Journal of the Taiwan Institute of Chemical Engineers 96 (2019) 256–263

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Biodegradability enhancement of real antibiotic metronidazole wastewater by a modified electrochemical Fenton

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ARTICLE INFO

Article history:
Received 28 August 2018
Revised 29 October 2018
Accepted 12 November 2018
Available online 27 November 2018

Keywords:
Modified electrochemical Fenton
Hydroxyl radical
Antibiotic metronidazole
Reduction reaction
Biodegradability enhancement

ABSTRACT

This paper proposes a modified electrochemical Fenton method with a pair of iron electrodes, which Fe anode is electrodisolved supplying stoichiometric Fe^{2+}. Then the electrodisolved Fe^{2+} reacts with H_2O_2 to generate hydroxyl radical (· OH). The experiment shows that 62.6% of chemical oxygen demand (COD) is removed and the ratio of the five-day biochemical oxygen demand (BOD_5) to COD increases from 0.17 to 0.45 under the optimal experimental conditions (current density of 30 mA/cm^2, electrolysis time of 15 min, H_2O_2 dosage of 75 mmol/L, pH 3.00 and stirring time of 2.5 hours). Meanwhile, the high concentration of metronidazole (1000 mg/L) is dramatically decreased (> 95%). In order to explore the mineralization pathway for metronidazole, the intermediate by-products of the modified electrochemical Fenton process are investigated by GC/MS, FTIR and HPLC. Good results are achieved in treatment of the real metronidazole wastewater by the proposed method, BOD_5/COD increases from 0.17 to 0.35. This method has been successfully applied to a large scale industrial treatment of real metronidazole wastewater as a pretreatment process for the biochemical treatment.

1. Introduction

Metronidazole is a kind of nitroimidazoles antibiotics which is introduced by Cosar and Julou in Europe as a trichomonicide in 1959 [1]. Metronidazole is mainly used to the treatment of the infections of the anaerobic bacteria and protozoa, which is not only applied to humans, but also for animal husbandry and aquaculture [2]. Extensive usage of metronidazole and high solubility in water leads to the accumulation in food-chains, freshwater and marine sediment. Metronidazole and metabolic products have potential toxicological effects, including mutagenic and carcinogenic properties [3–6]. It is necessary to seek an effective and economical method to remove metronidazole.

Removal of metronidazole from water is difficult due to its high solubility and non-biodegradability [3,7]. Up to now, multiple methods, including sorption [8,9], chemical Fenton, Sono-Fenton and electro-Fenton [10–12], photocatalytic degradation [13–16], nanoscale zero-valent iron particles catalytic degradation [17,18], ozonation [19], electrochemical oxidation technology [20–22] and electroreduction technology [23] are applied to dispose metronidazole from aqueous solutions. Among these methods, adsorption just transfers the pollutants.

The electro-Fenton (EF) stands out for the degradation of metronidazole wastewater. The COD removal rate reach to 39% in four hours, and the BOD_5/COD ratio in metronidazole wastewater increases from 0.23 to 0.34 [12]. The end products formed during EF tend to be recalcitrant to oxidative chemicals, but these end-products are readily biodegradable, Thus, EF could be applied as a pre-treatment to enhance biodegradability and reduce toxicity [24].

The electro-Fenton method is a particularly attractive technology which can generate part or whole of the Fenton's reagent in situ. It has been effectively applied to the treatment of many pollutants, such as synthetic dyes wastewater [25], landfill leachate [26] and pharmaceutical effluents [27]. The electro-Fenton process is based on the continuous electro-generation of H_2O_2 at the cathode fed with dissolved O_2 or air. By adding a catalytic amount of $Fe^{2+}$to the contaminated solution, ·OH is produced via Fenton's reaction, and Fe^{2+} is recycled by electro-chemical reduction of Fe^{3+} [28].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_0 = 0.67\,V \text{ vs. SHE} \tag{1}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E_0 = 0.77\,V \text{ vs.SHE} \tag{2}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \cdot OH \tag{3}$$

Compared to the traditional Fenton method, the electro-Fenton method can generally avoid the storage and the transportation

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https://doi.org/10.1016/j.jtice.2018.11.019
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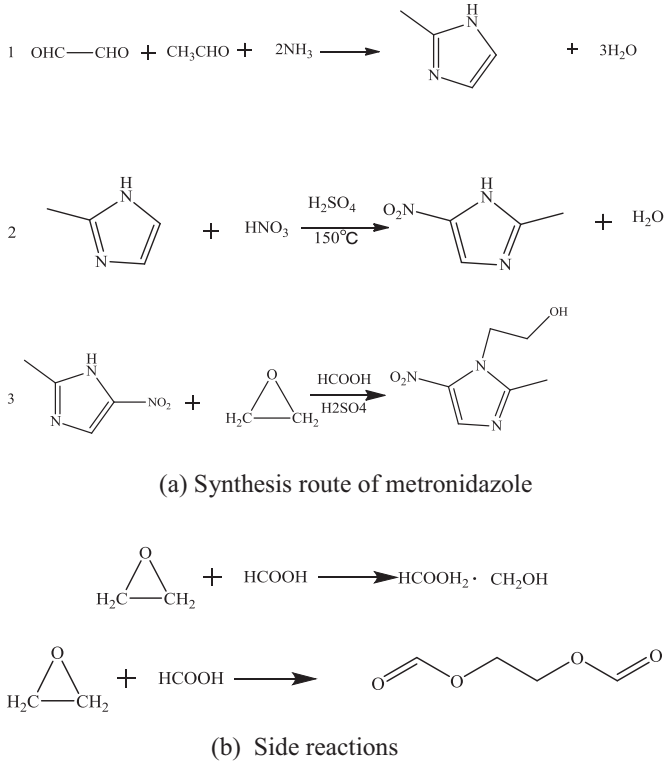

Fig. 1. Synthesis route of Hubei Hongyuan Pharmaceutical Technology Co, Ltd.

of hydrogen peroxide. But the yield of hydrogen peroxide is low due to the low solubility of O_2 in aqueous solution [29]. To overcome the above mentioned problem, the gas diffusion electrode is employed to generate H_2O_2. However the electro-Fenton method using gas diffusion electrode requires a more complicated electrochemical cell and higher costs [30], resulting in its difficulty to apply in real practice.

This paper proposes a modified electrochemical Fenton method with a pair of iron electrodes which Fe anode is electrodisolved supplying stoichiometric Fe^{2+},then Fe^{2+} reacts with H_2O_2 to generate hydroxyl radical (·OH), which has advantages of moderate cost and simple operation. The experimental parameters such as H_2O_2 concentration, pH, apparent current density and electrolytic time are investigated for degradation of the simulated metronidazole wastewater. And the biodegradability of wastewater is evaluated after processing. Furthermore this method has been successfully applied as a pretreatment process for the treatment of real metronidazole wastewater.

2. Materials and methods

2.1. Materials

Metronidazole with purity of 99% was purchased from Aladdin. H_2O_2, $FeSO_4 \cdot 7H_2O$, Na_2SO_4 and H_2SO_4 were analytical reagent grade supplied by Sinopharm Chemical Reagent Co., Ltd. Aqueous solutions were prepared using deionized water. The real metronidazole wastewater was obtained from Hubei Hongyuan Pharmaceutical Technology Co, Ltd. Synthesis routes of metronidazole were shown in Fig. 1. The source of waste liquid came from the third step of reaction, the organic compounds of waste liquid mainly contained metronidazole, 2-methyl-5-nitroimidazole, ethylene glycol and formic acid. The purpose of this study was to improve the biodegradability for the follow-up biological treatment, so metronidazole and 2-methyl-5-nitroimidazole were the main contaminants to be considered. The biorefractory organics mentioned in the following text represented metronidazole and 2-methyl-5-nitroimidazole. Its main characteristics were summarized in Table 1.

Table 1
The characteristic of the real wastewater.

The real metronidazole wastewater	
COD (mg/L)	26,789.0
BOD_5 (mg/L)	4554.1
BOD_5/COD	0.17
The concentration of biorefractory organics (mg/L)	37.8
NH_4^+-N value (mg/L)	475
The chloride concentration (mg/L)	688

2.2. The modified electrochemical Fenton

The Modified electrochemical Fenton consisted of two steps. Firstly soluble Fe^{2+} electrochemically produced from sacrificial iron anode ($E_0 = -0.44$ V vs. SHE) was supplied to the solution. Ferric ions were reduced to ferrous ions and organic compound took place reduction reaction during electrolytic process. Secondly hydrogen peroxide was added to the beaker as one of the Fenton reagents to perform the Fenton reaction.

First step in the electrolytic cell:

$$\text{Anode}: Fe \rightarrow Fe^{2+} + 2e^- \quad (4)$$

$$\text{Cathode}: Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (5)$$

$$Organics + e^- \rightarrow Reductionof\ organic \quad (6)$$

Other chemical reaction:

$$Fe(OH)_2 + Organics \rightarrow Reductionof\ organic + Fe(OH)_3 \quad (7)$$

Second step in the beaker:

$$\text{Introduced } H_2O_2: Fe^{(2+)} + H_2O_2 + H^+ \rightarrow Fe^{(3+)} + H_2O + \cdot OH \quad (8)$$

Electrolytic process of the modified electrochemical Fenton method was carried out in one compartment rectangular plexiglas container with a pair of iron electrodes (2 cm × 10 cm) connecting to digital DC power supply. 200 ml capacity of wastewater was placed in this container. The pH was adjusted by adding appropriate amount of sulphuric acid or sodium hydroxide. 0.1 M Na_2SO_4 served as supporting electrolyte. After completion of the electrolytic process, simulated metronidazole wastewater was poured into the beaker to stir by adding hydrogen peroxide. The reaction was quenched by increasing pH to around 9. The modified electrochemical Fenton method was applied to the real metronidazole wastewater treatment, but the method was made some adjustments considering the distinction between the real metronidazole and simulated metronidazole wastewater. All the experiments were conducted in triplicate at room temperature and the date shown were averages.

2.3. Analytical techniques

COD was determined using Multi-parameter water analyzer from Lian-hua Tech co. Ltd of China. Biological oxygen demand (BOD_5) was measured by dilution and seeding method according to HJ 505–2009. The concentration of ammonia–nitrogen was determined by Nessler's reagent spectrophotometry according to HJ 535–2009. The determination of chloride content in wastewater adopted silver nitrate titration method.