Electrochemistry Communications 94 (2018) 55–58

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Double-potential electro-Fenton: A novel strategy coupling oxygen reduction reaction and Fe^{2+}/Fe^{3+} recycling

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ARTICLE INFO

Keywords:
Electro-Fenton
H_2O_2 generation
Fe^{3+} reduction
DMP mineralization

ABSTRACT

In general, the electro-Fenton degradation potential is set according to the optimal H_2O_2 generation potential without considering Fe^{2+}/Fe^{3+} electrocatalytic recycling, resulting in high-energy consumption and iron sludge. In this work, a novel double-potential strategy was provided by alternately applying the optimal H_2O_2 generation potential and Fe^{2+}/Fe^{3+} recycling potential during the degradation process. The double-potential method showed a coordination of *in-situ* H_2O_2 generation by oxygen reduction reaction (ORR) and Fe^{2+}/Fe^{3+} recycling. EPR detection indicated that more hydroxyl radicals were produced during the double-potential process compared with the one achieved by constant potential. An outstanding DMP mineralization rate of 94.0% was achieved within 30 min and corresponding energy consumption was 0.762×10^4 kJ kg TOC^{-1} while the constant potential method reached 73.4% at −0.5 V and corresponding energy consumption was 1.54×10^4 kJ kg TOC^{-1}.

1. Introduction

Electro-Fenton (E-Fenton) is one of the classic technologies in advanced oxidation processes [1,2]. The continuous generation of H_2O_2 (Eq. (1)) through the $2e^-$ oxygen reduction reaction ($2e^-$ORR) can eliminate the risk of H_2O_2 storage and transportation. After the catalytic action of Fe^{2+}, strong oxidizing hydroxyl radicals will be produced and mineralize organic pollutants (Eq. (2)). Generally, the optimal H_2O_2 generation potential was set as a constant potential universally and then applied during the whole E-Fenton degradation process according to the early researches [3,4]. Also, this research strategy is still in effect today [5,6]. Setting the best H_2O_2 production potential for degradation always seems to be an established process in E-Fenton research. However, three primary reaction steps exist in the whole E-Fenton process. Two occur on the surface of the cathode – not only the *in-situ* H_2O_2 generation but also the Fe^{3+} reduction (Eq. (3)) [7,8]. And Fe^{3+} reduction potential tends to be lower than H_2O_2 production potential [9]. In a word, multi-electrochemical processes in E-Fenton regulated and controlled by only one single potential seems to be unsubstantial. Though H_2O_2 can be produced in an appropriate condition, E-Fenton overall degradation efficiency is still depressed due to the inhibition of Fe^{3+} reduction at an excessive potential.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

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

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{5}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{6}$$

Herein, in this work an effective potential regulation strategy is provided to optimize the E-Fenton process, leading to an ideal result of higher degradation efficiency with lower energy consumption. Firstly, a classical cathode material ACF was chosen as the electrode model. The potential diversity between H_2O_2 generation and the Fe^{3+} reduction was tested and found. And then, the double-potential process was designed after analyzing Fe^{2+} content changing curves during degradation. Finally, TOC mineralization and relative energy consumption were tested and calculated, showing a rapid removal rate and less energy cost compared with conventional constant potential application.

2. Materials and methods

2.1. Measurement of H_2O_2

H_2O_2 producing yield was detected by the potassium titanium (IV)

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https://doi.org/10.1016/j.elecom.2018.08.006
Received 2 July 2018; Received in revised form 11 August 2018; Accepted 13 August 2018

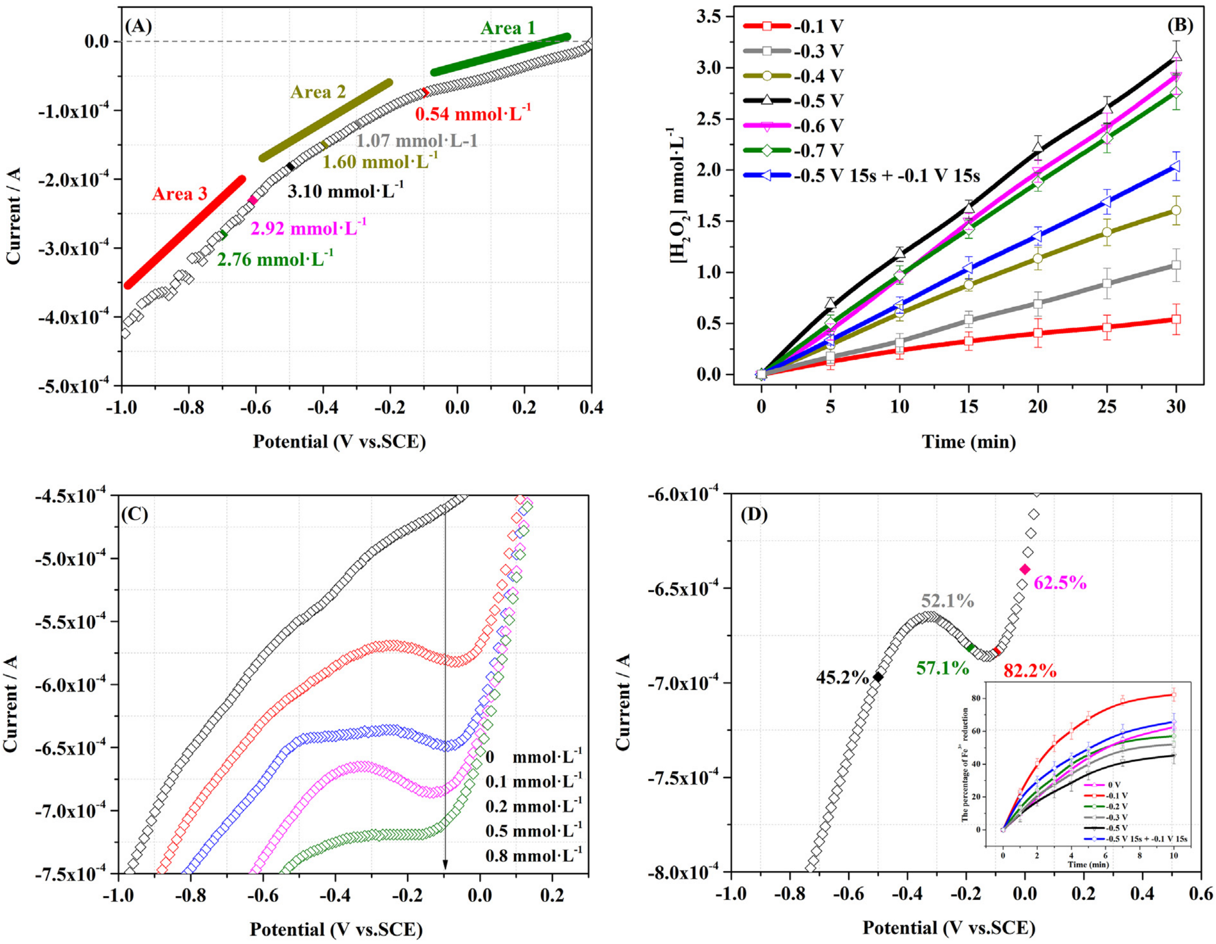

Fig. 1. (A) LSV curve achieved from 0.4 V to −1.0 V at a scan rate of 10 mv s^{-1}. (B) H_2O_2 generated at different potentials. (C) LSV curves achieved by adding 0 mmol L^{-1}, 0.1 mmol L^{-1}, 0.2 mmol L^{-1}, 0.5 mmol L^{-1} and 0.8 mmol L^{-1} Fe^{3+} (from equilibrium potential to −1.0 V at a scan rate of 10 mv s^{-1}). (D) LSV curves achieved after adding 0.5 mmol L^{-1} Fe^{3+} and reduction of Fe^{3+} at different potentials.

oxalate method: namely, 0.5 mL experiment solution mixed with 0.5 mL titanium reagent and 1.5 mL deionized water. Ultraviolet measuring wavelength was set at 400 nm [10].

2.2. Fe content detection

The concentration of Fe^{3+} and Fe^{2+} (adjusted by adding ferric sulfate and ferrous sulfate) was measured by the phenanthroline method at 510 nm. [11].

2.3. Spin trapping measurement of the hydroxyl radical

The formation of hydroxyl radical was indirectly monitored in the presence of the spin trap DMPO, the hydroxyl radicals produced in the E-Fenton reaction are trapped by analytical grade 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and the signal of the DMPO-OH adduct can be recorded with electron paramagnetic resonance (EPR, EMX NANO, USA).

2.4. Double-potential operation

The double-potential was operated by a square wave potential method with a period of 30 s: 15 s for −0.5 V and another 15 s for −0.1 V alternately applied on the cathode. Oxygen was provided during the whole reaction process.

2.5. TOC mineralization

Electrochemical workstation (CHI-650D, China) was used with a three-electrode system. ACF was applied as the working electrode. The counter electrode and reference electrode were platinum electrode and saturated calomel electrode, respectively. 50 mL, 0.1 mmol L^{-1}, pH = 3 (regulated by adding H_2SO_4) Na_2SO_4 electrolyte consisted of 1.0 mmol L^{-1} dimethyl phthalate (DMP) and 0.5 mmol L^{-1} $FeSO_4$ were carried out for E-Fenton degradation process. The distance between the cathode and anode was 1.5 cm. The working electrode was 3.0 cm × 2.0 cm ACF, and a platinum electrode was used as the counter electrode. Oxygen was supplied on the surface of the cathode at a flow rate of 0.4 L min^{-1} for O_2 saturated. TOC mineralization was measured by TOC tester (Analytik Jena, MULTI-NZ2100, Germany). The energy consumption of TOC removal was calculated and is expressed below [12,13]:

$$\text{Energy consumption} = \frac{U \times I \times T \times 3.6}{m_{\text{TOC}}}\ \text{kJ}\cdot\text{kgTOC}^{-1}$$

where U is the average cell voltage (V), I is the current (A), m_{TOC} is the amount of the mineralized TOC (kg), and T is the sewage treatment time (h).