Electrochimica Acta 182 (2015) 73–80

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhancement of oxygen diffusion process on a rotating disk electrode for the electro-Fenton degradation of tetracycline

Yan Zhang, Ming-Ming Gao*, Xin-Hua Wang, Shu-Guang Wang, Rui-Ting Liu

Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form 24 August 2015
Accepted 26 August 2015
Available online 14 September 2015

Keywords:
electro-Fenton
rotating disk electrode
tetracycline
oxygen transport
mineralization

ABSTRACT

An electro-Fenton process was developed for wastewater treatment in which hydrogen peroxide was generated in situ with a rotating graphite disk electrode as cathode. The maximum H_2O_2 generation rate for the RDE reached 0.90 mg/L/h/cm^2 under the rotation speed of 400 rpm at pH 3, and −0.8 V vs SCE. The performance of this electro-Fenton reactor was assessed by tetracycline degradation in an aqueous solution. Experimental results showed the rotation of disk cathode resulted in the efficient production of H_2O_2 without oxygen aeration, and excellent ability for degrading organic pollutants compared to the electro-Fenton system with fixed cathode. Tetracycline of 50 mg/L was degraded completely within 2 h with the addition of ferrous ion (1.0 mM). The chronoamperometry analysis was employed to investigate the oxygen diffusion on the rotating cathode. The results demonstrated that the diffusion coefficients of dissolved oxygen is 19.45×10^{-5} cm^2/s, which is greater than that reported in the literature. Further calculation indicated that oxygen is able to diffuse through the film on the rotating cathode within the contact time in each circle. This study proves that enhancement of oxygen diffusion on RDE is benefit for H_2O_2 generation, thus provides a promising method for organic pollutants degradation by the combination of RDE with electro-Fenton reactor and offers a new insight on the oxygen transform process in this new system.

1. Introduction

Advanced oxidation processes (AOPs) are regarded as the most attractive methods for the treatment of wastewater containing toxic and non-biodegradable pollutants [1–4]. Among all the processes, Fenton reagents (Fe^{2+} and H_2O_2) are particularly powerful for degrading recalcitrant organic pollutants due to the formation of hydroxyl radicals ($^{\bullet}OH$), which can non-selectively react with organic compounds leading to their mineralization to CO_2, water and inorganic ions [5]. However, it is expensive and dangerous for the production, transportation and storage of H_2O_2 [3–8]. In recent decades, electro-Fenton (EF) process has attracted great interests because of the in-situ electro-chemical production of H_2O_2 and the regeneration of Fe^{2+} at the cathode (via the reaction 1–3) [6–10]. This can solve the problems caused by the traditional Fenton processes, such as the storage and shipment of H_2O_2 and the generation of iron sludge [11–13].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Although EF process has been proposed as a promising environmental remediation technology, it encounters some drawbacks for further application. To our knowledge, the efficiency of H_2O_2 production is highly dependent on the diffusion of oxygen of the gaseous phase into the liquid phase [14–16]. Traditionally, the sparging of pure oxygen or air into the solution is usually considered to improve the insufficient of oxygen [7,17,18]. However, the reduction of oxygen in the cathode is controlled by the solubilisation of the molecular oxygen into the solution and then diffusion from the bulk to the electrode surface [19]. Due to the low solubility of oxygen, most oxygen bubbled into the solution cannot reach the electrode surface, resulting in the low oxygen utilization efficiency. As an example, the oxygen utilization efficiency, based on the fraction of oxygen that ended up in the H_2O_2 from the total amount of oxygen supplied through sparing, was less than 0.1% [20]. Furthermore, the high energy

* Corresponding author. Tel.: +86 531 88362802; fax: +86 531 88364513.
E-mail address: mmgao@sdu.edu.cn (M.-M. Gao).

http://dx.doi.org/10.1016/j.electacta.2015.08.134
0013-4686/

requirements of stirred tank and airlift would be a major waste in production process. Another way to increase the surface concentration of oxygen and reduce mass transfer limitations is the application of gas diffusion cathodes. As known, the gas diffusion cathode has excellent performance in the production of H_2O_2, but their size is commonly small, adding up to high cost and instability for long term operation [21]. Therefore, it is essential to develop a cost-effective EF system with much improved oxygen delivery efficiency.

Inspired by the rotating biological contactor and the rotating cathode microbial fuel cells [22–25], the use of rotating disk electrode (RDE) has been introduced in this EF process. In this system, the disk electrode was partially immersed in the solution and its upper part is contained in gas phase. So when a rotational movement is imposed to the disk, a liquid film is brought upwards over the surface of the disk, thus providing a contact of the liquid film with the oxygen. After moving downwards, the liquid film will be taken up again by the liquid in the reactor [26]. What's more, the contact between phases is generated by maintaining the liquid phase as thin film thus minimizing the mass transfer resistances from gas phase to the liquid phase [26]. A previous study [20] found that the RDE process is feasible in the application. The dissolved oxygen (DO) in this reactor does not impact on the generation rate of H_2O_2 because adequate amount of oxygen could be supplied during the air exposure cycle.

In this study, EF system was fabricated with graphite, a typical carbon material [27–29], as rotating disk cathode to give a common information for carbon-based RDE. The effects of pH, applied potential and rotating speed on the generation of hydrogen peroxide were studied. Then, the performance of this reactor was evaluated for the degradation of tetracycline (TC), compared with cathode-fixed EF process with gas–liquid stirred. Finally, the oxygen transform process was investigated to give an insight on the effects of rotating disk cathode on the generation of H_2O_2 and electro-Fenton process.

2. Experimental

2.1. EF system assembly

A schematic diagram of the RDE reactor used in this study is shown in Fig. 1. The electrochemical generation of hydrogen peroxide and the subsequent removal of TC concentrate were performed in the undivided cell of 250 mL capacity. The cell was made of 0.2 cm thick acrylic material, 10.0 cm high, and was 7.0 cm long and 5.0 cm wide. The electrodes in this study were prepared by spectroscopically pure graphite (SPG) (≥99.9% porosity, 1.85 g/cm^2 bulk density, 13 μΩ m electric resistivity, Shanghai Yifeng Co., Ltd.) without any modification. The prepared cathode of graphite disk (Ø 80 mm, thickness of 8 mm) was selected as the working electrode, a graphite column (Ø 20 mm) as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The disk cathode were mounted on a horizontal copper shaft (1.0 cm diameter) that was attached to a variable speed motor device by a plastic connector. The cathode disk was 40% submerged in the liquid and the distance between the cathode and the anode was 2.0 cm.

2.2. Operation conditions

The H_2O_2 electro-generation experiments were performed in the homemade RDE reactor in 0.05 M Na_2SO_4 solution at room temperature. The solution pH was adjusted to 3 using H_2SO_4 and NaOH and determined with a Sartorius PB-10 pH-meter. The electrical signal for the electrochemical experiments was controlled and recorded by a CHI760D electrochemical workstation (Shanghai Chenhua, China). The disk cathode was rotated at a controlled speed (100, 200, 300, 400 and 500 rpm) driven by a motor. At the 60th min, 2 mL samples were taken for analyzing the concentration of the H_2O_2.

The degradation of tetracycline hydrochloride (Analytical grade, 96% purity, Aladdin Industrial Corporation, Shanghai) by RDE process was carried out in the same apparatus at several initial concentrations (50, 100, 200 and 300 mg/L). After the solution pH was adjusted to 3, $FeSO_4$ was introduced to provide 1.0 mM Fe^{2+} in the solution as the catalyst and the rotation speed was kept 400 rpm. The TC samples were taken every 20 min and then filtered by 0.45 μm membrane for analysis, and the electric charges were recorded.

A comparative reaction for TC degradation was carried out in a conventional gas–liquid stirred tank reactor. A fixed graphite sheet (80 mm × 62 mm, 50.2 cm^2) was used as cathode, which has the same surface area as the RDE. Other operation parameters (such as pH, applied potential and Fe^{2+} concentration) were the same as the RDE reactor. The concentration of oxygen in the solution was maintained by continuously bubbling compressed air at 300 ml/min recommended as the optimum amount sparging rate in the EF process [30,31].

2.3. Analytical method

The concentration of H_2O_2 during such experiments was monitored by UV–Vis spectrophotometer (UV759, Shanghai instrument analysis Co., LTD.) using the potassium titanium (IV)

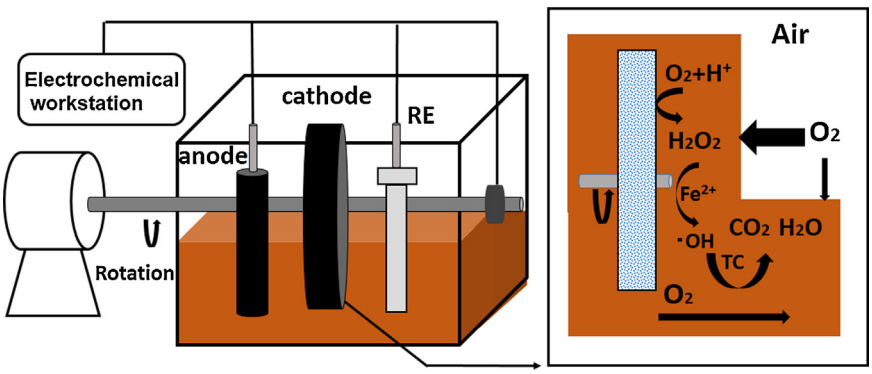

Fig. 1. Experimental setup of RDE reactor used for tetracycline degradation. The cell was 10 cm high, 7 cm long and 5 cm wide. The distance between the graphite disk cathode (Ø 80 mm, thickness of 8 mm) and the anode (Ø 20 mm) was 2 cm.