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A novel dual gas diffusion electrodes system for efficient hydrogen peroxide generation used in electro-Fenton

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HIGHLIGHTS

- A novel H_2O_2 generation reactor using dual gas diffusion electrode as cathode was proposed.
- It was confirmed to be more cost-effective in H_2O_2 yield and energy consumption.
- The effect of some parameters on H_2O_2 generation and cathode stability was studied.
- It performed well for high concentrated tartrazine degradation by electro-Fenton.

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ABSTRACT

Highly efficient H_2O_2 generation is greatly demanded in electro-Fenton process for organic pollutants degradation. In the present work, a novel H_2O_2 generation reactor using dual gas diffusion electrodes (GDEs) as cathodes was put forward, which was confirmed to be more cost-effective in H_2O_2 generation rate, O_2 utilization efficiency and energy consumption in comparison with other carbonaceous materials and reactors. The catalyst layer in GDE was characterized and optimized, and the accumulation of H_2O_2 reached to 566 mg/L in 0.05 M Na_2SO_4 at a current density of 7.1 mA/cm^2 and air flow rate of 0.5 L/min after 180 min. The operational parameters such as current density, pH and air flow rate were optimized, and after 10 times used the production of H_2O_2 was confirmed to be stable. This novel reactor was tested to degrade tartrazine, and even for a high initial concentration of 1000 mg/L, it could be completely decolorized within 60 min while the TOC removal efficiency could reach 66.1% within 120 min with a mineralization current efficiency of 65.1%, indicating its potential for the treatment of high-concentrated wastewaters.

1. Introduction

Advanced oxidation processes (AOPs) which mainly involve chemical, photo-chemical and electro-chemical techniques are known as promising methods to remove refractory pollutants in aquatic environment. The principal active specie in AOPs is hydroxyl radical (·OH), a highly powerful oxidizing agent that can unselectively react with organic contaminants until their degradation and mineralization. As an environmental friendly process, electro-Fenton (EF) is one of the most commonly used AOPs for the removal of persistent organic pollutants (POPs) [1–7]. The basic principle of EF is the reaction between the continuous in-situ electro-generation of H_2O_2 on the cathode (Eq. (1)) and the added iron catalyst, producing powerful oxidant ·OH (Eq. (2)) [8–12].

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

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

As a result, one key concern in the EF process is the cathode with effective production of H_2O_2. At present, carbonaceous materials such as graphite [13,14], carbon/graphite felt [15–21], reticulated vitreous carbon (RVC) [22], activated carbon fiber (ACF) [23], carbon nanotube [24], BDD [25] and gas diffusion electrode (GDE) [26–29] have been attempted as cathode, confirming that they

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possess some advantages such as non-toxicity, good stability, conductivity and chemical resistance [19,20]. However, traditional carbonaceous materials, for example, graphite, graphite felt and ACF, are not efficient in H_2O_2 production [13,20,23]. And many reports have confirmed that the performance of H_2O_2 electro-generation can be greatly improved by cathode modification [11,13,19]. Of all these materials, GDE has attracted great attention owing to its relatively high H_2O_2 production [10,28]. Because in this system the pumped air or oxygen can directly pass through the porous structure of GDE other than dissolve into the solution in other cathode systems, in which the low solubility of oxygen in the electrolyte is usually a key limitation that resulted in a low production of H_2O_2 [30].

So far, many studies using GDE as cathode for EF process have been mainly focused on process development (e.g., photoelectro-Fenton and photo-assisted electro-Fenton) and its application for degradation of different organic pollutants [10,28,31–33], usually omitting the cathodes system construction to improve process effectiveness [30,34]. It is supposed that the cathode performance is evaluated mainly by the H_2O_2 production rate, current efficiency and the energy consumption [30,34]. Depending different cathode materials and systems, the H_2O_2 yield and current efficiency differed much [10,26]. And more recently, it has been indicated that the O_2 utilization efficiency is also an important index since in many cathode system, it is lower than 0.1%, i.e., most of the oxygen is not effectively used for H_2O_2 yield [34]. In some literatures used GDE as cathode, the H_2O_2 yield is high but some other indexes such as current efficiency or energy consumption or oxygen utilization efficiency are not satisfactory [27,30]. Therefore, it is necessary to re-evaluate a cathode system by making a comprehensive study on these indexes.

In this work, a novel dual GDE using carbon fiber as substrate was developed, in which two GDE connected with one air input port was placed in parallel with anodes. Compared with the conventionally used GDE system, this one was readily to scale up, and was proved greatly enhancing current efficiency and O_2 utilization efficiency, and gave rise to a much higher H_2O_2 production rate with less energy consumption. This would be very important and promising for application in pollutants degradation by EF process. The influences of the loading of catalyst layer in GDE, current density, pH, and air flow rate on H_2O_2 production and current efficiency, as well as the cathode stability were investigated. The treatment performance by EF process was evaluated by the degradation of tartrazine, an azo dye that widely used to color the foods, beverages, drugs and cosmetics, and may do harm to the health of people especially children [33].

2. Experimental

2.1. GDE preparation

All chemicals used in this study were analytical grade and used as received without further purification. The carbon fiber (Jilin Shenzhou Carbon Material Co., Ltd.), used as substrate for GDE preparation, were firstly degreased in an ultrasonic bath with acetone and deionized water in sequence and then dried at 80 °C for 24 h. Then 0.15 g carbon black and 2 mL PTFE (30%) emulsion (Shanghai Hesen Electric Co., Ltd.) were mixed and deposited uniformly onto the surface of the pretreated carbon fiber. This coating is the so-called diffusion layer. Afterwards, it was put into a muffle oven to calcine at 350 °C for 30 min. The aforementioned process repeated two times and when it cooled down, the mixture of carbon black, absolute ethyl alcohol and PTFE (60%) emulsion were deposited as the catalyst layer, and still were put into a muffle oven to calcine at 350 °C for 30 min [26,29].

2.2. Cathode system and EF reactor

Fig. 1 shows the schematic diagram of setup. Reactor one is the proposed novel reactor with two pairs of anode and cathode placed in parallel. To make a comprehensive evaluation on H_2O_2 generation performance, it was compared with reactor two (one pair of anode and cathode) and reactor three, which was the most traditional reactor used in literatures with the surface of anode and cathode positioned vertically [28,31–33].

The H_2O_2 electro-generation experiments were performed in a 200 mL undivided cell. GDE (ϕ 3.0 cm) was used as cathode and DSA (2 cm × 4 cm) with IrO_2 coating was used as anode. The distance between the anode and cathode was 1.5 cm. An aqueous solution of 0.05 M Na_2SO_4 was used as supporting electrolyte and the pH value was adjusted by H_2SO_4 or NaOH. Prior to the electrolysis, air was pumped into the tube of GDE using a aerator machine at a desired flow rate for 10 min, then the power supply was switched on to start electrolysis. At certain intervals, 0.5 mL samples were taken to analyze the concentration of H_2O_2 formed.

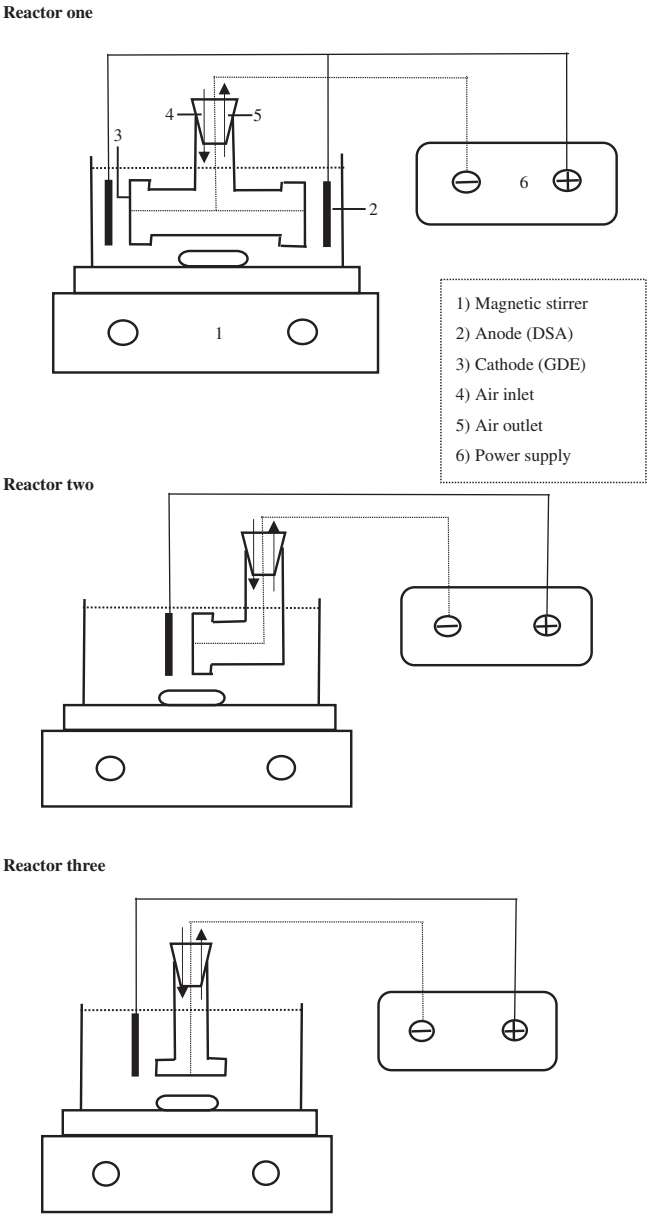

Fig. 1. The schematic diagram of the setup.