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Development of a trickle bed reactor of electro-Fenton process for wastewater treatment

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HIGHLIGHTS

- An electrochemical trickle bed reactor was composed of C-PTFE-coated graphite chips.
- The trickle bed reactor had a high H_2O_2 production rate in a dilute electrolyte.
- An azo dye was effectively decomposed by the electro-Fenton process in the reactor.

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ABSTRACT

To avoid electrolyte leakage and gas bubbles in the electro-Fenton (E-Fenton) reactors using a gas diffusion cathode, we developed a trickle bed cathode by coating a layer composed of carbon black and polytetrafluoroethylene (C-PTFE) onto graphite chips instead of carbon cloth. The trickle bed cathode was optimized by single-factor and orthogonal experiments, in which carbon black, PTFE, and a surfactant were considered as the determinant of the performance of graphite chips. In the reactor assembled by the trickle bed cathode, H_2O_2 was generated with a current of 0.3 A and a current efficiency of 60%. This performance was attributed to the fine distribution of electrolyte and air, as well as the effective oxygen transfer from the gas phase to the electrolyte–cathode interface. In terms of H_2O_2 generation and current efficiency, the developed trickle bed reactor had a performance comparable to that of the conventional E-Fenton reactor using a gas diffusion cathode. Further, 123 mg L^{-1} of reactive brilliant red X-3B in aqueous solution was decomposed in the optimized trickle bed reactor as E-Fenton reactor. The decolorization ratio reached 97% within 20 min, and the mineralization reached 87% within 3 h.

1. Introduction

The electro-Fenton (E-Fenton) process, during which hydrogen peroxide (H_2O_2) is electrochemically generated through the reduction reaction of oxygen on a cathode, is an effective advanced oxidation technology for the degradation of recalcitrant organic pollutants in water [1–7]. This process is acknowledged to involve the production of hydroxyl radicals ($^{\bullet}OH$) through the interaction between electro-generated H_2O_2 and added Fe^{2+}, which are extremely powerful and non-selective to destroy the organic substrates.

Cathode materials are crucial in the E-Fenton process given that H_2O_2 is generated on the cathode. Cathode performance is commonly evaluated in terms of H_2O_2 production rate and current efficiency (*CE*) ahead of the purification of polluted water. Some cathodes, including mercury, gold, and carbon [8], allow to output H_2O_2. Meanwhile, carbonaceous cathodes are recognized as more environmentally benign and economic [8,9], whereas problems lie in a low level of current density less than 1 mA cm^{-2} (equivalent to a H_2O_2 production rate of 20 μmol h^{-1} cm^{-2}) [8,10,11]. Such limitations are essentially caused by the low oxygen solubility and mass transport limitation [8,10,11]. Accordingly, three-dimensional electrodes, such as activated carbon fiber [12,13], reticulated vitreous carbon (RVC) [6,7,14–16], carbon felt [4,17], and gas diffusion electrodes (GDEs) [18–25], have been developed to accelerate the H_2O_2 production. In all three-dimensional electrodes, GDEs prepared with carbon black and polytetrafluoroethylene (C-PTFE) have the highest H_2O_2 production rate. However, GDEs continuously cause electrolyte leakage to the gas chamber at the bottom of the electrode or gas bubbles to the electrolyte chamber at the top of the electrode when the GDE height exceeds 0.25 m [9]. These problems result from an imbalance between the pressure levels in electrolyte and the gas phase.

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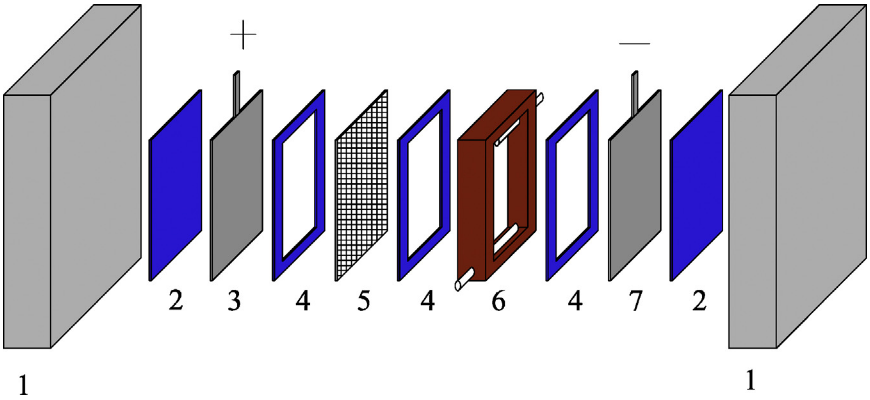

Fig. 1. Schematic diagram of the trickle bed reactor assembly. 1. Cell body, 2. Gasket, 3. Ti/PbO_2 anode, 4. Gasket ring, 5. Nylon diaphragm, 6. Cathode frame for loading graphite chips and 7. Ni plate.

To avoid electrolyte leakage and gas bubbles in the E-Fenton reactors using a GDE, we developed a trickle bed cathode by coating a layer composed of C-PTFE onto graphite chips instead of carbon cloth. The trickle bed reactor contains three phases of gas, liquid, and solid [26–28]. In this reactor, the flow rates of gas and liquid are adjusted to a low level, and the gas flows at a continuous state while the liquid flows through the bed in a trickle.

Provided that the trickle bed reactor is used to generate H_2O_2, the oxygen in the gas phase can be fully dissolved in the liquid phase, and then rapidly transfer to the solid–liquid interface, where the reduction reaction of oxygen occurs. As a result, a high rate of H_2O_2 production may be expected. Trickle bed cathodes composed of graphite particles and carbon felt have already been applied in the electrochemical generation of concentrated H_2O_2, which is further employed for pulp bleaching and organic synthesis [9,29,30]. Also important, the electrolyzer that contains the trickle bed cathode has more promising potential for scale-up than do conventional GDEs. For example, Yamada et al. [29] have developed a trickle bed electrolyzer for the electrochemical production of H_2O_2 in 2 mol L^{-1} NaOH solution with an apparent cathodic surface area as large as 0.8 m^2.

In this study, we developed a trickle bed cathode to generate H_2O_2 that was further employed in the E-Fenton system for wastewater treatment. The electrolyzer contained electrolyte more dilute than that used in the production of H_2O_2 for pulp bleaching and organic synthesis [9,29–31]. The trickle bed cathode was composed of composite graphite chips prepared by C-PTFE coating. Simulated wastewater containing an azo dye, i.e., reactive brilliant red X-3B (X-3B), was treated in the E-Fenton system with the cathode.

2. Experimental

2.1. Materials

X-3B ($C_{19}H_{10}Cl_2N_6Na_2O_7S_2$, 615 g mol^{-1}) was obtained from Beijing Chemical Reagents Co. (Beijing, China), and used as obtained. The graphite chips, with a size of 40 mesh (0.35–0.42 mm), were purchased from Tianhe Graphite Co. (Qingdao, China). The regular carbon black was purchased from Shanghai Carbon Co. (Shanghai, China). Carbon black Vulcan XC-72, Vulcan XC-72R, and Black Pearl 2000 (BP-2000) were obtained from Shanghai CABOT Chemical Co. (Shanghai, China). PTFE aqueous suspension (60 wt.%, FR301B) was purchased from 3F New Materials Co. (Shanghai, China). Other reagents were all of analytical grade. Deionized water was used to prepare the solutions in all experiments.

2.2. Electrochemical trickle bed reactor

As shown in Fig. 1, the electrochemical trickle bed reactor consists of a Ti/PbO_2 anode, a porous nylon diaphragm, a cathode frame containing C-PTFE-coated graphite chips (chips not shown in Fig. 1), and a nickel cathode plate. Three sealing gasket rings with empty parts (60 mm × 50 mm) are placed between each of the above-mentioned components. The cathode frame has two couplings that serve as a fluid feed and an outlet. The active dimensions of the cathode with the C-PTFE-coated graphite chips are 60 mm × 50 mm × 14 mm (width, height, thickness). Note that the graphite chips in the cathode frame closely contact with the nickel plate which acts as current collector. The entire assembly is tightly fitted between two carbon steel plates, which are insulated from electrodes by two rubber gaskets.

The composite graphite chips were prepared by coating carbon black and PTFE onto crude graphite chips [30,32]. The carbon black used in the coating was pretreated by 30 wt.% hydrochloric acid (Fig. S1). The coating process involved three steps: mixing, evaporation, and sintering. Mixing: carbon black, 60 wt.% PTFE suspension, and 1.1 L deionized water were mixed and stirred for 30 min; then, 330 g of crude graphite chips were added and agitated for 2 h. Evaporation: the mixture was evaporated in a rotary evaporator at 60 °C for 1.5 h and then at 90 °C for 1 h in vacuum. Sintering: the dried residue was sintered at 360 °C for 2 h without inert gas protection. Without inert gas protection, partial oxidation of carbon might occur, which was reported to bringing about more functional groups such as quinone groups [33,34]. Fortunately, these groups are considered to benefit the H_2O_2 generation [35]. The once-coated graphite chips were treated again by the same process, except that Triton X-100 was added to the deionized water. The composite graphite chip used in the repeated procedure in Section 3.2 was prepared with 14.0 g of pretreated Vulcan XC-72, 25 mL of PTFE in each coating, and 0.5 mL of Triton X-100 in the second coating. The Ti/PbO_2 anode was prepared by the anodic electro-deposition of PbO_2 onto a Ti plate [36].

2.3. Electrolysis process for H_2O_2 generation

Fig. 2 illustrates the process flow for the generation of H_2O_2 in dilute Na_2SO_4 solution. Air and electrolyte were combined in a tee and delivered in a two-phase flow to the trickle bed reactor through the upper coupling of the cathode frame. The gas–liquid fluid flowed downward through the cathode bed. The electrolyte flowing out the reactor through the lower coupling was sampled directly in continuous flow mode (CFM, A in Fig. 2) or circulated back to the initial electrolyte in batch mode (BM, B in Fig. 2). The injected air flowed out of the reactor with the electrolyte through