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Electrogeneration of hydrogen peroxide for electro-Fenton via oxygen reduction using polyacrylonitrile-based carbon fiber brush cathode

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ABSTRACT

Polyacrylonitrile-based carbon fiber brush (PAN-CFB) cathode was used to electrogenerate hydrogen peroxide (H_2O_2) via oxygen reduction reaction (ORR) and to degrade phenol in electro-Fenton system. Due to inherent N-containing structure, PAN-CFB cathode generated H_2O_2 efficiently (current efficiency at 300 mA >90%), showing high selectivity toward 2-electron ORR independent of medium (H_2SO_4, Na_2SO_4 or NaOH). Moreover, the influence of parameters such as applied current, cathodic potential, electrolyte concentration and volume as well as electrode distance on H_2O_2 electrogeneration was investigated in detail. Finally, the degradation of phenol was evaluated by ultraviolet (UV) spectra analysis and COD measurement. 86.2% of COD removal was achieved under the optimum conditions (pH 3, I = 300 mA, 0.3 mmol L^{-1} Fe^{2+}) after 240 min, meaning the almost complete degradation of phenol via electro-Fenton process using PAN-CFB cathode.

1. Introduction

H_2O_2 is one of the most essential and versatile chemicals for pulp bleaching, waste treatment and numerous compounds manufacture [1–3], and it is promising for green chemistry and environmental control, especially for effluents treatment because it decomposes solely into water and oxygen, leaving no hazardous residues [4–6]. It can be employed either alone or in combination with UV or metal salts to significantly enhance the oxidizing efficiency. In particular, the aqueous mixture of H_2O_2 and Fe^{2+}, known as Fenton's reagent, is one of the most effective environmental treatments [2,6,7]. It generates hydroxyl radical ($^{\bullet}OH$) which can degrade most organic pollutants into CO_2, H_2O and inorganic ions under acidic conditions in a nonselective way [8–10].

The current large-scale manufacture of H_2O_2, multi-step anthraquinone oxidation (AO) method, has disadvantages of high energy consumption and waste discharge [1,3,4,11], therefore extensive efforts have been devoted to directly synthesizing H_2O_2 in situ to reduce the cost and potential risks in purchasing, transporting, storaging and handling of concentrated H_2O_2 [5,6,12]. Two strategies have aroused wide attention. One is a direct synthesis from hydrogen (H_2) and oxygen (O_2) via precious-metal catalysts (Pd, Au, or Au-Pd) [11,13,14] but with too much undesired side reactions (Reactions (1) and (2)) [3,15] and serious problems such as unfavorable high-pressure and danger of explosion [3,11].

$$H_2 + 1/2\ O_2 \rightarrow H_2O \quad (1)$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \quad (2)$$

The other strategy resorts to an electrochemical synthesis via a 2-electron ORR [16] where only O_2 or air is needed to be reduced on suitable electrode with simple steps and no hazardous products is generated.

Electro-Fenton process with characteristics of cathodic regeneration of Fe^{2+} and less sludge can guarantee continuous in-situ generation of H_2O_2 [17] in acidic medium whose efficiency is largely dependent on the effect of cathode materials. Several electrodes such as mercury [18], graphite [16,19], carbon felt [20,21], activated carbon fiber (ACF) [22–25], reticulated vitreous carbon (RVC) [26], carbon sponge [27] and carbon nanotube [28] were tried, and particularly, gas diffusion electrode (GDE) is an effective one [2,29,30] but was limited by the high price and complex configuration for injection of O_2 [5,12,29]. Besides, the two-electron ORR on carbon cathodes in strong alkaline solution is a well-known efficient reaction, but an effective cathode to electrogenerate H_2O_2 for Fenton reaction in acidic medium is urgently needed [7].

Recently, N-doped carbon materials have attracted enormous interest as ORR catalysts [31,32]. Polyacrylonitrile-based carbon

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fiber (PAN-CF) is a typically commercial N-doped carbon material (N content: 2–6 wt. %) with excellent electric conductivity and corrosion resistance [33], so it is tried as cathode material of electro-Fenton to investigate its electrocatalytic activity toward ORR and the ability to electrogenerate H_2O_2 in situ. Furthermore, the influence of some parameters (applied current, cathodic potential, electrolyte concentration and volume as well as the distance between electrodes) on H_2O_2 electrogeneration was investigated in detail. Finally, the degradation of target compound—phenol via electro-Fenton process was evaluated at different Fe^{2+} concentration to verify the application in waste treatment.

2. Experimental

2.1. Chemicals

$K_2Cr_2O_7$ and potassium acid phthalate ($C_8H_5KO_4$) were of guaranteed grade. All other chemicals including potassium titanyl oxalate ($C_4K_2O_9Ti{\cdot}2H_2O$), phenol (C_6H_5OH), Na_2SO_4, H_2O_2, H_2SO_4, NaOH, Ag_2SO_4, $HgSO_4$, $FeSO_4{\cdot}7H_2O$ were of analytical grade. Deionized water was prepared by reverse osmosis system.

2.2. Electrochemical system

Electrolysis processes were conducted in three open and undivided cells (containing 2 L, 1 L, 0.5 L electrolyte) at room temperature. The anode was $Ti/IrO_x–TiO_2/IrO_2$ mesh electrode (6 cm × 4 cm) prepared as reference [34]. PAN-CFB cathode consisted of Ti wire(TA2, Φ1 mm) serving as current collector and 2 g PAN-CF (T300-12 K, Yancheng Xiangsheng carbon fiber plant, China) as described by Xu et al. [35], the brush was 30 mm in diameter and 180 mm in length (Fig. 1). During electrolysis, air was bubbled into the cell at a flow rate of 3 L min^{-1} by an air pump to feed oxygen needed for ORR. The initial pH was measured with a pH-meter (Mettler Toledo Delta-320) and the required pH was adjusted by dilute H_2SO_4 and NaOH solution. Electrolyses were performed at constant current or potential controlled by ZF-9 potentiostat/galvanostat (Shanghai Zhengfang Electric Appliance Co. Ltd).

2.3. Procedure

Linear sweep voltammetry (LSV) curves were respectively tested in 0.5 mol L^{-1} of H_2SO_4, Na_2SO_4 and NaOH by an electrochemical workstation (Zahner IM6ex, Germany) in a three-electrode system (Fig. 1 (I)), using PAN-CFB as working electrode, the $Ti/IrO_x–TiO_2/IrO_2$ mesh as counter electrode, and saturated calomel electrode (SCE) as reference electrode. The solution was saturated with N_2 or O_2 by feeding pure N_2 or air for 20 min before test and continuously bubbled throughout the measurement.

Electrogeneration of H_2O_2 was carried out in the same three-electrode system as above, and the concentration of H_2O_2 was determined by a UV–vis spectrophotometer (Shimadzu UV 2450, Japan) at 400 nm, using $C_4K_2O_9Ti$ as color indicator [36].

Electro-Fenton degradation of phenol was performed in a two-electrode system (Fig. 1 (II)) using $Ti/IrO_x–TiO_2/IrO_2$ mesh anode and PAN-CFB cathode in Na_2SO_4 solution containing phenol of 100 mg L^{-1}. $FeSO_4{\cdot}7H_2O$ was added to supply Fe^{2+}. The samples after different electrolysis time were taken out and filtered by 0.45 μm polyethersulphone (PES) membranes (Germany Membrane Co.), and then their absorption spectra were recorded by UV 2450 spectrophotometer. Chemical oxygen demand (COD) was measured according to Standard Methods for the Examination of Water and Wastewater (American Health Public Association, 20th ed., Washington DC, 2000.) using the colorimetric method at 420 nm by UV 2450 spectrophotometer.

2.4. Analytical method

X-ray photoelectron spectroscopy (XPS) was employed to determine the type of N-containing functional groups present on the surface of PAN-CF. The XPS spectra was obtained using ESCALAB250 surface analysis system (Thermo VG, USA) in an ultra-high vacuum set-up equipped with Al Kα X-ray source generated at 15 kV and 10 mA, the base pressure in the measurement chamber was about 5.5×10^{-8} mbar. XPS spectra were fitted by a nonlinear least-square curve-fitting program with the Gaussian/Lorentzian product function.

The current efficiency (CE) for electrogeneration of H_2O_2 is defined as follows [37]:

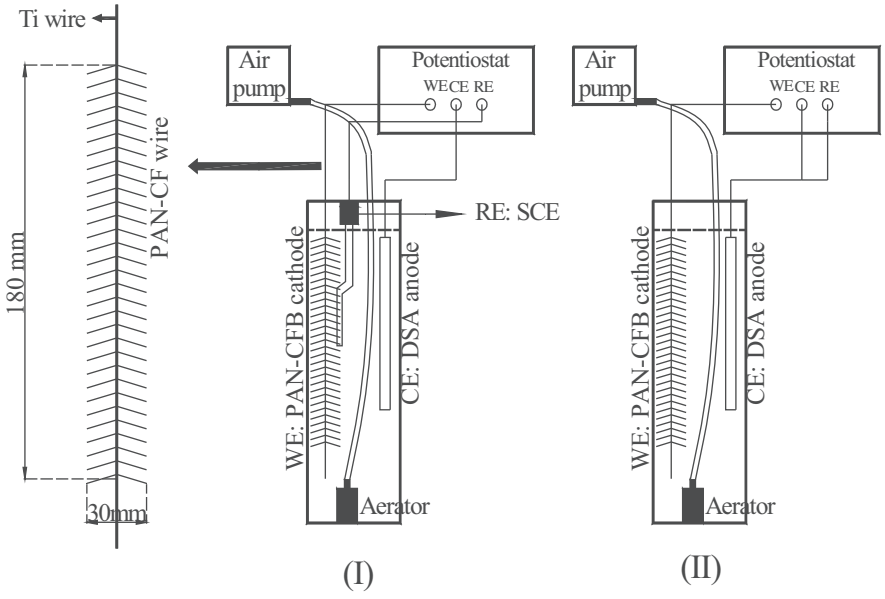

Fig. 1. Schematic of the electrolytic system used for (I) H_2O_2 electrogeneration and (II) electro-Fenton process.