A highly energy-efficient flow-through electro-Fenton process for organic pollutants degradation

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ABSTRACT

A highly energy-efficient flow-through Electro-Fenton (E-Fenton) reactor for oxidation of methylene blue (MB) from aqueous solution was designed using a perforated DSA as anode and the graphite felt modified by carbon black and polytetrafluoroethylene (PTFE) as cathode for the in situ generation of H_2O_2. The modified cathode had a high H_2O_2 production with low energy consumption, which was characterized by scanning electron microscopy (SEM), nitrogen adsorption-desorption study and contact angle. The flow-through E-Fenton system was compared to the flow-by and regular one, and confirmed to be best on MB removal and TOC degradation. The operational parameters such as current density, pH, Fe^{2+} concentration and flow rate were optimized. The MB and TOC removal efficiency of the effluents could keep above 90% and 50%, respectively, and the energy consumption was 23.0 kWh/kgTOC at the current density of 50 mA, pH 3, 0.3 mM Fe^{2+}, and the flow rate of 7 mL/min. $^\bullet$OH was proved to be the main oxidizing species in this system. After 5 times operation, the system, especially cathode, still showed good stability. Five more organic pollutants including orange II (OG), tartrazine, acetylsalicylic acid (ASA), tetracycline (TC) and 2,4-dichlorophen (2,4-DCP) were investigated and the electric energy consumption (EEC) was compared with literatures. All results demonstrated that this flow-through E-Fenton system was energy-efficient and potential for degradation of organic pollutants.

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1. Introduction

Fenton oxidation as a main type of advanced oxidation processes (AOPs), combining H_2O_2 and Fe^{2+} in the aqueous solution, is regarded as a promising and highly efficient technology for organic pollutants remediation based on the well-known free radical mechanism as shown in Eq. (1) [1]. Due to the high standard reduction potential (E° ($^\bullet$OH/H_2O) = 2.80 V/SHE) of hydroxyl radicals ($^\bullet$OH), it can oxidize most organics into CO_2, H_2O and inorganic ions via dehydrogenating or hydroxylating reaction [2]. Given their great oxidation capacity, many Fenton processes have been used to treat a great variety of industrial wastewaters (e.g., fine chemical industries). However, some drawbacks of the traditional Fenton process like storage and translation of H_2O_2, iron sludge, parasitic reactions still limit the application of Fenton oxidation at a degree [3,4].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{1}$$

To a certain extent, electro-Fenton (E-Fenton) overcomes the above drawbacks of traditional Fenton, which can continuously generate H_2O_2 in situ on suitable cathode via a two-electron reduction of oxygen (Eq. (2)).

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

The degradation efficiency of E-Fenton deeply depends on the productivity of H_2O_2, which is largely determined by the cathode properties. As a vital factor, much attention has been paid to the development of cathode materials, including graphite [5,6], BDD [7], and three-dimensional cathode like graphite felt [8], activated carbon filter [9,10], carbon nanotubes [3,11–13]. Considerable efforts have been made on cathode modification [14–21]. In particularly, gas diffusion electrode (GDE) has the properties of high porosity and hydrophobicity, providing lots of active surface sites for catalyzing oxygen reduction to H_2O_2, and allows air or

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oxygen cross the pore and contact with the active sites and the solution at cathode surface [22].

Usually this GDE is operated in a flow-by reactor [26,27], and recent studies indicated that a flow-through reactor, i.e., the solution flow through anode and cathode, could improve the degradation rate and efficiency because it enhanced the convective transfer of the pollutant molecule to the electrode surface [11,23]. In these works, the solution was pretreated by pumping air or pure oxygen to increase the concentration of the dissolved oxygen in solution [11,24,25]. However, due to the low concentration of dissolved oxygen in solution, this process has a main drawback of rather low yield of H_2O_2 which limits the Fenton oxidation rate. Therefore, it is necessary to invent a novel E-Fenton process that can satisfy the high yield of H_2O_2 and take the advantage of flow-through process.

Consequently a highly energy-efficient flow-through E-Fenton reactor was designed to degrade a model organic pollutant of methylene blue (MB), in which the synthetic wastewater flowed through the modified graphite felt cathode and the perforated DSA anode sequentially, companying the pumped air. The objective of work was to investigate the feasibility and advantage of this novel reactor, and to reveal the important parameters affecting the treatment performance such as current density, pH, initial Fe^{2+} concentration and flow rate. Characterized by scanning electron microscopy (SEM), nitrogen adsorption-desorption study and contact angle, a possible mechanism for the high H_2O_2 production with low energy on the modified cathode was presented. Moreover, the treatment performance was evaluated by five more organic pollutants, confirming this novel flow-through E-Fenton process owned great potential in wastewater treatment.

2. Experimental

2.1. Chemicals and materials

All chemicals used in this study were analytical grade and used as received without further purification. The graphite felts (Shanghai Qijie Carbon Material Co., Ltd.) and carbon black (Shanghai Hesen Electric Co., Ltd.) was used for cathode preparation. The MB (Beijing Solarbio Co., Ltd.) which was widely used in textile industry and as biological stain was regarded as the target pollutant. Orange II (OG), tartrazine, 2,4-dichlorophen (2,4-DCP), tetracycline (TC) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd and acetylsalicylic acid (ASA) was purchased from Shanghai Aladdin biological technology Co., Ltd. In all experiments, the electrolyte was 0.05 M Na_2SO_4 solution. H_2SO_4 (3 M) and NaOH (1 M) were used to adjust the pH of solution. $FeSO_4 \cdot 7H_2O$ was applied as Fenton catalyst. All experiments were operated at room temperature.

2.2. Flow-through E-Fenton reactor

Fig. 1 shows the schematic diagram of the flow-through E-Fenton reactor. In anodic area, a perforated DSA anode (1) was connected with a titanium ring (2) for electrical connectivity, and a insulating rubber rings (3) was used for sealing to prevent the wastewater flow out from the edge of the electrode. Under the anodic area and closed to the influent, it was the modified graphite felt cathode (4) with carbon black and polytetrafluoroethylene (PTFE), which was prepared as that in previous study [8]. The perforated DSA with same area (φ 3 cm) with IrO_2 and RuO_2 coating was used as anode (Baoji Changli Co. Ltd) and the holes (φ 2 mm) distributed evenly on it. The distance of the cathode and anode was 8 mm.

In the flow-through experiment, the influent and pumped air flowed through the cathodic area including (4), (2), (3) and the
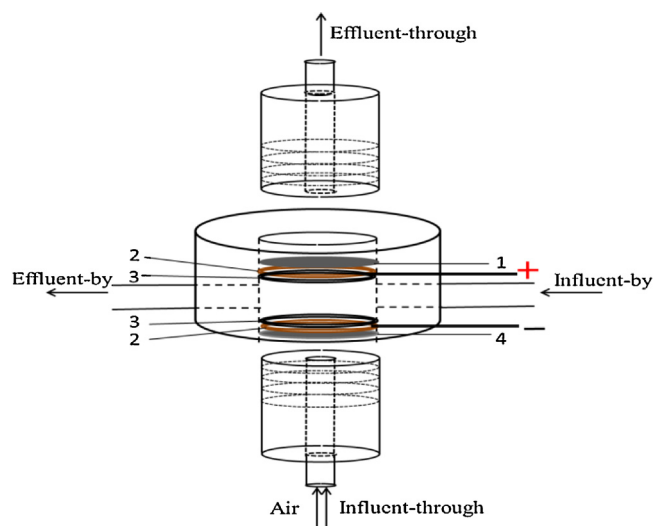

Fig. 1. The schematic diagram of the reactor consisting of (1) a perforated DSA anode, (2) the titanium ring, (3) the insulating rubber ring, (4) the modified graphite felt cathode.

anodic area including (3), (2), (1) sequentially. In the flow-by experiment, the influent flowed by the electrode parallel as signed in Fig. 1. The flow direction was the only difference in the above two systems. The reactor was a beaker with 150 mL solution and kept the same electrode gap using the similar electrode in the regular system. All the operational conditions including the cell potential and pumped air rate, were identical to flow-through and flow-by experiment. All interval samples were taken from the exit of the reactor.

2.3. Analytic methods

The concentration of H_2O_2 was measured using the method of potassium titanium (IV) oxalate by UV–vis spectrophotometer (UV759, Shanghai Instrument Analysis Instrument Co., LTD.). The MB concentration was also analyzed by the same spectrophotometer above at the wavelength of 664 nm. The total organic carbon (TOC) is measured by TOC analyzer (Analytikjena multi N/C 3100, Germany). The current efficiency of H_2O_2 generation was calculated by the following formula (3) [6]:

$$CE(\%) = \frac{nFCV}{\int_0^t I dt} \times 100\% \tag{3}$$

where n is the number of electrons transferred for oxygen reduction for H_2O_2, F is the Faraday constant (96,485 C/mol), C is the concentration of H_2O_2 (mol/L), V is the bulk volume (L), I is the current (A), and t is the electrolysis time (s).

The electric energy consumption (EEC) was calculated by the following formula (4) [21]:

$$EEC(kWh/kgTOC) = \frac{1000 U I t}{V \Delta(TOC)_{exp}} \tag{4}$$

Where U is the voltage (V), I is the applied current (A), t is the electrolysis time (h), V is the volume (L) and $\Delta(TOC)_{exp}$ is the experimental TOC removal (mg/L).

The residence time (T) was calculated by the following formula (5):

$$T(s) = \frac{60 S L}{J} \tag{5}$$

Where S is the electrode area (cm^2), L is the electrode gap (cm), J is the flow rate (mL/min).