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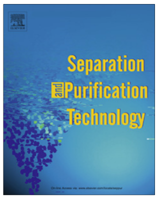

A dual-cell wastewater treatment system with combining anodic visible light driven photoelectro-catalytic oxidation and cathodic electro-Fenton oxidation

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ABSTRACT

In this study a dual-cell wastewater treatment system was constructed by coupling anodic photoelectrochemical/electro-Fenton (PEC) cell and cathodic electro-Fenton (EF) cell (D-PEC-EF), with the Bi_2WO_6 nanoplates deposited on fluorine-tin oxide glass as the anode (Bi_2WO_6/FTO) and Fe@Fe_2O_3 core–shell nanowires supported on activated carbon fiber (Fe@Fe_2O_3/ACF) as the gas diffusion cathode. The two separated cells could degrade rhodamine B (RhB) simultaneously and thus enhance the degradation efficiency and the TOC removal significantly in comparison with that of counterpart single-cell PEC-EF system (S-PEC-EF) because of more hydrogen peroxide electro-generated on the Fe@Fe_2O_3/ACF cathode by photo-generated electrons transferred from the Bi_2WO_6/FTO anode and less hydrogen peroxide consumed by anodic oxidation owing to the partition of two cells, which enhanced both PEC and EF oxidation ability and improved both photocatalytic quantum efficiency and overall current efficiency significantly. This study could not only provide a high effective and energy-saving advanced oxidation technology for wastewater treatment, but also deepen understanding of the synergic effect in dual-cell electrochemical process.

1. Introduction

The disposal of toxic and hazardous materials requires new technologies [1]. Advanced oxidation technologies (AOTs), which involved an *in situ* generation of highly potent chemical oxidants such as hydroxyl radicals ($^{\cdot}OH$), are regarded as an important class of technologies for non-selective oxidation of organic pollutants [2]. In view of their high cost and high energy consumption, it is still a great challenge to develop novel AOTs system for organic wastewater treatment.

Among AOTs, electrochemical oxidation has attracted a lot of attention due to its convenience, high efficiency and environmental compatibility [1–4]. Various electrochemical processes have been developed to decompose refractory organic pollutants that cannot be eliminated biologically. Among them, anodic oxidation method might be the earliest and most extensively used one [5]. Most of organics can be oxidized by the direct oxidation over the anode. However, the anodic oxidation technology suffers from the generation of more toxic and refractory intermediates [1]. Photocatalysis (PC) is promising for elimination of environmental pollutants, and many studies demonstrated that photo-electrochemical (PEC) combining electrochemical and photocatalytic processes can improve the photooxidation technique for wastewater purification effectively by decreasing the recombination of photogenerated charge carriers [6–10]. Later studies have demonstrated that applying a bias potential could decrease the recombination of photogenerated electron–hole pairs, and subsequently improve the efficiency of oxidizing organic contaminants, while the toxic and refractory intermediates generated during electrochemical oxidation could be decomposed by hydroxyl radicals from photocatalysis [11–16].

As a widely used AOT, Fenton reaction between ferrous iron and hydrogen peroxide could treat wastewater effectively [2,17]. However, high cost of H_2O_2 restricts its large scale application in wastewater treatment. Therefore, the electro-Fenton (EF) process based on cathodically generated hydrogen peroxide (H_2O_2) was developed to overcome high cost of the added H_2O_2 [1,18–21]. During the electro-Fenton process, H_2O_2 is continuously supplied to the contaminated solution via the two-electron reduction of oxygen (Eq. (1)), and then react with the added or *in situ* generated Fe^{2+}

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to form hydroxyl radicals (Eq. (2)), which could destruct refractory organic pollutants and even be applied for industrial wastewater treatment [20,22,23]. Although the extent of the reaction and the amount of hydrogen peroxide can be precisely controlled in this EF technique, the pollutant degradation is relatively slow due to the low concentration of electro-generated H_2O_2 [18].

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\cdot}OH + H_2O \quad (2)$$

EF oxidation is generally performed in conventional single-cell reactor [1,18], where H_2O_2 produced at the cathode in the single-cell system would diffuse to the anode and thus be destroyed there, leading to low treatment efficiency and high power input. In order to prevent the transportation of H_2O_2 to the anode, scientists turn to design dual-cell system (or dual electrode oxidation system) through separating the anode and cathode by using a membrane or an electrolyte bridge. Higher treatment efficiency could thus be obtained in the dual electrode oxidation system through simultaneous direct oxidation in the anodic cell and indirect Fenton oxidation in the cathodic cell [24].

Bi_2WO_6 is reported to be a promising photocatalyst because of its unique properties such as semiconductivity, photostability, chemical inertness, and environmentally friendly features [26–28], and it is also a superior candidate of photoelectrode during the treatment of organic pollutants [29,30]. Previously, in our group, a Bi_2WO_6/ITO nanoplate film electrode for PEC oxidation of Rhodamine B was prepared [25], and a novel iron reagent, core–shell Fe@Fe_2O_3 nanowires was also synthesized as to degrade RhB and pentachlorophenol in different Fenton systems including sono-Fenton [31–34] and EF systems using Fe@Fe_2O_3/ACF or Fe@Fe_2O_3/CNT/PEFE composite cathodes [35,36]. Recently, a photo-electrochemical/electro-Fenton oxidation system by coupling visible light driven photo-electrochemical oxidation (PEC) and electro-Fenton oxidation (EF) in a single cell (S-PEC-EF) and was reported, in which we found that the coupling of PEC and EF could enhance the degradation and the instantaneous current efficiencies (ICE) because of better separation of photo-generated carriers in the photo-anode and the transfer of photo-electrons to the oxygen diffusion cathode to generate more H_2O_2 and hydroxyl radicals on the Fenton cathode [37]. Liu et al. also designed a novel three-dimensional electro-Fenton system for wastewater treatment in which foam nickel particle electrodes could active molecular oxygen and generate more H_2O_2 and hydroxyl radicals [38]. This study demonstrated that coupling an anodic PEC cell with Bi_2WO_6/FTO anode and a cathodic EF cell with Fe@Fe_2O_3/ACF composite cathode with a salt bridge in two separated cells (D-PEC-EF) could further enhance both PEC and EF oxidation ability and thus improve both photocatalytic efficiency and overall current efficiency significantly. This D-PEC-EF system exhibited a high instantaneous current efficiency with a small electrode area and low potential. The reasons for the oxidation enhancement of D-PEC-EF were investigated in detail.

2. Experimental section

2.1. Chemicals

$Bi(NO_3)_3{\cdot}5H_2O$, Na_2WO_4, $NH_3{\cdot}H_2O$, H_2O_2, NaOH, Na_2SO_4, $FeCl_3{\cdot}6H_2O$, $NaBH_4$, NaOH, H_2SO_4 and other chemicals were all of analytical grade and purchased from Shanghai Chemical Reagents Company. Active carbon fiber (ACF) and titanium mesh were purchased from China Southern Chemicals Import and Export Corporation. Commercially available RhB was chosen as the model pollutant compound. Fluorine-tin oxide (FTO) glass with a thickness of 1.1 mm and a sheet resistance of 15 Ω/cm^2 employed as a substrate was purchased from China Southern Class Co. Ltd. The FTO glass was cleaned by sonication in acetone, ethanol, and deionized water for 30 min, respectively. All chemicals were used as received without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of the Bi_2WO_6/FTO nanoplate film photo-anode

The Bi_2WO_6/FTO film anode was prepared according to our previous report [25]. Typically, the FTO glass (2.0 cm × 1.5 cm) was rinsed in an ultrasonic bath with distilled water for 15 min, and then cleaned by immersing in a mixture solution of $NH_3{\cdot}H_2O$ and H_2O_2 for 20 min at 80 °C. The volume ratio of NH_3:H_2O_2:H_2O was 20:40:100. After the rinsing procedure was repeated, the FTO glass was finally dried in air. The Bi_2WO_6 particles were synthesized hydrothermally as follows: $Bi(NO_3)_3{\cdot}5H_2O$ and Na_2WO_4 with an equal molar stoichiometry were first dissolved in 75 mL of distilled water. After stirring for 15 min, the solution was then transferred into a 100-mL autoclave with a Teflon liner. The autoclave was maintained at 150 °C for 24 h and then air-cooled to room temperature. The yellow precipitate was collected and washed with deionized water thoroughly and then dried at 100 °C for 5 h. The Bi_2WO_6 nanoplate film electrode was prepared by a spin coating method. Typically, a 0.1 g of as-prepared Bi_2WO_6 powder and 0.5 mL of water was milled in the glass mortar for 10 min; then 0.5 mL of terpineol was added to the resulting slurry and mixed by milling until Bi_2WO_6 particle was well dispersed. The final suspension was dropped on the surface of the FTO glass to obtain Bi_2WO_6/FTO electrode through spin coating at 2400 rpm for 1 min (ART MICCRA D-3/PA). The Bi_2WO_6/FTO electrode was dried in air at 50 °C for 2 h and then calcined at 450 °C for 2 h.

2.3. Preparation of the Fe@Fe_2O_3/ACF composite cathode

The composite cathode was prepared by loading core–shell Fe@Fe_2O_3 nanostructures on ACF according to our previous reports [31,36]. Typically, 0.3 g of $FeCl_3{\cdot}6H_2O$ and 0.6 g of $NaBH_4$ were dissolved in 100 mL of distilled water to obtain ferric solution and $NaBH_4$ solution, respectively. After 20 min sonication of ACF (1.5 cm × 2 cm) in the resulting ferric solution, the $NaBH_4$ solution was dropped into the ferric solution to reduce ferric ions into metallic iron on ACF. The Fe@Fe_2O_3/ACF composite electrode was washed with deionized water thoroughly and then dried in nitrogen for further use. 0.1 g L^{-1} of Fe@Fe_2O_3 loading on the ACF was used in each experiment. The Fe@Fe_2O_3/ACF composite electrode was fixed with titanium mesh before use.

2.4. Configuration of D-PEC-EF System

The D-PEC-EF system was constructed by combining two cells connected by a saturated KCl salt bridge, as shown in Fig. 1a. Two semi-circular quartz glass cylinders with 7 cm in height and 7 cm in diameter were used as the reactors, and a CHI-660B electrochemical system (Shanghai, China) was used as the potentiostat at room temperature. The light source (300 W tungsten halogen lamp, $\lambda > 420$ nm) was fixed outside the reactor against photoelectrode surface about 15 cm in distance. For comparison, the counterpart single-cell system (S-PEC-EF) was constructed where both anode and cathode are placed in the same electrolytic cell (Fig. 1b).

2.5. RhB degradation

Degradation of RhB with initial concentration of 1.044×10^{-5} M was performed in the D-PEC-EF system using a Bi_2WO_6/FTO photo-electrochemical anode (1.5 cm × 2 cm) and a Fe@Fe_2O_3/