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In situ generation of H_2O_2 using MWCNT-Al/O_2 system and possible application for glyphosate degradation

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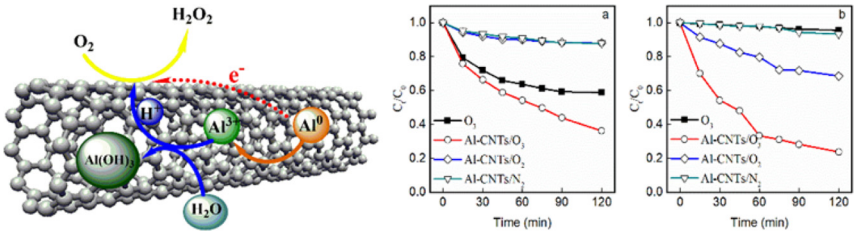
HIGHLIGHTS

- Al-CNTs composite was prepared by high-energy ball milling and sintering process.
- The accumulative concentration of H_2O_2 reached 947 mg/L in Al-CNTs/O_2 system.
- In situ generated H_2O_2 could be used for the degradation of glyphosate.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen peroxide (H_2O_2), as a green oxidant, has been widely applied into advanced oxidation processes (AOPs) for the degradation of toxic organic pollutants. The in situ generation of H_2O_2 can not only improve the storage and transportation safety of H_2O_2 but also reduce the capital and operation costs. In the present work, a novel system, i.e., multi-walled carbon nanotube aluminum (MWCNT-Al) composite was used to in situ generate H_2O_2 through micro-electrolysis. The MWCNT-Al composite was characterized and optimized. The accumulation concentration of H_2O_2 reached 947 mg/L at the initial pH of 9.0, the MWCNT-Al composite dosage of 8 g/L and oxygen gas flow rate of 400 mL/min after 60 min. The in situ generation of H_2O_2 was achieved by MWCNT-Al/O_2 system, mainly owing to the direct contact between Al^0 and MWCNT in MWCNT-Al composite, which accelerated the transfer of electrons from Al^0 to O_2, as well as the excellent electrocatalytic activity of MWCNT toward the two-electron reduction of oxygen. When H_2O_2 in situ generation technology was used in peroxone process (O_3/H_2O_2 process) to degrade glyphosate in aqueous solution, the removal efficiency of TOC and total phosphorus was 68.35% and 73.27%, respectively. Finally, the possible mechanism of in situ generation of H_2O_2 in MWCNT-Al/O_2 system was temporarily proposed.

1. Introduction

Advanced oxidation processes (AOPs) that use hydroxyl radical (•OH) with redox potential of 2.80 eV as principal active species for the degradation and mineralization of refractory pollutants are considered as promising methods of wastewater treatment (Wang and Xu, 2012; Wang and Bai, 2017). Hydrogen peroxide (H_2O_2) is used for •OH generation in many AOPs, such as H_2O_2/UV, H_2O_2/Fe^{2+}, H_2O_2/O_3, etc. (Neyens and Baeyens, 2003; Wan and Wang, 2016; Tang and Wang, 2018). In these H_2O_2-based AOPs, the potential safety risks from the transportation, and storage process of commercially available and concentrated H_2O_2 have received increasing attention due to its chemical instability (Asghar et al., 2015; Zhang et al., 2018). Therefore, a technology that can generate H_2O_2 in situ would be highly desirable.

Among various alternative approaches for the in situ generation of H_2O_2, the reduction of O_2 to H_2O_2 is the most attractive because O_2

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can be obtained conveniently from air. Many reducing agents have been used for the in situ generation of H_2O_2, such as hydrogen, hydrogen substituted organic compounds, photoelectron, cathode of electrochemical or microbial fuel cells, active metals, etc. (Asghar et al., 2015; Edwards et al., 2015; Fu et al., 2010; Annabi et al., 2016; Trovó et al., 2009; Luo et al., 2015; Yalfani et al., 2011; Liu et al., 2017). The direct reaction of hydrogen and oxygen to H_2O_2 is conceptually the most straightforward, however, there is potential problem of operational safety due to the wide explosive range of H_2/O_2 mixtures (Liu et al., 2018a). Hydrogen substituted organic compound such as hydrazine, formic acid and hydroxylamine has been suggested to overcome the shortcomings of direct method (Yalfani et al., 2011). However, incomplete conversion of organic compound may increase the toxicity of the treated wastewater and the decomposition of H_2O_2 over catalyst surface may decrease the process efficiency (Liu et al., 2018b). The photochemical reactions of semiconductors (ZnO, TiO_2 etc) can produce electrons and holes. The electron as a reducing agent, helps to the production of H_2O_2 and the holes helps to the degradation of organic contaminant (Hu et al., 2018; Clarizia et al., 2017). However, it cannot be considered as an alternative for in situ H_2O_2 generation because of its intensive energy demand (Asghar et al., 2015). The electrochemical synthesis via a 2-electron oxygen reduction reaction (ORR) on suitable cathode was confirmed to be more effective in H_2O_2 generation rate and O_2 utilization efficiency. The accumulation of H_2O_2 could reach 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 (Yu et al., 2015). The in situ generation of H_2O_2 in microbial fuel cells can reduce the intense energy requirement by the production of electricity (Zhuang et al., 2010; Chen et al., 2014). However, a lot of inorganic electrolyte was required in electrochemical system and many nutrient substances must be provided for microbial fuel cells. Active metals such as zinc, aluminum and iron have been known as an attractive reducers for reducing oxygen into H_2O_2 because of its simple steps and no extra cost on material and energy (Keenan and Sedlak, 2008; Fan et al., 2015; Wen et al., 2014). However, the maximal concentration of H_2O_2 was only 180 μM in Al/O_2 system at 250 min (Fan et al., 2015), which limited its application in the wastewater treatment.

The electrochemical corrosion theory implies that when the metals contact directly with other conducting material, with higher electrode potential, the galvanic-type corrosion cell will be formed, which will accelerate the corrosion rate of metal and most of the depolarizing agent reduction on the surface of metal will be transferred to cathode. Based on this theory, our group has successfully prepared zinc carbon nanotubes (Zn-CNTs) composite and used it to generate H_2O_2 in situ. The results showed that the maximum cumulative concentration of H_2O_2 in Zn-CNTs/O_2 system was 293.51 mg/L under the initial pH 3.0, Zn-CNTs dosage 2 g/L and O_2 flow rate 400 mL/min, which was 15 times of zinc alone (Gong et al., 2018). Aluminum has lower electrode potential and more abundant storage in the earth than zinc. The fresh aluminum compound produced by the corrosion of aluminum has strong flocculation properties and the ability of precipitation to remove phosphorus. Therefore, multi-walled carbon nanotubes-Al (MWCNT-Al) composite may have greater potential than Zn-CNTs composite for the in situ generation of H_2O_2 and for the removal of toxic contaminants from the wastewater.

Glyphosate (*N* (phosphonomethyl) glycine) is an organophosphorus compound, which has been extensively used as herbicide (Lan et al., 2016; Wang et al., 2016). Glyphosate has been classified as "probably carcinogenic in humans", which can cause a variety of symptoms including eye and skin irritation, contact dermatitis, eczema, cardiac and respiratory diseases and allergic reactions (Hu et al., 2011).

In this paper, we synthetized MWCNT-Al composite for the first time by high-energy ball milling and sintering the mixture of aluminum and MWCNT directly. XRD, SEM, EDS and Raman were used to characterize the as-prepared MWCNT-Al composite. The catalytic performance of MWCNT-Al composite for the in situ generation of H_2O_2 under oxygen aeration was investigated. Meanwhile, the effects of operational factors, such as the initial pH in solution, operating temperature and MWCNT-Al composites dosage, on the in situ generation of H_2O_2 were also discussed. The in situ generated H_2O_2 was used to peroxone process (O_3/H_2O_2 process) for the degradation of glyphosate in aqueous solution Glyphosate was selected as the model pollutant due to its high toxicity and extensive application (Koskinen et al., 2016; Ibáñez et al., 2005).

2. Experimental

2.1. Materials

All chemicals and reagents in this study were of analytical reagent grade or better and commercially available. Polyethylene glycol (4000) and aluminum powder were provided by the National Medicines Corporation Ltd., China. Hydroxylated multiwalled carbon nanotube (MWCNT) was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. Deionized (DI) water was used in all experiments. Glyphosate [*N* (phosphonomethyl) glycine] ($C_3H_8NO_5P$) was a sigma Aldrich product (≥99.0% purity).

2.2. Synthesis of MWCNT-Al composite

The synthesis procedure of MWCNT-Al composite was optimized and the final parameters for composite production were as follows: polyethylene glycol (4000), aluminum powder and MWCNT with given mass ratio (4:1–15:1) were mixed in a 500 mL ball mill tank and the powder mixtures were ball milled for 4 h via rotating at 400 rpm, using a ball-to-powder weight ratio of 91:1. All powder handling was carried out under argon atmosphere to minimize oxidation. The as-received and milled MWCNT/Al mixture was collected and transferred to combustion tube, and then heat-treated at the given temperature (500 °C–900 °C) in tube furnace for 1 h. The heating rate was 5 °C/min, and the high-purity argon as protective gas had a flow rate of 60 mL/min. After the sintering at high temperature, the obtained sample was cooled down to room temperature with continuous argon. Then it was ground into powder and labeled as MWCNT-Al.

2.3. Characterization of MWCNT-Al composite

Scanning electron microscope (SEM, JSM-7500F, Jeol, Japan) equipped with an energy-dispersive spectrometer (EDS, X-Max50, Oxford, England) was employed to measure the surface morphology and components of the obtained MWCNT-Al composite at an acceleration voltage of 20.0 kV. The surface was investigated by EDS in the scanning range of 0–4000 eV. X-ray diffraction (XRD) was carried out using a diffractometer (BrukeD8 Adv., Germany) with a filtered Cu Kα radiation source (λ = 1.54178 Å). Raman spectra were measured by a Laser Confocal Micro-Raman Spectroscopy (LabRAM HR800, France) using a continuous-wave He-Ne laser with an excitation wavelength of 632.8 nm and maximum power of 5 mW at the sample.

2.4. The generation and measurement of H_2O_2

The experiments for the in situ generation of H_2O_2 were carried out in a 250 mL glass beaker containing 150 mL of solution under oxygen aeration. A stirrer was put into the reactor at a constant rate of 300 rpm in order to facilitate convection. Prior to the experiment, the desired initial pH of the solution was adjusted using HCl (0.1 M) or NaOH (0.1 M) solution. Samples were taken and filtered by 0.20 μm filter membrane to determine the concentrations of the H_2O_2 or aluminum ion at pre-set intervals time. The concentration of generated H_2O_2 was detected by a photometric method, which used potassium titanium oxalate as chromogenic reagent and performed on an UV–vis spectrometer (Alpha-1500, Shanghai, China) at 400 nm. The concentration of aluminum (Al^{3+}) in solution was measured by inductively