Research article

Fenton-like oxidation of 4-chlorophenol using H_2O_2 in situ generated by Zn-Fe-CNTs composite

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ABSTRACT

In this paper, a zinc-iron-carbon nanotubes (Zn-Fe-CNTs) composite was prepared, characterized and used to develop a Fenton-like system of Zn-Fe-CNTs/O_2 for the degradation of 4-chlorophenol (4-CP), in which H_2O_2 was generated in situ from zinc-carbon galvanic cells and oxygen in aqueous solution was activated by iron attached on the surface of CNTs to produce ·OH radicals for the oxidation of 4-CP. The experimental results showed that the particles of Zn and Fe in Zn-Fe-CNTs composite were adhered to the surface of CNTs, which accelerated the electron transfer process. The BET area of Zn-Fe-CNTs composite was 32.9 m^2/g. The contents of Zn and Fe (% w) in the composite were 44.7% and 4.2%, respectively. The removal efficiency of 4-CP and TOC in Zn-Fe-CNTs/O_2 system was 90.8% and 52.9%, respectively, with the initial pH of 2.0, O_2 flow rate of 800 mL/min, Zn-Fe-CNTs dosage of 1.0 g/L, 4-CP concentration of 50 mg/L and reaction time of 20 min. Based on the analysis of the degradation intermediate products with LC-MS and IC, a possible degradation pathway of 4-CP in Zn-Fe-CNTs/O_2 system was proposed.

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1. Introduction

Hydrogen peroxide (H_2O_2) is a strong oxidant with the standard potential of 1.80 and 0.87 V at pH 0 and 14, respectively (Campos-Martin et al., 2006; Pu Rtolas et al., 2015). H_2O_2 is widely used in environmental protection, particularly in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, chlorine, etc (Campos-Martin et al., 2006). The use of H_2O_2 is regarded as an environmentally friendly wastewater treatment method since the end products of H_2O_2 decomposition were water and oxygen. However, H_2O_2 alone is not effective for the treatment of high concentration of certain refractory contaminants such as highly chlorinated aromatic compounds (Neyens and Baeyens, 2003). Improvements can be achieved by using transition metal salts (e.g. iron salts) or ozone and UV-light to activate H_2O_2 and form hydroxyl radicals (·OH) with redox potential of 2.80 V, which can oxidize many organic contaminants rapidly (Pera-Titus et al., 2004; Wang and Xu, 2012). Oxidation process with activation of H_2O_2 by iron salts, classically

referred to as Fenton reagent, has gained attention because of rapid formation of ·OH at ambient temperature and pressure (Mirzaei et al., 2017; Wang and Wang, 2016, 2018). However, the high cost of industrial grade H_2O_2 (c.a. $390–500 per ton) and the potential risk associated with the transport, handling and storage of bulk quantities of H_2O_2, have made the process unsafe and economically challenging (Asghar et al., 2015). One way to overcome this problem is the use of in situ generated H_2O_2 for Fenton process as an alternative to pre-manufactured H_2O_2 (Yalfani et al., 2010; Santana Martínez et al., 2016).

The reduction of oxygen by certain reducers has been used for in-situ generation of H_2O_2 in aqueous solution, such as hydrogen (Lunsford, 2003), zero valent iron (Fe^0) (Chang et al., 2009), electrons present in conductive band (Liu et al., 2015), cathode of electrolytic cell (Pizzutilo et al., 2017) and cathode of microbial fuel cells (Fu et al., 2010). The direct synthesis of H_2O_2 from hydrogen and oxygen must deal with the risk of explosion of hydrogen/oxygen mixture (Lunsford, 2003). Although, hydrazine, formic acid and hydroxylamine as hydrogen substitutes for H_2O_2 production can overcome the limitations encountered in hydrogen direct reduction method, incomplete conversion of organic compound in the H_2O_2 production process may increase the toxicity of the treated wastewater (Choudhary and Jana, 2007; Yalfani et al., 2011). The iron species for transformation of oxygen into H_2O_2 include
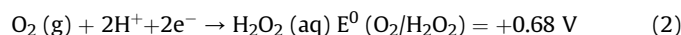
iron pyrite, magnetic nano-particles, zero valent iron (Fe^0) and Fe^{2+} (Borda et al., 2003; Chang et al., 2009; Fang et al., 2013). The H_2O_2 generated in-situ can react with iron species in bulk medium to produce ·OH through Fenton reaction. In-situ H_2O_2 production by iron catalyzed process is also cost-effective due to the advantage of forming Fenton oxidation system in itself. The in-situ generation of H_2O_2 by photocatalysis (Zhang et al., 2006; Liu et al., 2015) or electrochemical oxidation process (Panizza and Cerisola, 2009; Zhang et al., 2012; Pizzutilo et al., 2017) is not economically viable, which requires intense energy consumption (Mehrjouei et al., 2014). Microbial fuel cells can provide an environmental friendly and cost-effective solution for in-situ H_2O_2 production, but it needs to be further explored to increase the H_2O_2 production efficiency (Rozendal et al., 2009; Fu et al., 2010). Therefore, the concept of in-situ generation of H_2O_2 requires further research to optimize the methodology.

Currently, many researchers focus on the in-situ generation of H_2O_2 by internal micro-electrolysis (IME) process. IME is believed to operate on a principle very similar to that of the traditional electrolysis, except that the electrons are supplied from the galvanic corrosion of many micro-scale sacrificial anodes instead of external power (Cheng et al., 2007; Ying et al., 2013). Fe-based catalysts are widely used in the advanced oxidation processes (AOPs) for the water and wastewater treatment (Su et al., 2016; Wang and Bai, 2017). In the case of the Fe^0/C IME system, when a mixture of iron chips and carbon particles are in contact with wastewater, numerous microscopic galvanic cells are formed between the particles of iron (anode) and carbon (cathode) because of their electrode potential difference (Fan et al., 2009; Qin et al., 2012; Lai, 2013; Wu et al., 2013; Lu et al., 2016; Singh et al., 2016). The in situ generation of H_2O_2 can be obtained by Fe^0/C IME process in the presence of O_2, which can be described as follows:

Iron anode (oxidation):

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E^0 (Fe^{2+}/Fe) = -0.44\,V \quad (1)$$
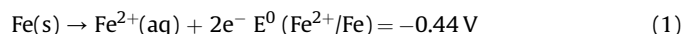
Carbon cathode (reduction):

$$O_2\,(g) + 2H^+ + 2e^- \rightarrow H_2O_2\,(aq) \quad E^0 (O_2/H_2O_2) = +0.68\,V \quad (2)$$

The generated H_2O_2 subsequently combines with Fe^{2+}, forming Fenton's reagent that is capable of oxidizing contaminants in the wastewater (Ying et al., 2012; Zhu et al., 2014; Wu et al., 2016). However, the concentration of H_2O_2 generated in situ was still low according to previous researches (below 9×10^{-6} M with DO concentration of 9 mg/L and carbon nanotubes as cathode) (Zhang et al., 2013). The efficiency of these IME-Fenton reactors is also unsatisfied. For example, about 50% COD removal efficiency was obtained by an iron-mediated aeration reactor (Deng and Englehardt, 2008). Therefore, it is necessary to develop an efficient IME process to generate sufficient amount of H_2O_2 in situ (Liu et al., 2012).

Zinc is an earth abundant element and zero-valent zinc (Zn^0) is a strongly reducible metal. The standard electrode potential of Zn^{2+}/Zn was -0.76 V, which is lower than that of Fe^{2+}/Fe (-0.44 V). This suggests that Zn^0 has stronger reduction ability for O_2 than Fe^0. Moreover, the in-situ generation of H_2O_2 by the reaction between Zn^0 and O_2 were confirmed by Wen et al. (2014) and Liu et al. (2016). Based on the electrochemical corrosion theory, the rate of redox reactions occurred on the surface of metal could be accelerated in the galvanic-type corrosion cell. Therefore, the H_2O_2 yield from the reduction of O_2 in Zn^0/C corrosion cell may be higher than that of Fe^0/C corrosion cell. Zn^0/C corrosion cell may be a promising material for efficient IME process to generate H_2O_2 in situ.

Chlorophenol, such as 4-chlorophenol (4-CP), is widely applied as fungicide and in a wide range of other products, including oils, adhesives, textiles, leather and pharmaceutical products, which is a toxic and recalcitrant contaminant and often used as model contaminant. Various technologies have been used for the degradation of 4-CP in wastewater (Kuo and Wu, 2010; Kurian and Nair, 2015).

The objective of this study was to investigate the performance of Zn^0–carbon galvanic cells for the in situ generation of H_2O_2 in the presence of O_2. The in situ generated H_2O_2 was applied in the degradation of 4-CP through a Fenton-like reaction. Zn-Fe-CNTs composite was synthesized and characterized by TEM, XRD, XPS and N_2 adsorption/desorption experiment. The efficiency of this Fenton-like process was evaluated by means of 4-CP degradation. The effect of several parameters including initial concentration of 4-CP, initial pH and Zn-Fe-CNTs dosage on 4-CP removal was examined. A possible degradation pathway of 4-CP by the Fenton-like process and the reaction mechanism were proposed.

2. Materials and methods

2.1. Chemicals

Hydroxyl-containing multi-walled CNTs ($d < 8$ nm, $l = 10-30\,\mu m$) (Beijing deke daojing Nano-Company, China), polyethyleneglycol 4000 (National Medicines Corporation Ltd., China), 4-chlorophenol (Sigma-Aldrich Corporation Ltd., China), Zinc powder (Shandong Xiya, Corporation Ltd., China) and other reagent, including H_2SO_4, NaOH, $FeSO_4 \cdot 7H_2O$ and $C_4K_2O_9Ti \cdot 2H_2O$, and H_2O_2 used in this study were all analytical grade and provided by National Medicines Corporation Ltd., China. HPLC-grade acetonitrile (Merck) and formic acid (Fluka) were used for HPLC analyses and HPLC-MS analyses.

2.2. Preparation and characterization of Zn-Fe-CNTs

Zn-Fe-CNTs composite was prepared by the infiltration fusion followed by chemical precipitation. Briefly, CNTs particles, zinc powder and 40% w polyethyleneglycol 4000 solution with the mass ratio of 1:3:2 were mixed together. The obtained slurry was then dried at room temperature under argon atmosphere. The dried solid sintered in the tube furnace at 550 °C for 120 min with the heating rate of 10 °C/min and the N_2 flow rate of 60 mL/min. The obtained precursor was then slow cooling to room temperature and marked as Zn-CNTs. 1.0 g of Zn-CNTs was added into a four-necked flask containing 100 mL of 1% w $FeSO_4 \cdot 7H_2O$ solution with violent stirring under Ar protection at 25 °C. After 1 h of reaction, solid-liquid separation was employed and the solid was washed with oxygen-free deionized water for three times, and dried in a vacuum freeze dryer. Fe-CNTs was prepared by the same method as Zn-CNTs.

Transmission electron microscopy (TEM) (HRTEM, JEM 2100 and JEOL) was used to investigate the microstructure of the as prepared composites. The Brunauer, Emmett and Teller (BET) surface area was determined using Nova 3200e Surface area instrument and the pore-size distribution was obtained using the Barrett, Joyner and Halenda (BJH) equation. X-Ray diffraction (XRD) patterns were obtained via a D8-Advancediffraction meter at 40 kV and 40 mA employing Cu Kα radiation and step-scanning over the 2θ range 10–90°. The measurement of X-ray photoelectron spectroscopy (XPS) was carried out using an AXIS-Ultra instrument (Kratos Analytical, UK) with monochromatic Al Kα radiation (225 W, 15 mA, 15 kV).