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An integrated catalyst of Pd supported on magnetic Fe_3O_4 nanoparticles: Simultaneous production of H_2O_2 and Fe^{2+} for efficient electro-Fenton degradation of organic contaminants

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ABSTRACT

A novel electro-Fenton process based on Pd-catalytic production of H_2O_2 from H_2 and O_2 has been proposed recently for transforming organic contaminants in wastewaters and groundwater. However, addition of Fe(II) complicates the operation, and it is difficult to recycle Pd catalyst after treatment. This study attempts to synthesize an integrated catalyst by loading Pd onto magnetic Fe_3O_4 nanoparticles (Pd/MNPs) so that H_2O_2 and Fe^{2+} can be produced simultaneously in the electrolytic system. In an undivided electrolytic cell, phenol, a probe organic contaminant, is degraded by 98% within 60 min under conditions of 50 mA, 1 g/L Pd/MNPs (5 wt% Pd), pH 3 and 20 mg/L initial concentration. The degradation rate peaks at pH 3, increases with increasing Pd loading and electric current and decreases with increasing initial concentration. A distinct mechanism, reductive dissolution of solid Fe(III) in Fe_3O_4 by atomic H chemisorbed on Pd surface, is responsible for Fe^{2+} production from Pd/MNPs. The efficiency of phenol degradation can be sustained at the same level for ten times of repeated treatment using the Pd/MNPs catalyst. The variations of main crystal structure and magnetic property of catalysts are minimal after treatment, but low concentrations of Pd leached, which needs further evaluation.

1. Introduction

Chemical oxidation has been extensively used for wastewater treatment and groundwater remediation. Among all the oxidants, Fenton reagents (dissolved Fe^{2+} and H_2O_2) are particularly powerful for degrading recalcitrant organic pollutants due to formation of nonselective hydroxyl radicals (•OH, oxidation potential: 2.8 V) by Reaction 1 (Gogate and Pandit, 2004; Neyens and Baeyens, 2003; Pignatello et al., 2006). However, it is expensive and dangerous for the production, transportation and storage of H_2O_2. In recent decades, electro-Fenton (E-Fenton) process has attracted great interests (Brillas et al., 2009; Feng et al., 2010; Gözmen et al., 2003; Liu et al., 2007; Yuan and Lu, 2005; Zhang et al., 2006) because H_2O_2 can be continuously produced in situ from the two-electron reduction of O_2 on the cathode under acidic conditions

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(Reaction 2). By the addition of Fe^{2+}, H_2O_2 is decomposed to •OH (Reaction 1), which oxidizes or even mineralizes organic contaminants. Nonetheless, the efficiency of H_2O_2 production is highly dependent on the type of cathode materials. Effective production of H_2O_2 needs relatively expensive gas diffusion electrodes (Brillas et al., 2009), which have low mechanical stability. Moreover, Fe^{2+} addition and pH adjustments, i.e., acidification and neutralization before and after treatment, complicate the implementation process and increase the cost.

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + {\bullet}OH + H_2O \quad (1)$$

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

Recently, a novel E-Fenton process, termed Pd-based E-Fenton, was developed based on Pd-catalytic production of H_2O_2 from electro-generated H_2 and O_2 (Yuan et al., 2011, 2012, 2013; Liao et al., 2013). Water electrolysis produces O_2 and H^+ on the anode (Reaction 3), while produces H_2 and OH^- on the cathode (Reaction 4). Under acidic conditions, H_2O_2 is produced from the combination of H_2 and O_2 on the surface of Pd catalyst (Reaction 5) (Edwards et al., 2009; Samanta, 2008). In the presence of Fe^{2+}, •OH is produced by Reaction 1. To avoid pH adjustments by the addition of acids and bases, the authors configured a special three-electrode system, in which locally acidic conditions automatically developed in the degradation zone (Yuan et al., 2013; Liao et al., 2013). This process has shown high performance on degrading many organic contaminants including rhodamine B, trichloroethyelene, phenol and toluene in wastewater and groundwater (Yuan et al., 2011, 2012, 2013). The barriers of this Pd-based E-Fenton process include the recycle of Pd catalysts and the supply of appropriate concentrations of Fe(II). It is difficult to recycle the expensive Pd catalysts because they were supplied in the form of powder Pd/Al_2O_3 or Pd/C. In addition, Fe^{2+} was added manually in the form of ferrous salts. A low concentration of Fe^{2+} limits the production of •OH from H_2O_2 (Yuan et al., 2012), while a high concentration of Fe^{2+} compete with contaminants for •OH (Reaction 6, Brillas et al., 2009). It is difficult to provide the appropriate concentration of Fe^{2+} for contaminant degradation by manual addition of ferrous salts, particularly for the in situ groundwater remediation. Thus, it is essential to synthesize an integrated catalyst supplying both Pd and Fe with recyclability.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)$$

$$H_2 + O_2 \xrightarrow{Pd} H_2O_2 \quad (5)$$

$$Fe^{2+} + \quad (6)$$

In recent years, there has been an increasing use of magnetic nanoparticles (MNPs) for water treatment (Tang and Lo, 2013; Teja and Koh, 2009). Magnetite (Fe_3O_4) is one of the most widely used MNPs. Fe_3O_4 MNPs have been widely used as adsorbents for contaminants removal from wastewaters and groundwater (Tang and Lo, 2013; Yang et al., 2010; Zhang et al., 2011) and support of catalysts in environmental applications (Alvarez et al., 2010; Hildebrand et al., 2009; Salehizadeh et al., 2012) because they are porous and can be easily recycled by magnetic separation. Fe_3O_4 MNPs also catalysed H_2O_2 decomposition in Fenton-like processes due to the existence of surface Fe(II) and the leaching of soluble Fe^{2+} (Matta et al., 2007; Rusevova et al., 2012). Therefore, it is rational to hypothesize that supporting Pd on Fe_3O_4 MNPs (Pd/MNPs) can simultaneously catalyse the production of H_2O_2 from H_2 and O_2 by the component of Pd as well as the decomposition of H_2O_2 to •OH by the component of iron. Furthermore, the magnetic property of Pd/MNPs provides a possible approach to recycling the catalyst after treatment.

In this study, a new integrated catalyst of Pd/MNPs containing both Pd and Fe with magnetic property is synthesized and characterized. The performance of this new catalyst on simultaneously producing H_2O_2 and Fe^{2+} is evaluated for the Pd-based E-Fenton degradation of organic contaminants. Using phenol as a probe organic contaminant, the effects of operation parameters including solution pH, Pd loading in Pd/MNPs, electric current and initial contaminant concentration are investigated. The mechanisms of production of Fe^{2+} and reactive oxidizing species (ROS) are elucidated. Ultimately, repeated degradation of phenol was conducted using recycled Pd/MNPs. It is mainly aimed to provide an integrated catalyst for the simultaneous production of H_2O_2 and Fe^{2+} in the Pd-based E-Fenton process.

2. Methods and materials

2.1. Chemicals

Phenol (>99.5%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Rhodamine B (RhB), methyleneblue (MB) and isopropanol of analytic grade were supplied by Guoyao Group Chemical Reagent Co. Ltd., China. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was provided by Aldrich. Palladium acetate was purchased from Shanxi Kaida Chemical Reagent Co. Ltd., China. Pd/Al_2O_3 powder (5% wt. Pd, Shanxi Kaida Chemical Ltd, China), with particle size of 1.5–5 μm, was used for comparison. Deionized water (18.0 mΩ cm) was obtained from a Millipore Milli-Q system and used in all the experiments. All other chemicals used in this study were higher than analytical grade.

2.2. Synthesis of Pd/MNPs catalyst

For the synthesis of Pd/MNPs catalyst, 0.6951 g of $FeSO_4 \cdot 7H_2O$ and 1.3500 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 100 mL of deionized water. The mixture was slowly added by 20 mL of ammonia solution under vigorous stirring conditions. Upon completion of the reaction, the suspended solution was filtered. The precipitates were washed with deionized water for several times until neutral. A magnet was used to separate the particles during washing. The obtained MNPs were dried under vacuum at 40 °C overnight. Pd was then supported onto the as-synthesized MNPs through the following procedure.