



Technical Note

Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide

Libing Chu^a, Jianlong Wang^{a,b,*}, Jing Dong^a, Haiyang Liu^a, Xulin Sun^c

^a Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China

^b Beijing Key Laboratory of Fine Ceramics, Tsinghua University, Beijing 100084, PR China

^c Air Liquide (China) Holding Co. Ltd., Shanghai 200233, PR China

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ABSTRACT

In this study the treatment of coking wastewater was investigated by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Particular attention was paid to the effect of initial pH, dosage of H₂O₂ and to improvement in biodegradation. The results showed that higher COD and total phenol removal rates were achieved with a decrease in initial pH and an increase in H₂O₂ dosage. At an initial pH of less than 6.5 and H₂O₂ concentration of 0.3 M, COD removal reached 44–50% and approximately 95% of total phenol removal was achieved at a reaction time of 1 h. The oxygen uptake rate of the effluent measured at a reaction time of 1 h increased by approximately 65% compared to that of the raw coking wastewater. This indicated that biodegradation of the coking wastewater was significantly improved. Several organic compounds, including bifuran, quinoline, resorcinol and benzofuranol were removed completely as determined by GC–MS analysis. The advanced Fenton oxidation process is an effective pretreatment method for the removal of organic pollutants from coking wastewater. This process increases biodegradation, and may be combined with a classical biological process to achieve effluent of high quality.

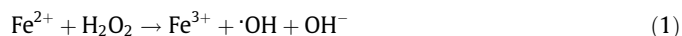
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1. Introduction

Coal is the major energy resource in China. Recently, due to rapid economic development, the amount of coke produced has increased significantly. Coking wastewater from coal coking, coal gas purification and by-product recovery processes in the coke plant has become one of the most severe environmental problems in China. According to the 2009 environmental statistics, the amount of wastewater COD discharged from the coke industry accounted for 1.3% of the total discharged COD in China (SEPA, 2009). The coking wastewater is a complex cocktail of individual pollutants comprising hundreds/thousands of organic pollutants including phenolics, cyanide, ammonia, polynuclear aromatic hydrocarbons and nitrogen-, oxygen- and sulfur-containing heterocyclic compounds (Wang et al., 2002). Most of the compounds in the coking wastewater are highly concentrated, toxic, mutagenic and carcinogenic and may have long-term environmental and ecological impacts.

The treatment processes used for coking wastewater generally include pretreatment involving steam stripping and solvent extraction, followed by biological treatment involving anoxic–oxic,

anaerobic–anoxic–oxic and activated sludge processes (Li et al., 2011; Wang et al., 2011). The presence of refractory and inhibitory compounds was found to inhibit the efficiency of anaerobic digestion and make the coking wastewater recalcitrant to biological degradation (Lai et al., 2009). In some cases, advanced oxidation processes (AOPs) are considered as effective alternatives for converting the bio-refractory contaminants into less harmful or lower chain compounds which can then be treated biologically (Ruppert et al., 1994; Esplugas et al., 2002). AOPs are based on the formation of highly reactive hydroxyl radical. Among the AOPs, the Fenton process is one of the most promising processes due to its advantages which include the use of inexpensive chemicals, ease of operation and high oxidation performance (Chakinala et al., 2008). One of the disadvantages of this process is the large amount of Fe(II) salts added which can result in troublesome sludge problems (Namkung et al., 2008).

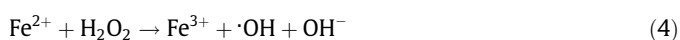
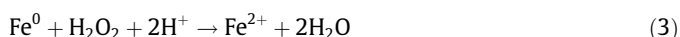
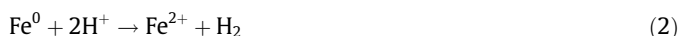


The conventional Fenton reaction uses hydrogen peroxide in conjunction with iron(II) salts under acidic conditions to produce highly reactive hydroxyl radicals which can oxidize organic compounds in solution (Eq. (1)). Recently, studies have been carried out to enhance the classical Fenton oxidation process (Doong and Chang, 1998; Lucking et al., 1998; Namkung et al., 2005;

* Corresponding author at: Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 62784843; fax: +86 10 62771150.

E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

Pignatello et al., 2006). One of the alternatives is the use of zero-valent iron to replace ferrous salts in the solution. The substitution of solid Fe(0) powder/grains for dissolved Fe(II)-salts entails the replacement of homogenous Fenton reaction by heterogenous type. The proposed reaction mechanism is shown in Eqs. (2)–(6) based on the Fenton reaction and iron-surface mediated reactions (Namkung et al., 2005). Initially iron metal is corroded in the presence of H₂O₂ under acidic conditions oxidizing Fe⁰ to Fe²⁺, which then further reacts with H₂O₂ in a Fenton-like process to generate hydroxyl radicals and Fe³⁺. The Fe⁰ then reduces the Fe³⁺ back to Fe²⁺ and the cycle continues (Chakinala et al., 2007). The particular advantages of this process are the cost-savings due to the use of metal iron compared to iron salts and the faster recycling of ferric iron at the iron surface (Eq. (5)).



Advanced Fenton processes based on the use of zero-valent iron and H₂O₂ have been reported in the degradation of phenolic compounds involving phenol and pentachlorophenol, dyes, insecticides such as parathion and some industrial wastewaters (Doong and Chang, 1998; Liao et al., 2007; Chakinala et al., 2008). Bremner et al. (2006) studied the degradation of phenol by using iron bars and H₂O₂. In the presence of metallic iron, acidic conditions and concentrated 9.5 M H₂O₂, almost 100% of phenol was removed after 15 min. The intermediates in oxidation were identified as catechol, hydroquinone and benzoquinone. Tang and Chen (1996) used iron powder and H₂O₂ to decolorize commercial dyes. They reported that this process was more favorable for decolorization of dye than Fenton reagent due to the continuous dissolution of iron and adsorption of dyes on the iron surface. Kallel et al. (2009) studied the degradation of olive mill wastewater using hydroxyl radicals generated from iron metal in a spiral form and H₂O₂. The optimal experimental conditions were found to be the continuous presence of iron metal, acidic pH (2.0–4.0), and relatively concentrated H₂O₂ (9.5 M). Coloration of olive mill wastewater disappeared and phenolic compounds decreased to 50% of the initial concentration after 3 h reaction time.

In this study, the application of advanced Fenton processes with zero-valent iron powder for the pretreatment of coking wastewater was investigated. We explored the interaction of iron powder and H₂O₂, the effects of initial pH and H₂O₂ dosage on the treatment performance in terms of COD and total phenol removal, and the evolution of biodegradation of the coking wastewater during the oxidation. The changes in composition of the coking wastewater during oxidation were identified qualitatively by GC–MS. With this information, the aim was to deepen our understanding of the advanced Fenton reaction in treating coking wastewater and provide a new alternative for the pretreatment method.

2. Materials and methods

2.1. Materials

The coking wastewater was obtained from a coke plant in northern China. Table 1 shows the characteristics of the coking wastewater after ammonia stripping. The wastewater was heavily colored with a high strength of COD. From GC–MC analysis,

Table 1
Characteristics of the raw coking wastewater.

Item	Value (mg L ⁻¹)
COD	7500–8400
Total phenol	1700–1900
Ammonium	400–480
Cyanide	7.5–8.5
pH	9.1–9.3

phenolic compounds including phenol, methyl phenol and dimethyl phenol were the major organic constituents.

Hydrogen peroxide (30%, w/v) and metallic iron powder were of analytical grade. The size of iron powder used was 30–70 μm and the purity was higher than 98%.

2.2. Experimental procedure

Experiments were performed in 500 mL Erlenmeyer flasks in batch mode. 50% sulfuric acid (v/v) was used to adjust the wastewater pH to the desired levels. Approximately 300 mL of coking wastewater plus iron powder were added to the reactors. Following the introduction of a volume of H₂O₂, the reactors were opened and placed in an air shaker at 150 rpm and 25 °C. Supernatant samples were taken periodically and pH, COD and total phenol concentrations were measured. Batch tests were carried out in duplicate.

2.3. Analytical methods

COD, phenol, ammonium and cyanide contents were determined according to Chinese SEPA standard methods (SEPA, 2002). TOC and TN were evaluated by a TOC analyzer (multi N/C 2100, Analytik Jena, Germany). pH was measured using an Orion model 868 pH meter. The surface morphology of the fresh and oxidized iron powder was examined by a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan).

In order to assess the effect of oxidation on biodegradation of the coking wastewater, the oxygen uptake rate (OUR) of the raw coking wastewater and oxidized effluent was determined using a Warburg respirometer (Yu et al., 1998; Mezzanotte et al., 2003). Effluent taken from the advanced Fenton reactors with reaction time up to 150 min was diluted to appropriate concentration about 500 mg COD L⁻¹ and then fed to the respirator reactors with a volume of 1 mL. During the OUR tests, the pH was maintained at

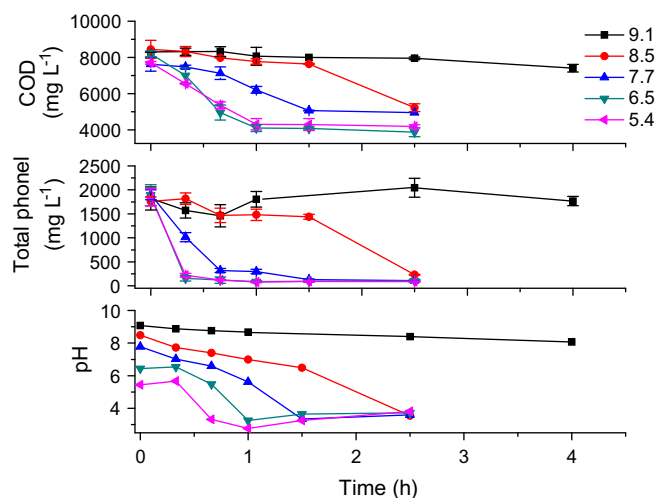


Fig. 1. Changes in pH and removal profile of COD and total phenol during oxidation at different initial pH values (iron powder 3.0 g L⁻¹, H₂O₂ 0.3 M).

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