Study of phenol removal using fluidized-bed Fenton process

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ABSTRACT

In this paper, the removal of phenol from simulated wastewater was studied using gas–liquid fluidized bed with the Fenton reagent. The factors that affect the removal rate of phenol were investigated, including the initial concentrations of hydrogen peroxide $[H_2O_2]$ and $[Fe^{2+}]$, the molar ratio of $[Fe^{2+}]/[H_2O_2]$, pH value, temperatures, reaction time, and the ventilation volume. It was found that the optimal operating conditions existed as: $[H_2O_2] = 12\,mmol/L$, $[H_2O_2]/[Fe^{2+}] = 4:1$, pH = 4, $T = 60\,°C$, reaction time of 30 min, and a ventilation volume of $0.12\,m^3/h$. Under these conditions, the phenol removal rate of about 96% was obtained.
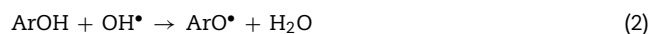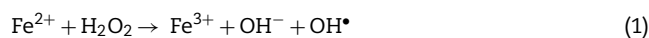
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1. Introduction

Advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing hazardous and recalcitrant organic compounds such as pesticides, surfactants, and pharmaceuticals and endocrine disrupting chemicals. They have also been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes. A great number of methods are classified under the broad definition of AOPs based on the oxidizing agents applied. Most of them use a combination of strong oxidizing agents (e.g. H_2O_2, O_3) with catalysts (e.g. transition metal ions) and irradiation (e.g. ultraviolet, visible). Among these methods, The Fenton process has been one of the most popular technologies for wastewater treatment (Neyens and Baeyens, 2003; Anotai et al., 2009; Brillas and Casado, 2002; Alnaizy and Akgerman, 2000; Masomboon et al., 2009; Huling et al., 2007, 2008; Huiling et al., 2000, 2001; Wang et al., 2010). However, the Fenton process produces a large amount of ferric hydroxide $(Fe(OH)_3)$ sludge, which requires additional separation and disposal. The disadvantages limit the further application of the Fenton process in treating wastewater. Therefore, the fluidized-bed Fenton process has been developed to reduce the production of iron sludge (Anotai et al., 2010).

The main mechanism of the Fenton process is the generation of highly reactive free radicals – hydroxyl radicals (HO•), which are derived from the ferrous catalyzed H_2O_2 (Walling, 1973). Hydroxyl radicals (HO•) are effective in destroying organic chemicals. Once generated, the hydroxyl radicals can attack organic chemicals by radical addition, hydrogen abstraction and electron transfer to degrade macromolecules into small organic or inorganic molecules, such as CO_2 and H_2O. The detail mechanism was proved to be as the following (Ma et al., 2009):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

$$ArOH + OH^\bullet \rightarrow ArO^\bullet + H_2O \qquad (2)$$

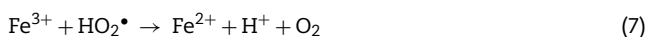$$ArO^\bullet + Fe^{3+} \rightarrow Fe^{2+} + products \qquad (3)$$

According to the above mechanisms, the hydroxyl radicals from depleted H_2O_2 have been used for the oxidation of organic substances. In general, a high concentration of H_2O_2 can improve the organo-oxidation to form low carbon chemicals. Gogate and Pandit (2004a,b) reported that the efficiency of the oxidation process is affected by a solution's pH, temperature, H_2O_2 concentration, the concentration of Fe^{2+}, and the initial concentration of the contaminants. They also found

that there is an optimum concentration ratio between $[Fe^{2+}]$ and $[H_2O_2]$ to maximize the phenol removal rate. Any excess of either $[Fe^{2+}]$ or $[H_2O_2]$ reduced the efficiency of the reaction due to side reactions. The excessive $[H_2O_2]$ reacts further with $OH^{\bullet}$ radicals to form a new radical $HO_2^{\bullet}$, which dramatically decreases the $OH^{\bullet}$ radical concentration in solution. Similarly, excessive amount of $[Fe^{2+}]$ also has the scavenging action to $OH^{\bullet}$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{4}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{5}$$

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^{+} + HO^{\bullet} \tag{6}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \tag{7}$$

Phenol has been chosen as the model pollutant in this study because it is one of the most prevalent forms of toxins and weakly biodegradable chemical pollutants from industrial activities. It is considered as an important raw material for organic synthesis, and widely used in industrial manufacturing processes (Huling et al., 2008; Ma and Peng, 2007; Zhang et al., 2006a,b). Since phenol is highly toxic, carcinogenic, teratogenic, and potentially mutagenic to gene structures, many countries in the world have put identified phenol as a primarily controlled pollutant in water (Ma et al., 2009; Basso and Cukierman, 2005). The content of phenols ranges from 0.12–4.2 mg/L in leather industrial wastewater, up to a high concentration of 700–12,000 mg/L in ammonia industrial wastewater. To effectively remove phenols from wastewater pollution is one of the most important issues in environmental protection. Currently, methods to remove phenol from wastewater include physical adsorption method (Prez et al., 2002; Wang et al., 2008), chemical oxidation (Temmink and Grolle, 2005; Fang et al., 2006; Zhang et al., 2006a,b; Comninellis et al., 2008; De et al., 1999; Esplugas et al., 2002; Joglekar et al., 1991; Santos et al., 2006; Rubalcaba et al., 2007), and biological treatment (Stone, 1987; Li et al., 1998), and so on. In the oxidation wastewater treatment, the organic molecules are decomposed in a relatively short period of time into CO_2, H_2O and other small molecules or low molecular weight inorganic compounds. The characteristics of the oxidation method include high rate and no secondary pollution. It also overcomes the drawback of the long treatment time in biological treatment, and it has become the primary technique in phenol removal from wastewater.

The Fenton technologies such as photo-Fenton, electron-Fenton, and fluidized-bed Fenton processes have been already investigated for degradation of a number of organic pollutants (Huling et al., 2008; Anotai et al., 2010; Lu et al., 2005; Anotai et al., 2006; Brillas et al., 1996). Multiphase gas–liquid–solid fluidized-bed reactors have been widely used in all types of research such as physics, chemistry, energy, environment, medicine, and materials. The advantages of the fluidized-bed reactors have been proved as its excellent mass and heat transfer characteristics, high rates of reaction resulting from the close contact between the different phases, and the continuous operation (Katsuhiko and Fan, 1985). The application of fluidized-beds in the oxidation treatment of phenol removal in wastewater has not been studied extensively. Therefore, this study researched the effects of concentration of reactants including ferrous, hydroperoxide,
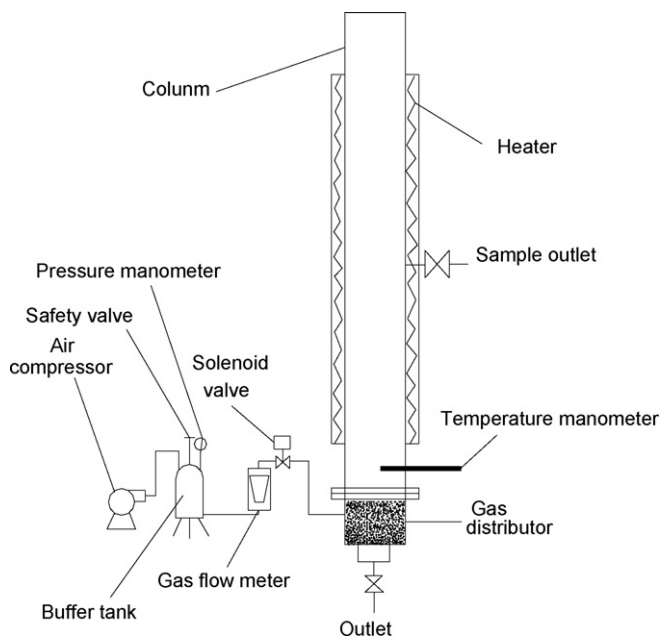

Fig. 1 – Schematic diagram of the experimental apparatus.

the pH of the solution, and other reaction conditions on the oxidation efficiencies of phenol in a simulated wastewater using a self-made gas–liquid fluidized-bed with the Fenton process.

2. Experimental

2.1. The apparatus

The experimental apparatus included a self-designed gas–liquid–solid fluidized-bed reactor, as shown in Fig. 1. The reactor is composed of a plexiglass column with a diameter of 40 mm and a height of 1500 mm. It is equipped with a gas–liquid distributor at the bottom, and a round water bath surrounding the column. The gas–liquid distributor is connected to the gas compressor through a gas flow meter. A buffer tank is also included to prevent backflashing of air and fluid in the reactor. Air flows through gas–liquid distributor to the reaction column to form air bubbles in diameter of about 1–2 mm.

Other equipment and chemicals included S22-type spectrophotometer, WM-2H-type oil-free air compressor, PH3-3C pH meter; $FeSO_4 \cdot 7H_2O$, 30 wt% H_2O_2, and phenols. All chemicals are analytically pure.

2.2. Experimental methods

The simulated wastewater was prepared in the laboratory with a concentration of the phenol of 100 mg/L. After the cylinder reached constant temperature, the oxidant was added, and the pH of the solution was adjusted to a pre-determined value. Air was then compressed through and flew through the bottom of the column, and the flow rate was adjusted to form bubbles with diameters of 1–2 mm. Samples were taken as predetermined intervals, and the phenol content was analyzed using 4-amino-antipyrine spectrophotometric measurement.