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Degradation of acetaminophen by Fenton and electro-Fenton processes in aerator reactor

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ABSTRACT

This study investigated the degradation of acetaminophen (ACTP) in the Fenton and electro-Fenton processes in an aerator reactor. The influences of important parameters on acetaminophen degradation were studied and described in details. The experimental results show that the Fenton and electro-Fenton processes had maximum ACTP degradation efficiencies of 99% and 100%, respectively. The ACTP degradation efficiency of Fenton process and electro-Fenton process were apparently increased at pH 2 and 4, respectively; ACTP degradation efficiency increased 72% at pH 2 in the Fenton process and 74% at pH 4 in the electro-Fenton process when fixed H_2O_2 dosage (15 mM) and Fe^{2+} dosage was increased from 0.01 to 0.1 mM. The Box–Behnken design results indicated that the relative effects of the studied parameters on ACTP degradation in Fenton and electro-Fenton processes were $Fe^{2+} > H_2O_2 > pH$. The initial rate of ACTP degradation (r) and ACTP degradation efficiency in the electro-Fenton process were apparently higher than those in the Fenton process at pH 2, as a high H_2O_2-to-Fe^{2+} molar ratio (1500) was used. The COD and TOC obtained by electro-Fenton process were 12% and 65% higher, respectively, than those in the Fenton process.

1. Introduction

Huge amounts of commercial pharmaceuticals are used worldwide for medical and agricultural purposes. A current environmental issue is the effects of pharmaceuticals and personal care products (PPCPs). Human use of PPCPs results in excretion of unchanged constituents of PPCP through urine and faeces or as metabolites via municipal sewage systems. The PPCPs have been detected in waste streams and effluents from hospitals, wastewater treatment plants and livestock [1–3] and are considered a major emerging contaminant [4].

The various treatment technologies for removing or degrading PPCPs include advanced oxidation processes (AOPs) [5], which were defined in a 1987 study by Glaze et al. [6]. These processes generate hydroxyl radicals ($^{\cdot}OH$) [7–9], which are powerful nonselective oxidants. Therefore, they can oxidize and mineralize almost all organic compounds into CO_2 and inorganic ions [10–14]. A common AOP is the Fenton process, which is initiated by hydroxyl radicals formation during a Fenton reaction (Eq. (1)) [15].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad k_1 = 70\ M^{-1}\ S^{-1} \tag{1}$$

In an acidic medium, this serial complex reaction generates the radicals shown in the following equations:

$$^{\cdot}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad k_2 = 3.2 \times 10^8\ M^{-1}\ S^{-1} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad k_3 = 0.001 - 0.01\ M^{-1}\ S^{-1} \tag{3}$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + {}^{\cdot}O_2H \tag{4}$$

$$Fe^{2+} + {}^{\cdot}O_2H \rightarrow Fe^{3+} + HO_2^- \quad k_5 = 1.3 \times 10^6\ M^{-1}\ S^{-1} \tag{5}$$

$$Fe^{3+} + {}^{\cdot}O_2H \rightarrow Fe^{2+} + O_2 + H^+ \quad k_6 = 1.2 \times 10^6\ M^{-1}\ S^{-1} \tag{6}$$

$$^{\cdot}OH + H_2O_2 \rightarrow H_2O + {}^{\cdot}O_2H \quad k_7 = 3.3 \times 10^7\ M^{-1}\ S^{-1} \tag{7}$$

$$^{\cdot}OH + \text{organics} \rightarrow H_2O + \text{production} \tag{8}$$

In the Fenton process, the ferrous ion (Fe^{2+}) dosage is added to catalyze hydroxy peroxide (H_2O_2), which generates ferric hydroxide sludges that require an additional separation process and disposal. Application of the electrochemical method in Fenton process, which is known as the electro-Fenton (EF) process, can be performed in three ways [16]. The first approach is to apply ferrous ions so that hydrogen peroxide and ferrous ion are concurrently generated at the cathode. The second approach is to apply hydrogen peroxide and use an iron anode as a ferrous ion source

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[16] or to electrogenerate ferrous ion by reducing ferric hydroxide sludge [17]. The third approach is to electrogenerate ferrous ion and hydrogen peroxide at a sacrificial anode and cathode, respectively [18]. The studies have shown that toxic and refractory organics including dyes in wastewater can be destroyed by the electro-Fenton application [19,20].

In the pharmaceuticals and personal care industries, acetaminophen paracetamol (ACTP) is among the most used and abused drugs in the world today. Recent studies have attempted to use AOPs for acetaminophen treatment [21–25]. These works have shown that electro-Fenton process can regenerated Fe^{2+} at the cathode, which also minimizes sludge production. However, no studies have compared acetaminophen degradation between Fenton and electro-Fenton processes. This study therefore compared acetaminophen degradation, chemical oxygen demand (COD) and total organic carbon (TOC) between the Fenton and electro-Fenton processes under similar batch mode experimental conditions. The Box–Behnken statistical design was applied to determine the optimum conditions for acetaminophen degradation.

2. Materials and methods

2.1. Materials and reactor

Acetaminophen ($C_8H_9NO_2$, Merck), hydrogen peroxide (H_2O_2, 35%, Merck), and ferrous sulfate hepta-hydrated ($FeSO_4{\cdot}7H_2O$, Merck) were reagent grade and used without further purification. Fig. 1 presents the Fenton and electro-Fenton which were contained in a Plexiglas reservoir with dimensions of 21.5 × 15 × 25 cm^3 with a volume of 8 L. Both processes were performed at room temperature in bath mode. To improve agitation, the stirrer was replaced by an aerator at the bottom of the reactor. Sludge was removed through an outlet inside the reactor. The anodes and cathodes were mesh-type titanium metal coated with IrO_2/RuO_2 and stainless steel, respectively. Both the cathode and anode had a working area of 300 cm^2 (20 cm × 15 cm). The electrodes were connected to a Topward 33010D power supply operated at the desired electric currents.

2.2. Experimental method

Synthetic wastewater containing 5 mM acetaminophen was prepared in the reactor. The pH was then adjusted to a predetermined value (2–4) by adding perchloric acid ($HClO_4$). After adding ferrous ions (0.01–0.1 mM) to the reactor, H_2O_2 (5–25 mM) was added to start the reaction. The experiment started when electrical power was switched on. The aerator at the bottom of the reactor was used to improve agitation. At selected time intervals, a 4 mL sample was taken from the reactor and immediately injected into a 1 M NaOH solution to terminate the reaction. Each sample was filtered through a 0.2 μm membrane filter to remove precipitates before analysis.

2.3. Analytical method

Acetaminophen concentrations were measured by high-performance liquid chromatography (HPLC) with a spectra system. A model SN4000 pump and an Asahipak ODP-506D column (150 mm × 6 mm × 5 μm) was used with a mobile phase of 85% ortho-phosphoric acid (H_3PO_4) and 15% acetonitrile (CH_3CN). The H_2O_2 concentration was measured by iodometric titration with $Na_2S_2O_3$ solution [26]. Design Expert 7 software (Stat-Ease, Inc., Minneapolis, USA) was used to determine the optimal parameters for acetaminophen removal. To prevent H_2O_2 concentrations from affecting the COD measurement, the samples were left overnight to eliminate residual hydrogen peroxide remaining in the sample solution. Chemical oxygen demand (COD) was determined using a closed reflux titrimetric method from the Standard Methods [27]. The TOC was analyzed using an Elementar-liqui TOC analyzer.

2.4. Box–Behnken design experiment

The effects of significant factors were tested by Box–Behnken design (BBD), a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial analysis. The analyzed factors and ranges were pH from 2 to 4, concentration of Fe^{2+} from 0.01 to 0.1 mM and H_2O_2 from 5 to 25 mM. For each factor, a high, moderate, and low value was designated 1, 0 and −1, respectively. Acetaminophen degradation was the selected response factor.

3. Results and discussion

3.1. Effect of operating parameters on acetaminophen degradation

The initial pH was limited to a range of 2–4. Fig. 2 shows how initial pH affected ACTP removal efficiency. At pH 2, ACTP removal efficiency increased with time and reached 91% at 90 min (Fig. 2a). The same trend was observed at pH 3 and 4. The ACTP removal efficiencies rapidly increased in first 10 min and then began to decrease after 10 min. At pH 3 and 4, removal efficiency approximated 80% at 10 min. The decreased ACTP removal efficiency at low pH probably resulted from formation of $Fe(OH)^+$, which showed more activity compared to Fe^{2+} in the electro-Fenton process. Compared to Fe^{2+}, $Fe(OH)^+$ has a slower reaction with H_2O_2. Therefore, H_2O_2 was slowly gradually consumed over time (Fig. 2b).

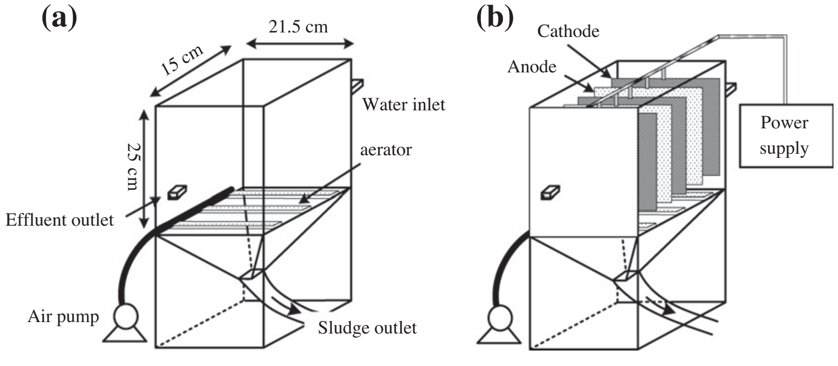

Fig. 1. Schematic diagram of (a) Fenton and (b) electro-Fenton reactors.