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Kinetics of acetaminophen degradation by Fenton oxidation in a fluidized-bed reactor

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HIGHLIGHTS

- Fluidized-bed Fenton process was used to treat synthetic acetaminophen solutions.
- The effects of Fe^{2+} dosage and $[Fe^{2+}]/[H_2O_2]$ (*FH* ratio) were integrated in the kinetic model.
- Acetaminophen degradation conformed to a pseudo reaction kinetics.
- A reaction pathway was proposed.

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ABSTRACT

Acetaminophen (ACT), an analgesic and antipyretic substance, is one of the most commonly detected pharmaceutical compound in surface waters and wastewaters. In this study, fluidized-bed Fenton (FB-Fenton) was used to decompose ACT into its final degradation products. The 1.45-L cylindrical glass reactor had inlet, outlet and recirculating sections. SiO_2 carrier particles were supported by glass beads with 2–4 mm in diameter. ACT concentration was determined by high performance liquid chromatography (HPLC). During the first 40 min of reaction, a fast initial ACT removal was observed and the "two-stage" ACT degradation conformed to a pseudo reaction kinetics. The effects of ferrous ion dosage and $[Fe^{2+}]/[H_2O_2]$ (*FH* ratio) were integrated into the derived pseudo second-order kinetic model. A reaction pathway was proposed based on the intermediates detected through SPME/GC–MS. The aromatic intermediates identified were hydroquinone, benzaldehydes and benzoic acids while the non-aromatic substances include alcohols, ketones, aldehydes and carboxylic acids. Rapid initial ACT degradation rate can be accomplished by high initial ferrous ion concentration and/or low *FH* ratio.

1. Introduction

Acetaminophen (ACT) is the main active ingredient of widely used analgesic and antipyretic drugs that can be purchased in most countries even without medical prescription. As unregulated trace pollutant from ng L^{-1} to μg L^{-1}, ACT is widely-present in the aquatic environment (Yang et al., 2008; Lin and Tsai, 2009). When ingested in therapeutic dosage, 58–68% of the original ACT compound is excreted by the body unaltered (Muir et al., 1997). The removal of ACT from contaminated waters by conventional biological treatment remains incomplete as several 100 ng L^{-1} of ACT continue to be detected in the final effluent (Jones et al., 2007).

Known for its powerful non-selective oxidizing agents called hydroxyl radicals (·OH), Fenton oxidation has been proven more effective than biological methods in degrading organic molecules including acetaminophen. Hydroxyl radicals can decompose ACT into simple and less harmful compounds within min to a few h (Zhang et al., 2008; Almeida et al., 2011; de Luna et al., 2012).

Organic pollutant degradation by Fenton oxidation is a multifaceted phenomenon (Masomboon et al., 2009), involving various interacting chemical species including the target compound, hydroxyl radicals, hydrogen peroxide, Fe^{2+} and Fe^{3+} among others. Despite its apparent complexity, Fenton oxidation has been modeled using simple pseudo first-order kinetics (Durán et al., 2011) and pseudo second-order kinetics (Chan and Chu, 2005) for the initial reaction time where rapid production of hydroxyl radicals (·OH) leads to faster pollutant degradation (Almeida et al., 2011; Zhang et al., 2011a, 2011b). Almeida et al. (2011) found that ACT

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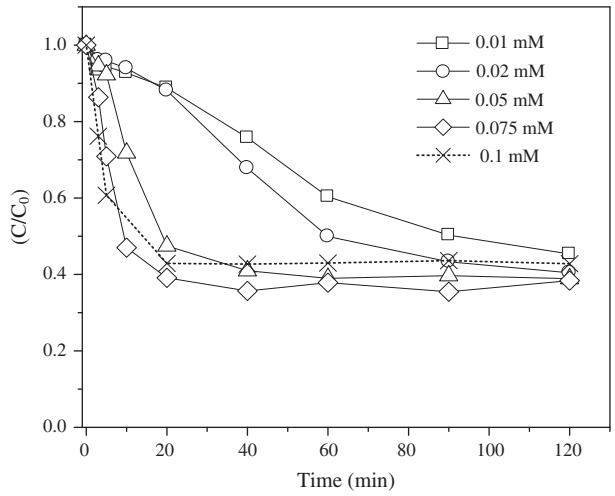

Fig. 1. Degradation profiles at varying [Fe^{2+}]: [ACT] = 5 mM, pH = 3 and [H_2O_2] = 5 mM.

decay via solar photoelectro-Fenton can be modeled using a pseudo-first order kinetics with a rate constant of 1.04×10^{-3} s^{-1}.

The primary intermediates of ACT oxidation include acetamide and aromatic compounds hydroquinone and *p*-benzoquinone. Prior to complete mineralization, the conjugated double bonds of the ring structures are subsequently subjected to additional radical attack resulting in the formation of dicarboxylic acids namely, ketomalonic, maleic, fumaric and oxalic acids while acetamide is converted into oxamic acid (Brillas et al., 2009).

In this study, ACT degradation in synthetic pharmaceutical wastewater was carried out via Fenton oxidation in a fluidized-bed (FB) reactor. Pseudo-reaction kinetics was used to model ACT degradation during the initial 40 min where rapid decomposition of ACT molecules was observed. The effect of initial ferrous ion concentration to hydrogen peroxide dosage (*FH* ratio) was analyzed and subsequently incorporated into the derived kinetic model. FH ranged from 0.0004 to 0.1. Within this range, an optimum FH ratio was observed wherein further increasing [Fe^{2+}] (causing FH ratio to increase) would cause ACT degradation to decrease. Also, [Fe^{2+}] is high enough (0.05–0.1 mM) wherein an initial rapid degradation was observed. In addition, a reaction pathway was proposed based on the intermediates identified during the various stages of ACT oxidation.

2. Materials and methods

2.1. Chemicals and analytical methods

All chemicals used were of reagent grade and purchased from Merck. All aqueous solutions were prepared using Millipore system deionized water with a resistivity of 18.2 MΩ cm. ACT concentration was determined with SpectraSYSTEM SN4000 HPLC equipped with Asahipak ODP-50 6D using 20 mM phosphoric acid and acetonitrile at 85:15 (v/v), flow rate of 1 mL min^{-1} and the detector set at 220 nm. Residual H_2O_2 was evaluated by the titanium oxalate method where absorbance was measured at 400 nm using a Thermo Spectronic Genesys 20 spectrophotometer. The intermediate analysis and identification were carried out through gas chromatography–mass spectrometry (GC–MS, Agilent Technologies, 7890A GC system/5975C MSD) with a flame ionization detector following the procedures from Möder et al. (1997) and Shoemaker et al. (1999). The solid-phase microextraction technique employed utilized polyacrylate and polydimethylsiloxane (PDMS) fibers purchased from Supelco.

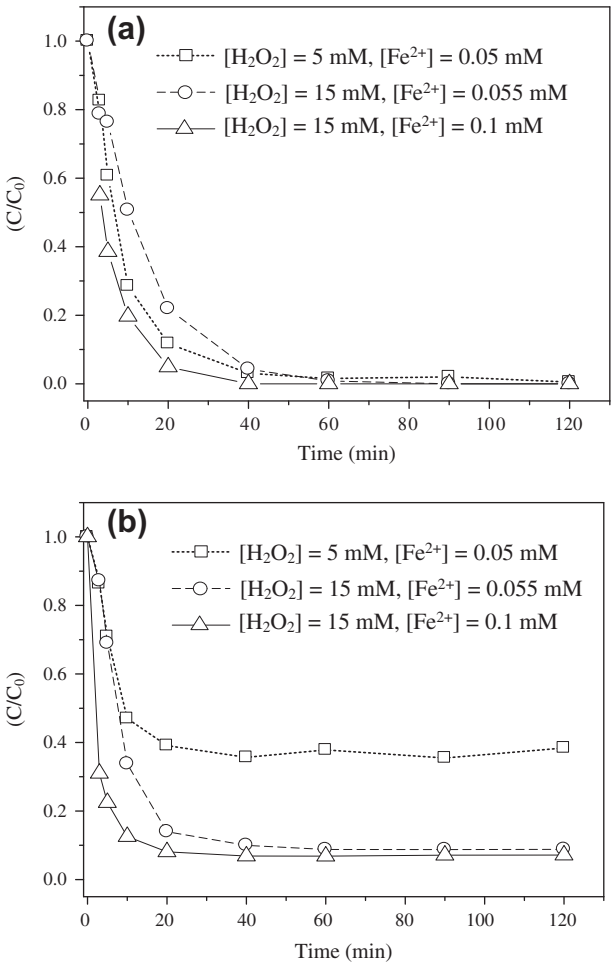

Fig. 2. (a) H_2O_2 and (b) ACT profiles for some runs at pH = 3 and [ACT] = 5 mM.

2.2. FB-Fenton experiments

The cylindrical glass reactor used in all FB-Fenton experiments had a working volume of 1.45-L and was equipped with a pH probe and a pump for recirculation and fluidization. Synthetic acetaminophen wastewater at 5 mM was poured into the reactor prior to pump operation and subsequent addition of known amount of $FeSO_4 \cdot H_2O$ as catalyst source. Glass beds of diameters 4 mm and 2 mm were added in sequence as support material for the 0.5-mm SiO_2 carriers. Initial pH was adjusted to 3 by either concentrated $HClO_4$ or 0.1 N NaOH. Fenton oxidation was initiated with a predetermined dose of hydrogen peroxide. Samples taken from the top of the reactor at various time intervals were mixed with NaOH to quench the Fenton reaction prior to chemical analysis.

3. Results and discussion

3.1. Two-stage ACT degradation

The blank experiment showed that the adsorption of acetaminophen in the fluidized-bed reactor was less than 5%. The result confirmed that acetaminophen could not be effectively removed under the fluidized-bed reactor without Fenton reagent. At low [Fe^{2+}] (<0.02 mM), ACT degradation proceeded in a single-stage as residual ACT concentration followed a steady decline (Fig. 1). In contrast, at ferrous ion dosage greater than 0.05 mM, ACT