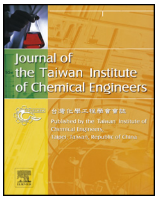
Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 565–570

Contents lists available at SciVerse ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice



Factors that influence degradation of acetaminophen by Fenton processes

Mark Daniel G. de Luna [a,b], Mersabel L. Veciana [b], James I. Colades [a], Chia-Chi Su [c], Ming-Chun Lu [c,*]

[a] Department of Chemical Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines
[b] Environmental Engineering Graduate Program, University of the Philippines, 1101 Diliman, Quezon City, Philippines
[c] Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 22 May 2013
Accepted 26 May 2013
Available online 28 June 2013

Keywords:
Advanced oxidation process
Acetaminophen degradation
Electro-Fenton
Photoelectro-Fenton

ABSTRACT

The effects of important parameters, Fe^{2+}, H_2O_2 and initial acetaminophen concentrations, on the initial rate and efficiency of ACT degradation in the electro-Fenton (EF) and photoelectro-Fenton (PEF) processes were investigated. The effect of organic acids on the degradation of ACT molecules was also studied. Experimental results show that the initial rate and removal efficiency of ACT in the EF and PEF processes varied insignificantly with Fe^{2+} concentration. The initial rate and removal efficiency of ACT in the PEF process were higher than those in the EF process. At a high initial ACT concentration, the initial rate of ACT degradation in the EF process was lower than that in the PEF process. Acetic acid improved ACT degradation efficiency while malonic and oxalic acids reduced it. Oxalic acid exhibited the strongest inhibitory effect, reducing ACT degradation efficiency by 18%. In the presence of oxalic acid in solution, EF yielded a degradation efficiency of 79%, which should be compared to efficiencies of 9% and 3%, for the fluidized-bed and conventional Fenton processes, respectively, showing that the EF process involves beneficial Fe^{2+} regeneration.

1. Introduction

Acetaminophen (ACT), more popularly known as paracetamol (n-acetyl-p-aminophenol), is the main component of various widely used antipyretic and analgesic drugs [1]. ACT molecules have been detected in the effluents of sewage treatment plants, and in both surface and drinking waters [2]. They have also been found to remain in bodies of water without degradation for 15 days [3]. ACT has been found in European Sewage Treatment Plant (STP) effluents with a concentration of 6–11.3 ppb [4]. Up to 6.8 ppb was detected in wastewater treatment plant (WWTP) influents Korea [5] and more than 65 ppb in UK Tyne river [6].

The inability of conventional biological methods to degrade completely pharmaceutical compounds, such as acetaminophen, has shifted the focus of research to more powerful treatment methods. The Fenton process, a well-established advance oxidation process (AOP), is known for its effectiveness in degrading a wide variety of organic pollutants [7]. The Fenton process, which is usually applied to wastewaters with COD concentrations from 100 mg/L to 5000 mg/L, generates hydroxyl radicals ($^{\bullet}OH$) from hydrogen peroxide (H_2O_2) in the presence of ferrous ions (Fe^{2+}) catalysts by Eq. (1) [2] even at normal temperature and atmospheric pressure [8].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad k = 53\text{–}76\,M^{-1}s^{-1} \tag{1}$$

Hydroxyl radicals are powerful non-selective oxidants with an oxidizing potential that is at least 50% greater than that of hydrogen peroxide (1.78 V) [9] and 40% greater than that of ozone [10]. These chemical species are highly energetic and reactive – vanishing as rapidly as they are formed [10]. The reaction of hydroxyl radicals with the target organic compound can result in its complete mineralization into simple and harmless products, following Eq. (2). The concentration of the produced hydroxyl radicals and the mass transfer of these species to organic molecules determine the extent of pollutant degradation [11]. The previous study shows that the acetaminophen was degraded efficiently in an aerated Fenton reactor [12].

$${}^{\bullet}OH + \text{organics} \rightarrow \text{products} \tag{2}$$

The propagation of the Fenton reaction relies on the conversion of excess ferric species into ferrous ions through their reaction with hydrogen peroxide, according to Eq. (3). The large difference between the rate constants of Eqs. (1) and (3) shows that ferrous ions are consumed more rapidly than they are formed. As a result,

---

* Corresponding author. Tel.: +886 6 2660489; fax: +886 6 2663411.
E-mail addresses: mmclu@mail.chna.edu.tw, mclu@ms17.hinet.net (M.-C. Lu).

1876-1070/$ – see front matter
http://dx.doi.org/10.1016/j.jtice.2013.05.020

the conventional Fenton process produces large amounts of ferric hydroxide sludge during the neutralization stage, requiring additional treatment and separation steps prior to sludge disposal [13].

$$\mathrm{H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+}, \qquad k = 0.01\,\mathrm{M^{-1}} \qquad (3)$$

The electro-Fenton (EF) process was developed to solve the above problem. In the EF process, electric current is applied to induce the reduction of ferric ions to ferrous ions on the cathode according to Eq. (4). Electric current in an EF system not only improves the regeneration of the catalyst and consequent sludge reduction but also enhances the generation of hydroxyl radicals that further degrade organic pollutants [14].

$$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} \qquad (4)$$

The EF reaction in the bulk solution with ultraviolet (UV) irradiation is called the photoelectro-Fenton (PEF) process. UV irradiation can result in increased hydroxyl radicals generation by the photo-reduction of $\mathrm{Fe(OH)^{2+}}$, which contains the $\mathrm{Fe^{3+}}$ species that predominates between pH 2 and 3 [15], according to Eq. (5) [16]. Another consequence of UV irradiation is the photolysis of the $\mathrm{Fe^{3+}}$ complex with generated carboxylic acids, according to Eq. (6) [16].

$$\mathrm{Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH} \qquad (5)$$

$$\mathrm{(RHCO_2) - Fe^{3+} \xrightarrow{h\nu} (RH^{\bullet}) + Fe^{2+} + CO_2} \qquad (6)$$

In this study, the effectiveness of the electro-Fenton (EF) and photoelectro-Fenton (PEF) processes in the treatment of pharmaceutical wastewater using acetaminophen as the model pollutant was investigated. The effects of the operating parameters – namely ferrous ions dosage, hydrogen peroxide dosage and initial ACT concentration – on ACT removal and the initial degradation rate of ACT were verified. The influences of organic acids such as oxalic, maleic, fumaric, malonic, acetic and formic acids on the treatment process were also examined.

2. Materials and methods

2.1. Chemicals and analytical methods

Acetaminophen ($\mathrm{C_8H_9NO_2}$, 99%, Merck), hydrogen peroxide ($\mathrm{H_2O_2}$, 35%, Merck) and ferrous sulfate heptahydrate ($\mathrm{FeSO_4 \cdot 7H_2O}$, Merck) were of reagent grade and used without further purification. Stock solutions were prepared using deionized water from a Millipore system with resistivity of 18.2 MΩ. The acetaminophen concentration was measured using a high-performance liquid chromatography (HPLC) with Spectra SYSTEM model SN4000 pump and an Asahipak ODP-506D column (150 mm × 6 mm × 5 mm), where the mobile phase was 60% acetonitrile with 40% DI water. Closed-reflux titration was used to measure the chemical oxygen demand (COD). Samples were stored for 12 h before COD analysis to eliminate the effect of residual hydrogen peroxide.

2.2. Experimental set-up

The 4 L electrochemical reactor (diameter: 13 cm and height: 35 cm) comprised two stainless steel cathodes with inside diameters of 2 cm and 13 cm, respectively, and a titanium-coated $\mathrm{RuO_2/IrO_2}$-coated DSA anode with an inside diameter of 7 cm. This reactor was operated in constant current mode. In the PEF process, the irradiation source was a set of 16 3 W UVA lamps (Sunbeamtech.com) that were fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate). Each UV lamp had a maximum wavelength of 360 nm. The same reactor was used by elsewhere by de Luna *et al.* used the same reactor [17].

2.3. Experiments using EF and PEF processes

Synthetic ACT-containing wastewater was treated by both EF and PEF processes. A predetermined amount of $\mathrm{FeSO_4 \cdot 7H_2O}$ was added to the ACT solution. The initial pH was adjusted using either concentrated $\mathrm{HClO_4}$ or 0.1 N NaOH. The simultaneous introduction of hydrogen peroxide and a constant current into the system initiated the EF reaction. All experiments were conducted at room temperature and were run for 2 h. Samples that were taken at specified time intervals were then mixed with NaOH and filtered using 0.2 μm filters to remove possible precipitates prior to chemical analysis. The same procedure as above was followed for PEF experiments with the addition of UV irradiation.

2.4. Interference studies

Oxalic, maleic, fumaric, malonic, acetic and formic acids are among the common intermediates that are formed during the degradation of organic pollutants by the Fenton reaction [17–21]. In this study, 1 mM organic acid was added to 5 mM acetaminophen-containing synthetic wastewater to examine the degradation of ACT.

3. Results and discussion

3.1. Effect of $\mathrm{Fe^{2+}}$, $\mathrm{H_2O_2}$ and ACT concentrations on ACT degradation

The effects of $\mathrm{Fe^{2+}}$, $\mathrm{H_2O_2}$ and ACT concentrations on ACT degradation were investigated and shown in Fig. 1. Continuous degradation was observed when a $\mathrm{Fe^{2+}}$ concentration of 0.01 mM was used in the EF process (Fig. 1(a)). The ACT degraded quite rapidly for the first 40 min of treatment when the $\mathrm{Fe^{2+}}$ concentration was increased from 0.05 mM to 0.2 mM. Fig. 1(a) indicates that the same treatment efficiency as $\mathrm{Fe^{2+}}$ of 0.2 mM can be achieved at a lower initial $\mathrm{Fe^{2+}}$ concentration. The difference between ACT removal efficiency is insignificant. Hydrogen peroxide is the Fenton's reagent that is used to produce hydroxyl radicals that oxidize the organics in wastewater. The effect of $\mathrm{H_2O_2}$ concentration on ACT degradation in the EF process was investigated (Fig. 1 (b)). The results thus obtained show that the ACT degradation in the EF process increased with reaction time but decreased with increasing $\mathrm{H_2O_2}$ concentration. This phenomenon was attributed to the scavenging effect, according to Eq. (7). Hence, few available hydroxyl radicals in the solution degraded ACT.

$$\mathrm{{}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}O_2H + H_2O}, \qquad k = 2.7 \times 10^7\,\mathrm{M^{-1}s^{-1}} \qquad (7)$$

Fig. 1(c) shows the degradation of ACT in the EF process at various ACT concentrations. The degradation of ACT at low concentration (5 mM) was more efficient than that at high concentration, because increasing the ACT concentration increased the number of ACT molecules but not the hydroxyl radical concentration, reducing the degradation efficiency.

3.2. Comparison between EF and PEF processes

Fig. 1(a) shows that the ACT degradation was very rapid in the first 2 min. The reaction that occurred in the first 2 min is discussed in terms of the initial rate. Fig. 2 plots the effects of $\mathrm{Fe^{2+}}$, $\mathrm{H_2O_2}$ and initial ACT concentrations on the ACT degradation efficiency and the initial rate of ACT degradation in the EF and PEF processes. Increasing the $\mathrm{Fe^{2+}}$ loading drastically increased the