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Degradation of acetaminophen by different Fenton processes

Luzvisminda M. Bellotindos[a], An-Tzu Chang[b], Ming-Chun Lu[b,*]

[a]*Archie Eustaquio Research Laboratory, Universidad de Zamboanga, Zamboanga City 7000, Philippines*
[b]*Department of Environmental Resources Management, Chia-Nan University of Pharmacy and Sciences, Tainan 71710, Taiwan, Tel. +886 6 2660489; Fax: +886 6 2663411; email: mmclu@mail.chna.edu.tw (M.-C. Lu)*

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ABSTRACT

A new approach for increasing ferric reduction efficiency by the use of UVA lights and electric current as electron donors in a Fenton process has been developed to degrade organic toxic chemicals. The process can be applied to treat emerging pollutants such as pharmaceuticals and personal care products. Acetaminophen (ACT) was the target compound in this study. Effects of initial pH, Fe^{2+} loading, and H_2O_2 concentration were determined to test and validate a kinetic model for the oxidation of ACT by the photoelectro-Fenton process (PEF). Increasing the ferrous ion concentration from 0.01 to 0.1 mM increased the hydroxyl radicals and then increased the degradation efficiency of ACT. The optimal H_2O_2 concentration for ACT degradation in this study was 25 mM. The ACT removal efficiency for electro-Fenton and PEFs were 90% and 91%, respectively, as compared to 12% ACT removal efficiency using Fenton process.

Keywords: Acetaminophen; Advanced oxidation processes; Electro-Fenton process; Photoelectro-Fenton process

1. Introduction

Human and veterinary pharmaceuticals and personal care products (PPCPs) have received increasing attention as persistent organic pollutants (POPs) in waters. These compounds, known as emergent pollutants, include prescription and non-prescription human and veterinary pharmaceutical compounds as well as PPCPs. Conventional sewage treatment plants provide very inefficient destruction of PPCPs because they are usually resistant to biodegradation, which means the use of oxidation technologies is needed to ensure their removal from the environment. Chemical oxidants, such as Cl_2, ClO_2, and O_3, can react with drugs and their metabolites but are unable to promote their total mineralization [1–3]. Electrochemical advanced oxidation processes (EAOPs) based on Fenton's reaction chemistry are emerging technologies for water treatment. Of the EAOPs, the most popular is the electro-Fenton (EF) process, and combined EF method, such as photoelectro-Fenton (PEF) process, has also been reported for wastewater remediation [1]. Over the past decade, there have been significant developments showing great effectiveness for the decontamination of wastewater polluted with toxic and persistent pesticides, organic synthetic dyes, pharmaceuticals and PPCPs, and a great deal of industrial pollutants [1].

The Fenton method makes use of a mixture of Fe^{2+} and H_2O_2 (Fenton's reagent) to degrade the POPs. The efficiency of this method is increased by coupling this

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*Corresponding author.

with electrochemistry [1]. In the EF process, H_2O_2 is generated at the cathode with O_2 or air feeding. While an iron catalyst (Fe^{2+}, Fe^{3+}, or iron oxides) is added to the effluent while in the PEF process, the solution is treated under EF conditions and simultaneously irradiated with UVA light to accelerate the mineralization rate of the organics [1], which minimizes the disadvantages of the conventional Fenton process, one of which is the production of excess amount of ferric hydroxide sludge that needs further separation and disposal [4,5]. In a study on the technical and economic feasibilities of three AOPs [6], the operating cost of Fenton process was lower and the investment cost for the ozonation process was higher. In another study that compared the different AOPs in treating antibiotics aqueous solution from technical and economic point of view [7], photo-Fenton process appeared to be the most cost effective.

$[Fe(OH)]^{2+}$ ion, the pre-eminent form of Fe(III) at pH 2.8–3.5, plays a key role when the dark Fenton process is photo assisted by UV irradiation leading to the photo-Fenton process. This procedure can utilize UVA ($\lambda = 315$–400 nm), UVB ($\lambda = 285$–315 nm), and UVC ($\lambda < 285$ nm) lights as energy source, although the intensity and wavelength of radiation have significant influence on the destruction rate of organic pollutants. A disadvantage of this process is the excessive cost arising from the use of artificial light. Recent work has shown that the alternative use of sunlight ($\lambda > 300$ nm) as a free and renewable energy source in the so-called solar photo-Fenton process is also useful for wastewater remediation [8,9].

For this work, acetaminophen (ACT), which is the raw material for pharmaceuticals like Panadol (Tylenol), was used as the target compound. In this study, the performances of Fenton, EF, and PEF processes on the degradation of ACT were compared. Effects of initial pH (pH_i), Fe^{2+} loading, and H_2O_2 concentration were determined.

2. Materials and methods

2.1. Chemicals and analytical method

The reagents used in the experiments were of analytical quality (Merck). All the preparations and experiments were conducted at room temperature. The samples taken at predetermined time intervals were immediately injected into tubes containing sodium hydroxide solution to quench the reaction by increasing the pH to 11 [10]. All the samples were filtered with PALL 0.2 μm mixed cellulose ester filters before analysis. The ACT was analyzed by Spectra SYSTEM model SN4000, high-performance liquid chromatography, with an Asahipak ODP-506D column (150 mm × 6 mm × 5 μm). The Fe^{2+} concentration was determined by light absorbance measurement at 510 nm after complexing with 1,10-phenanthroline using a SHIMADZU UV-1201UV–vis spectrophotometer [11]. The TOC was determined with an Elementer-liquid TOC (Germany) total organic carbon analyzer. The H_2O_2 concentration was measured using a standard Iodometric method with potassium iodide and $Na_2S_2O_3$ [12].

2.2. Experimental apparatus

Fig. 1 shows the schematic experimental setup of this study. The rectangular parallelepiped reactor (length: 21.5 cm, width: 15 cm, and height: 50 cm) was operated at a constant current mode. The acrylic reactor has a total volume of 8 L.

2.3. EF process

Solutions with 5 mM ACT as background electrolyte were treated by all Fenton processes for comparison. The ferrous ion was added after the pH was adjusted to the desired value. The pH of the solution was not controlled during the reaction. After the power supply was turned on, hydrogen peroxide was added to initiate the reaction. The oxidation reaction was stopped instantly by adding NaOH to the reaction mixtures after sampling. The samples were then filtered with 0.2 μm filters to remove precipitates before analysis.

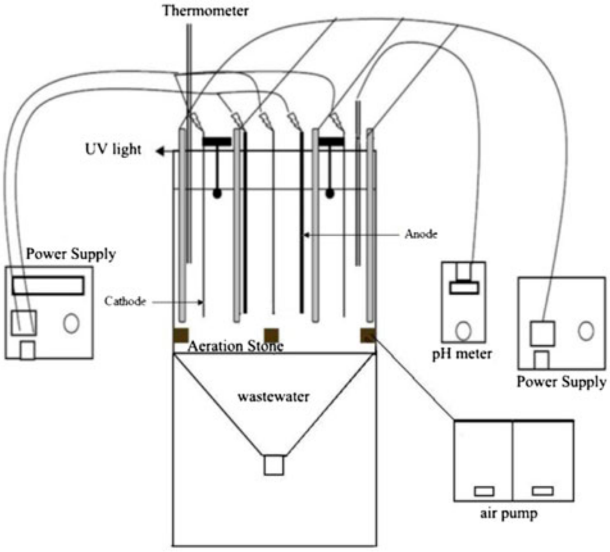

Fig. 1. Schematic diagram of reaction system.

2.4. PEF process

The irradiation source was a set of eight 3-W UVA lamps (Sunbeamtech.com) fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate). In addition to all the experimental conditions mentioned above, UV light with maximum wavelength of 360 nm supplied a photoionization energy input of 24 W to the solution.

3. Results and discussion

3.1. Effect of pH_i

The Fenton reaction has the highest efficiency when the pH is around 2–4 [9]. The pH of the solution controls the production of the hydroxyl radical and the concentration of ferrous ions [13–16]. Hence, pH is an important parameter for the PEF process. The typical range for the PEF process is in the acidic range [17]. Thus, it is essential to determine the optimum pH for the Fenton process which can provide the best performance. Figs. 2a–2c show the effect of pH_i on the degradation of ACT at different concentrations of Fe^{2+} and H_2O_2. The experiments were performed at pH_i of 2.0, 3.0, and 4.0. The results are shown in Fig. 2a. There was no significant difference in the oxidation rate at pH 3.0, a slightly higher removal rate was noted. The optimum pH was found to be about 2. It is in good agreement with early reports [18–22].

The effect of pH on the degradation of ACT is shown in Fig. 2b. Increasing the pH_i from 2.0 to 4.0 decreased the remaining ACT from 94 to 27% in 2 h. Fig. 2c showed the same trend as in Fig. 2b; lower pH value of ACT also increased the removal efficiency.

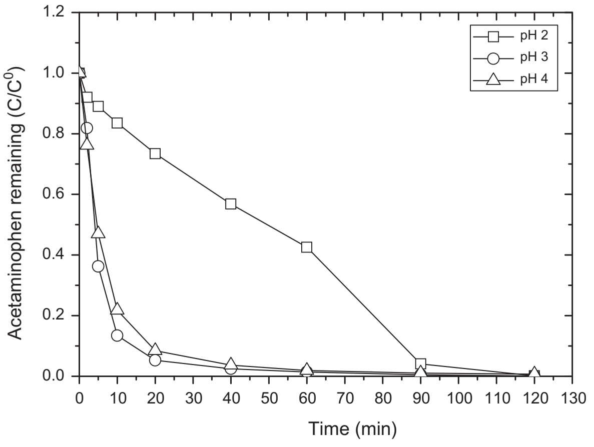

Fig. 2a. Effect of pH_i on the ACT degradation. ([ACT] = 5 mM; Fe^{2+} = 0.1 mM; H_2O_2 = 25 mM; current = 1.5 A; and UVA lamps = 8.)

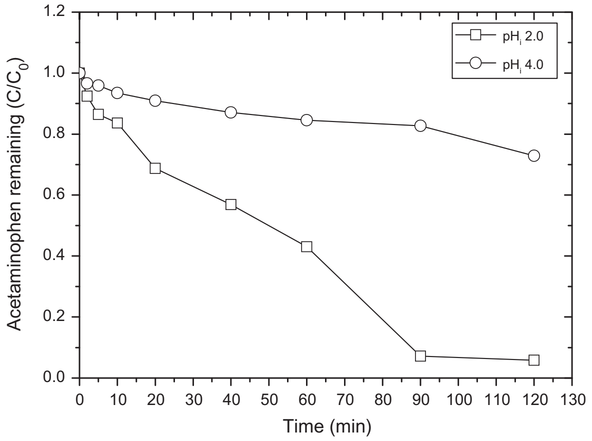

Fig. 2b. Effect of pH_i on the ACT degradation. ([ACT] = 5 mM; Fe^{2+} = 0.01 mM; H_2O_2 = 15 mM; current = 1.5 A; and UVA lamps = 8.)

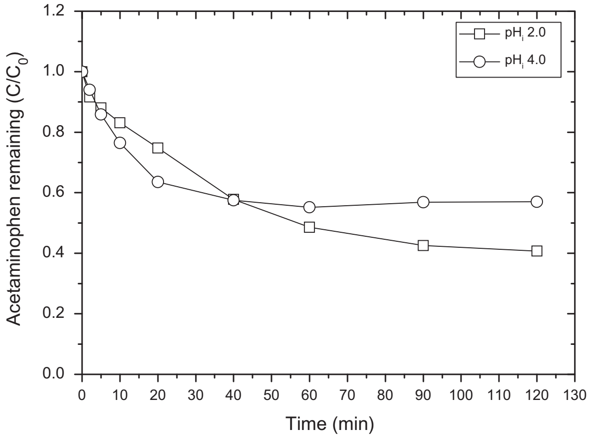

Fig. 2c. Effect of pH_i on the ACT degradation. ([ACT] = 5 mM; Fe^{2+} = 0.05 mM; H_2O_2 = 5 mM; current = 1.5 A; and UVA lamps = 8.)

The poor degradation of ACT at a high pH range (>2.0) was caused by the formation of ferric and ferric hydroxide complexes with much lower catalytic capability than Fe^{2+} [15]. Furthermore, a low pH also promotes hydrogen evolution, according to Eq. (6), thus reducing the number of active sites for generating ferrous ions.

The proposed reactions in the electrolytic system are [18]:

On the anode side:

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \tag{1}$$

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^- \tag{2}$$

Table 1
Effect of pH_i of ACT removal and degradation rate by PEF process

Run	pH	Fe^{2+} (mM)	H_2O_2 (mM)	$[Fe^{2+}]/[H_2O_2]$	ACT degradation rate (mM min^{-1})	ACT removal (%)
1	2	0.10	25	0.0040	0.082	100
2	3	0.10	25	0.0040	0.433	100
3	4	0.10	25	0.0040	0.394	100
4	2	0.01	15	0.0007	0.082	94
5	4	0.01	15	0.0007	0.033	27
6	2	0.05	5	0.0100	0.084	59
7	4	0.05	5	0.0100	0.118	43

Note: Degradation rate: at 10 min of reaction time.

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (3)$$

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

On the cathode side:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (5)$$

$$H_2O + e^- \rightarrow 1/2H_2 + OH^- \quad (6)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (7)$$

Table 1 shows the effect of pH_i of ACT removal and degradation rate by PEF process. For runs 1–3, at high concentrations of ferrous and hydrogen peroxide, the ACT removal efficiency was at 100%. At pH 2, although the degradation rate was slow, the ACT removal was high. Also, at pH 2, using low concentration of ferrous and hydrogen peroxide, the ACT removal was better than at pH 4.

3.2. Effect of Fe^{2+} initial loading

Ferrous ion is the catalyst in the Fenton process. Its main purpose is the catalysis of hydrogen peroxide resulting in hydroxyl radical formation. This is due to the fact that Fe^{2+} plays a very important role in initiating the decomposition of H_2O_2 to generate the $\cdot OH$ in the Fenton process.

When the concentrations of Fe^{2+} and $\cdot OH$ are high, Fe^{2+} can react with the $\cdot OH$ according to Eq. (8).

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (8)$$

Hence, the excess ferrous ions consumed the hydroxyl radicals with a high oxidative potential. It caused the ferric reduction efficiency to be lower than in Eq. (8). However, it is not a good idea to use over high concentration of Fe^{2+}. A large quantity of ferric oxide sludge will be generated, which needs further separation and disposal.

Fig. 3 shows the poor degradation of ACT at a low Fe^{2+} (0.01 mM). For the ferrous ion concentrations of 0.01 , 0.05 , and 0.1 mM, the removal efficiencies of ACT were 49, 83, and 100%, respectively.

Table 2 shows the effect of initial Fe^{2+} on the ACT removal and degradation rate by PEF process. An increase in the concentration of ferrous ion resulted in the increase in ACT removal. As can be seen from the table, an increase in ferrous ion concentration from 0.01 to 0.10 mM resulted in an increase of 10 times in the rate of degradation.

3.3. Effect of H_2O_2 initial concentration

The initial concentration of H_2O_2 plays an important role in the EF process. The effect of the H_2O_2 concentration on the ACT degradation is shown in Fig. 4.

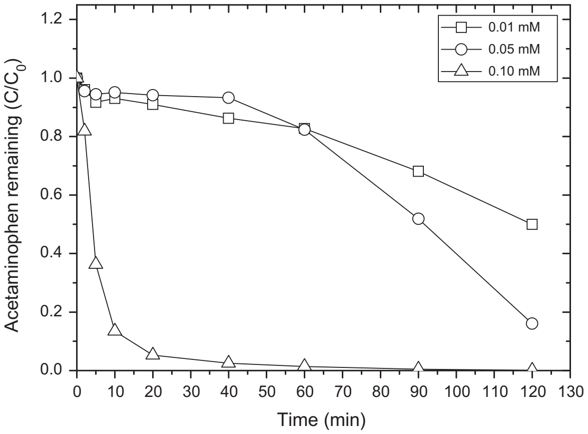

Fig. 3. Effect of Fe^{2+} on the ACT degradation. ([ACT] = 5 mM; pH_i = 3.0; H_2O_2 = 25 mM; current = 1.5 A; UVA lamps = 8.)

Table 2
Effect of initial Fe^{2+} on the ACT removal and degradation rate by PEF process

Run	pH	Fe^{2+} (mM)	H_2O_2 (mM)	$[Fe^{2+}]/[H_2O_2]$	ACT degradation rate (mM min^{-1})	ACT removal (%)
1	3	0.01	25	0.0004	0.043	50
2	3	0.05	25	0.0200	0.024	84
3	3	0.10	25	0.0040	0.433	100

Note: Degradation rate: at 10 min of reaction time.

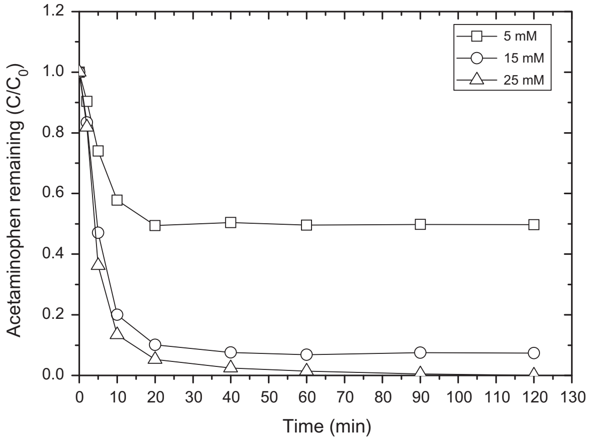

Fig. 4. Effect of H_2O_2 on the ACT degradation. ([ACT] = 5 mM; $pH_i = 3.0$; $Fe^{2+} = 0.1$ mM; current = 1.5 A; and UVA lamps = 8.)

The removal efficiencies for 5 , 15 , and 25 mM are 50, 90, and 100%, respectively. This increase in the removal efficiency was due to the increase in hydroxyl radical concentration as a result of the addition of H_2O_2. However, at a high dosage of H_2O_2, the decrease in removal efficiency was due to the hydroxyl radical scavenging effect of H_2O_2 (Eqs. (9) and (10)) and the recombination of the hydroxyl radical (Eq. (11)) [14].

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}HO_2 \tag{9}$$

$$^{\cdot}HO_2 + {}^{\cdot}OH \rightarrow H_2O + O_2 \tag{10}$$

$$^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \tag{11}$$

Table 3 shows the effect of initial H_2O_2 on ACT removal and degradation rate by PEF process. The degradation rate of ACT was doubled when the concentration of hydrogen peroxide was increased from 5 to 25 mM, and the ACT removal efficiency increased from 50 to 100%.

3.4. Degradation of ACT in different processes

In their studies of ACT degradation, Su et al. [10,23] have compared performances of Fenton and EF processes. In this study, Fenton, EF, and PEF

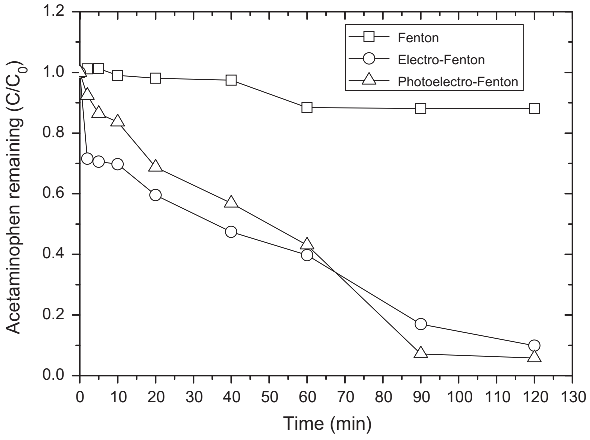

Fig. 5. Effect of different processes on the ACT degradation. ([ACT] = 5 mM; $pH_i = 2.0$; $Fe^{2+} = 0.01$ mM; $H_2O_2 = 15$ mM; current = 1.5 A; and UVA lamps = 8.)

Table 3
Effect of H_2O_2 on ACT removal and degradation rate by PEF process

Run	pH	H_2O_2 (mM)	Fe^{2+} (mM)	$[Fe^{2+}]/[H_2O_2]$	ACT degradation rate (mM min^{-1})	ACT removal (%)
1	3	5	0.1	0.0020	0.211	50
2	3	15	0.1	0.0067	0.400	93
3	3	25	0.1	0.0040	0.433	100

Note: Degradation rate: at 10 min of reaction time.

Table 4
ACT removal and degradation rate by different Fenton processes

Number	Process	Fe^{2+} (mM)	H_2O_2 (mM)	pH	$[Fe^{2+}]/[H_2O_2]$	ACT degradation rate* (mM min^{-1})	ACT removal (%)
1	Fenton	0.01	15	2	0.0007	0.005	12
	EF					0.151	90
	PEF					0.081	94

*At 10 min of reaction time.

experiments were conducted to investigate the synergistic effect of combined photo and electrochemical methods. Fig. 5 shows the effect of the different processes on the degradation. As shown in Fig. 5, the Fenton method alone could remove 12% of ACT in 2 h. The 90% removal efficiency achieved by the EF process was nearly 78% higher than that of the Fenton's reagent alone. Meanwhile, in the PEF process, 94% of ACT was removed in 2 h. The PEF process achieved a removal efficiency that was 4% higher than that of the EF process. This indicates that the PEF method had a synergistic effect for ACT degradation.

Table 4 shows the ACT removal and degradation rate by different Fenton processes. It can be seen that the degradation rate and the ACT removal efficiency using Fenton process are very low compared to the EF and PEF processes.

4. Conclusions

The optimal pH_i in this study was 2. At $pH > 2$, Fe^{3+} started to precipitate in the form of amorphous $Fe(OH)_{3(s)}$. The formation of $Fe(OH)_{3(s)}$ decreased the dissolved Fe^{3+} concentration and inhibited Fe^{2+} regeneration by partially coating the electrode surface. Increasing ferrous ions increased the hydroxyl radicals and increased the oxidation efficiency of ACT. The optimal hydrogen peroxide concentration and ferrous ion concentration for ACT degradation were 25 and 0.1 mM, respectively. The ACT removal efficiencies for EF and PEF processes were 90% and 94%, respectively, as compared to 12% ACT removal efficiency using Fenton process. This shows that this new approach for increasing ferric reduction, in addition to reduction in sludge formation, will be an economical alternative in removing other emerging pollutants.

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