Acetaminophen degradation by electro-Fenton and photoelectro-Fenton using a double cathode electrochemical cell

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ABSTRACT

Acetaminophen is a widely used drug worldwide and is one of the most frequently detected in bodies of water making it a high priority trace pollutant. This study investigated the applicability of the electro-Fenton and photoelectro-Fenton processes using a double cathode electrochemical cell in the treatment of acetaminophen containing wastewater. The Box–Behnken design was used to determine the effects of initial Fe^{2+} and H_2O_2 concentrations and applied current density. Results showed that all parameters positively affected the degradation efficiency of acetaminophen with the initial Fe^{2+} concentration being the most significant parameter for both processes. The acetaminophen removal efficiency for electro-Fenton was 98% and chemical oxygen demand (COD) removal of 43% while a 97% acetaminophen removal and 42% COD removal were observed for the photoelectro-Fenton method operated at optimum conditions. The electro-Fenton process was only able to obtain 19% total organic carbon (TOC) removal while the photoelectro-Fenton process obtained 20%. Due to negligible difference between the treatment efficiencies of the two processes, the electro-Fenton method was proven to be more economically advantageous. The models obtained from the study were applicable to a wide range of acetaminophen concentrations and can be used in scale-ups. Thirteen different types of intermediates were identified and a degradation pathway was proposed.

1. Introduction

Acetaminophen (ACT) is one of the most frequently used drugs worldwide. It is one of the most often detected pharmaceutical products in sewage treatment plant effluents, surface water and drinking water [1]. It is considered adverse environmental effects [2]. Detection of this compound is greater at highly populated areas such as urban centers where drug usage is expected to reach elevated proportions.

Advanced oxidation processes (AOPs) are now preferred to biological treatment especially for industrial effluents. AOPs generate powerful non-selective oxidants, hydroxyl radicals ($^\bullet$OH). Hydroxyl radicals can degrade and mineralize a wide variety of pollutants [3]. This is often operated at near ambient temperature and air pressure [4]. These techniques degrade the pollutants into harmless compounds making them more practical than other existing technologies [5].

One of the widely used AOP is the Fenton process which uses hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in the generation of hydroxyl radicals which can degrade and mineralize a wide variety of pollutants [6–8]. In this process, hydrogen peroxide is catalyzed by the ferrous ion to produce the hydroxyl radicals as shown in reaction (1) [9].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {^\bullet}OH, \quad k = 70\,M^{-1}\,s^{-1} \tag{1}$$
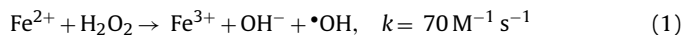
These hydroxyl radicals then react with pollutants like organic compounds resulting to its degradation and mineralization.

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

Ferrous ions are able to regenerate through the reduction of ferric species (Fe^{3+}) by hydrogen peroxide as shown in reaction (3). This enables the propagation of the Fenton reaction.

$$H_2O_2 + Fe^{3+} \rightarrow FeOOH^{2+} + H^+, \quad k = 0.001\text{–}0.01\,M^{-1}\,s^{-1} \tag{3}$$
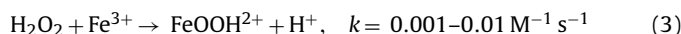
One of the major disadvantages of the Fenton process is the large production of ferric hydroxide sludge during the neutralization stage of the process. As can be observed in reactions (1) and (3), there is a large difference between the rate constants which show that ferrous ions are more rapidly consumed than

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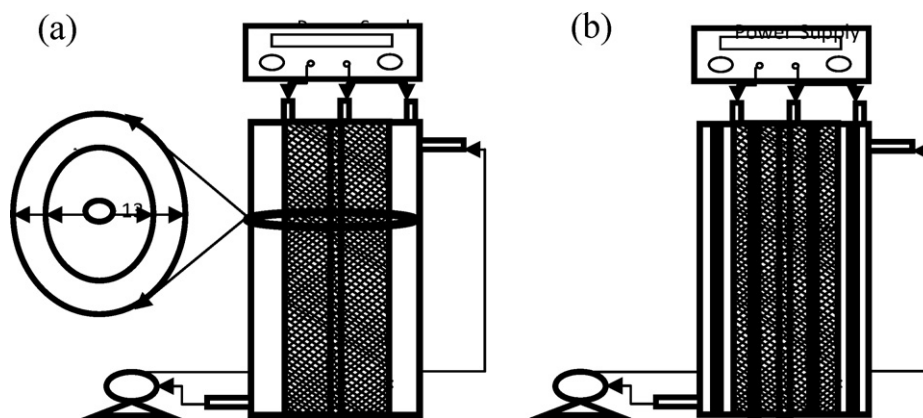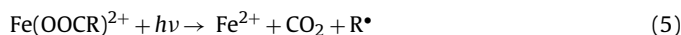[1] Tel.: +63 9493138631.

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

regenerated. Because of this, additional treatment and separation process is needed before the sludge can be disposed [10].

The electro-Fenton (EF) process was developed to address this disadvantage. In this process, electrical current is applied to induce the reduction of ferric hydrogen sludge to form ferrous ions on the cathode. This does not only reduce the amount of sludge formed but also enhance the degradation of target compounds [3,11]. Another electrochemical process being studied is the photoelectro-Fenton (PEF) process. It is a type of Fenton technology which uses the same conditions as that of the electro-Fenton process with simultaneous irradiation of UVA light. This accelerates the degradation rate of organic pollutants in the reaction and also increases the regeneration rate of Fe^{2+}. Additional $^{\bullet}OH$ can also be observed due to the photolysis of $[Fe(OH)]^{2+}$ and Fe(III) complexes that forms carboxylic acids which are the products of ACT degradation as presented in reactions (4) and (5) [12].

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (4)$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \qquad (5)$$

Advanced oxidation methods are being applied to treat acetaminophen containing wastewater [13–16]. A study on the use of solarphoto-Fenton to remove acetaminophen resulted in a removal efficiency of 16.3% [17]. Photo-Fenton process uses UV light to increase the production of hydroxyl radicals thereby increasing the efficiency of the treatment process [18]. For the case of solarphoto-Fenton, solar energy is used as light source. Heterogeneous AOPs were also applied in the treatment of acetaminophen. This includes TiO_2 photocatalysis with 95% removal in 80 min [19]. Photocatalytic methods include the illumination of semiconductors such as titanium dioxide (TiO_2) with high energy photons. This process produces hydroxyl radical which then oxidizes the target pollutants [5,20,21]. Other methods include photodegradation of ACT in TiO_2 suspended solution which was able to remove 95% ACT in 100 min [22].

In this study the applicability of electrochemical Fenton processes in the treatment of acetaminophen containing wastewater was investigated. Electro-Fenton and photoelectro-Fenton processes have the ability to treat even high concentrations of wastewater making its application possible as a pre-treatment process before the actual treatment. The effects of important operating parameters were also studied and the system was optimized to obtain the maximum removal at the most economical conditions.

2. Materials and methods

2.1. Chemicals and analytical methods

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 of reagent-grade and used without further purification.

Acetaminophen concentration was measured using a high performance liquid chromatography (HPLC) with Spectra SYSTEM model SN4000 pump with the operating flow rate at 1 ml/min through and Asahipak ODP-506D column (150 mm $\times$ 6 mm $\times$ 5 mm) where the mobile phase was 60% acetonitrile with 40% DI water. The 254 nm output from UV1000 detector was measured. 20 μL of sample was injected. Optimization of parameters was done for maximum acetaminophen removal using Design Expert 7 software (Stat-Ease, Inc., Minneapolis, USA). Closed-reflux titration based from standard methods was used for COD measurement. Samples were kept for 12 h before the analysis to remove the effect of H_2O_2 on the COD data. TOC was analyzed using an Elementar-liqui TOC analyzer. GC–MS (7890A GC system/5975 C MSD) with a flame ionization detector and an HP-5 column (25 m $\times$ 0.25 mm; film thickness of 0.25 μm) was used to determine intermediates. The GC injection port temperature was 250 °C, and the column temperature was fixed at 70 °C for 2 min, and then programmed from 70 to 250 °C at 10 °C/min, and hold for 5 min.

2.2. Experimental apparatus

A cylindrical reactor having concentric electrodes was used in this study as shown in Fig. 1. Two stainless steel cathodes having inside diameters of 2 cm and 13 cm respectively and a titanium coated RuO_2/IrO_2-coated DSA anode with an inside diameter of 7 cm comprised the 3.5 L electrochemical-cell reactor (diameter: 13 cm and height: 35 cm). This was operated at constant current mode. In the photoelectro-Fenton process, the irradiation source was a set of sixteen 3 W UVA lamps (Sunbeamtech.com) fixed inside a cylindrical Pyrex tube (allowing wavelengths $\lambda > 320$ nm to penetrate). Each light supplies photoionization energy of 3 W amounting to a total of 48 W. UV light with maximum wavelength of 360 nm was irradiated inside the reactor.

2.3. Electro-Fenton and photoelectro-Fenton processes

All experiments were conducted at room temperature. According to the previous study [23], high concentration acetaminophen

Table 1
ACT removal and rate constant of ACT degradation in the electro-Fenton and photoelectron-Fenton processes designed by the Box–Behnken program.

Run number	[Fe^{2+}] (mol/m^3)	[H$_2$O$_2$] (mol/m^3)	Current density (A/m^2)	ACT removal (%)[a]		Rate constant[b] ($\times 10^{-2}$ m^3/mol min)	
				EF process	PEF process	EF process	PEF process
1	0.01	5	75	68	79	0.33	0.44
2	0.10	5	75	81	80	1.07	1.80
3	0.10	25	75	100	100	22.06	14.79
4	0.01	25	75	64	82	0.13	0.13
5	0.055	25	38	98	98	5.08	1.50
6	0.055	25	113	99	99	2.09	1.28
7	0.055	5	113	86	86	1.36	1.96
8	0.055	5	38	70	80	1.02	0.96
9	0.01	15	38	49	55	0.22	0.06
10	0.01	15	113	82	91	0.51	0.87
11	0.10	15	113	98	99	11.26	3.59
12	0.10	15	38	97	99	13.32	10.63

[a] Data obtained at 120 min.
[b] Data obtained at 20 min.

(around 8 mM) had even been investigated. In this study, initial concentration of 5 mM ACT was treated by both processes. Moreover, the electro-Fenton and photoelectron-Fenton processes are well suited to treat high concentration organic contaminants. Hence, the experimental condition of 50 mM ACT was also been explored. Pre-determined amount of FeSO$_4$·7H$_2$O was added into the reactor. The pH was then adjusted to 3 before turning on the power supply at desired current. Samples were taken before the addition of H$_2$O$_2$ to get the initial conditions of the system. The time starts after the addition of the H$_2$O$_2$ to initiate the reaction. Samples taken at specified time intervals were then mixed with NaOH solution and then filtered using 0.2 μm filters to remove possible precipitates. Same experimental conditions were carried out using the photoelectro-Fenton process.

2.4. Box–Behnken experimental design

The Box–Behnken design (BBD) statistical experiment had been used on the advanced oxidation of pollutant [24]. BBD is the optimization of analytical methods [25]. Hence, BBD was used to investigate the effects of important operating parameters in the degradation of acetaminophen and to optimize the system. This is a type of response surface method (RSM) which is based on three-level incomplete factorial designs. It requires fewer runs when compared to other RSM designs making its application more economical. The Design-Expert software version 7.0 (Stat-Ease, Inc., Minneapolis, USA) was used for determining the optimum condition of acetaminophen degradation. The optimization procedure involves studying the response of statistically designed combination, estimating the coefficients by fitting experimental data to the response functions and predicting the response of fit mode. Lower and upper limits of these parameters were as follows: 0.01–0.1 mol/m^3, 5–25 mol/m^3 and 38–113 A/m^2 for initial [Fe^{2+}], initial [H$_2$O$_2$] and applied current density respectively. The high, middle and low levels were designated with 1, 0 and −1 respectively. This range was chosen based from prior experiments. The degradation of ACT was selected as a response factor. The rate constant and removal of ACT degradation for each run were selected as

the response factor. Application of different kinetic models (zero-order, first order, and second order) showed that the second-order model exhibited the highest r^2 values. Thus, a second order model was used for the rate constant calculation. Although each run lasted for 2 h each, the kinetic data were only evaluated at the first 20 min of each runs during the fast degradation stage of the process.

3. Results and discussion

Three experimental factors, namely Fe^{2+}, H$_2$O$_2$ and current density were varied for this study. These factors were chosen because these greatly affect the treatment efficiency of the processes being investigated. Twelve experimental runs were performed and presented in Table 1. The experimental results show that a minimum ACT degradation of 49% and 55% were observed for the electro-Fenton and photoelectro-Fenton processes, respectively. A 100% removal was observed for the electro-Fenton process and a 100% removal was achieved by the photoelectro-Fenton process after 2 h of treatment. It was found that increasing Fe^{2+} concentration increased ACT removal efficiency. When 0.01 mol/m^3 Fe^{2+}, 25 mol/m^3 H$_2$O$_2$ and 75 A/m^2 were applied, the ACT removal was only 64% and 82% (run 4) for electro-Fenton and photoelectron-Fenton processes, respectively. However, Fe^{2+} concentration increased from 0.01 to 0.1 mol/m^3, ACT removal increased 36% and 18% (run 3) for electro-Fenton and photoelectron-Fenton processes, respectively, indicating that Fe^{2+} has a significant effect on ACT degradation. The results also show that H$_2$O$_2$ concentration and current density can improve degradation efficiencies. When 0.055 mol/m^3 Fe^{2+} and 5 mol/m^3 H$_2$O$_2$ with 38 A/m^2 were used, ACT removals were 70% and 80% (run 8) for electro-Fenton and photoelectron-Fenton processes, respectively. Furthermore, H$_2$O$_2$ concentration increased from 5 to 25 mol/m^3, ACT removal was 98% (run 5) for both processes. At low Fe^{2+} concentration (0.01 mol/m^3), ACT removal efficiency was significantly increased with increasing current density. When 0.01 mol/m^3 Fe^{2+}, 15 mol/m^3 H$_2$O$_2$ and 38 A/m^2 were used, ACT removal was 49% and 55% (run 9) for electro-Fenton and photoelectron-Fenton processes, respectively. When current density was increased

Table 2
The levels of variables and the value of correlation on acetaminophen removal efficiency and rate constant from BBD.

Variables	Symbol	Variable level			Correlation factor			
		Low (−1)	Center (0)	High (+1)	ACT removal (%)		Rate constant (m^3/mol min)	
					EF process	PEF process	EF process	PEF process
[Fe^{2+}] (mol/m^3)	A	0.01	0.055	0.1	0.662	0.520	0.694	0.662
[H$_2$O$_2$] (mol/m^3)	B	5	15	25	0.318	0.395	0.367	0.283
Current density (A/m^2)	C	38	75	113	0.296	0.320	−0.065	−0.123

Table 3
Comparison of acetaminophen, COD and TOC removal efficiencies of each process at optimum conditions (electro-Fenton and Fenton processes operated at EF optimum: $[Fe^{2+}] = 0.087$ mM, $[H_2O_2] = 16.3$ mM, current density = 38 A/m^2; photoelectro-Fenton and Fenton process operated at PEF optimum: $[Fe^{2+}] = 0.08$ mM, $[H_2O_2] = 14.8$ mM, current density = 38 A/m^2).

Process	Removal efficiency (%)					Initial rate[a] (mM min^{-1}) (1–2 min)	Rate constant[a] ($\times 10^{-2}$ mM^{-1} min^{-1}) (1–40 min)
	ACT[a] (5 mM)	ACT (50 mM)	COD[a] (5 mM)	COD (50 mM)	TOD[a] (5 mM)		
Electro-Fenton	98	95	43	41	19	0.39	8.3
Fenton (EF-optimum)	96	95	28	30	15	0.17	7.2
Photoelectro-Fenton	97	–	42	–	21	0.50	9.1
Fenton (PEF-optimum)	96	–	29	–	–	0.14	7.1

[a] Means that operation was done at 5 mM acetaminophen.

from 38 to 113 A/m^2, ACT removal increased 33% and 37% (run 10) for electro-Fenton and photoelectron-Fenton processes, respectively. The increasing in Fenton's reagent led to an increase in the rate constant of ACT degradation. In addition, an interesting result concerning the rate constant was observed when current density increased. The rate constant of ACT degradation decreased with increasing current density at a high Fe^{2+} (0.1 mM) or H_2O_2 (25 mM) concentrations. When current density increased from 38 to 113 A/m^2, the rate constant decreased from 5.08×10^{-2} to 2.09×10^{-2} m^3/mol min at 25 mM of H_2O_2 (runs 5 and 6) and 13.32×10^{-2} to 11.26×10^{-2} m^3/mol min at 0.1 mM of Fe^{2+} for electro-Fenton process. This result implies that the ACT degradation at the first 20 min was inhibited at a high current density and Fenton's reagent. The difference between the ACT degradation efficiencies of these two processes decreases as the concentrations of the Fenton reagents increases. At higher concentrations of Fenton's reagent, an enough supply of hydroxyl radicals are produced which is enough for the treatment of the pollutant.

3.1. Effect of various parameters in acetaminophen degradation efficiency

Table 2 shows the levels of the three factors on BBD and correlation factor using the kinetic rate constant and ACT removal efficiency. These correlation values can have a value of +1 to −1 where a positive number indicates that it has a direct effect on the acetaminophen degradation efficiency and a negative value means that it affects the efficiency in reverse. A higher value would also mean that it has a greater effect on the response. All of the factors showed a positive effect on the treatment efficiency of both

processes. In the contrary, the current density has a negative effect on the rate constants obtained from both processes. An increase in the initial concentrations of both Fe^{2+} and H_2O_2 can produce more hydroxyl radicals as shown in reaction (1). More radicals mean that more pollutant can be degraded resulting to a higher treatment efficiency of the process. On the other hand, increasing the amount of applied current density can result to faster regeneration of the Fe^{2+} ions as presented in reactions (6) and (7), thereby making more Fe^{2+} ions available for hydroxyl radical production [3].

On cathode side:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{6}$$

On anode side:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{7}$$

Based from these factors, the initial Fe^{2+} concentration was the most significant factor among the three for both processes. The initial Fe^{2+} concentration dictates the behavior of degradation of acetaminophen. Also, the effect of varying Fe^{2+} concentration was more pronounced in the electro-Fenton process than the photoelectro-Fenton process having a correlation factor of 0.694 for rate constant and 0.662 for ACT removal compared to 0.662 for rate constant and 0.520 for ACT removal. In the electro-Fenton process, the Fe^{3+} ions are continuously regenerated in the cathode side. This increases the regeneration rate of Fe^{2+} ions thereby increasing the treatment efficiency of the process. However, the photoelectro-Fenton process also has the ability of regenerating Fe^{2+} ions from ferric complexes such as $Fe(OH)^{2+}$ aside from its regeneration in the cathode side as shown in reactions (4) and (5) [12]. In this way, the regeneration efficiency of Fe^{2+} is higher in the photoelectro-Fenton process than in the electro-Fenton process. This is the reason why
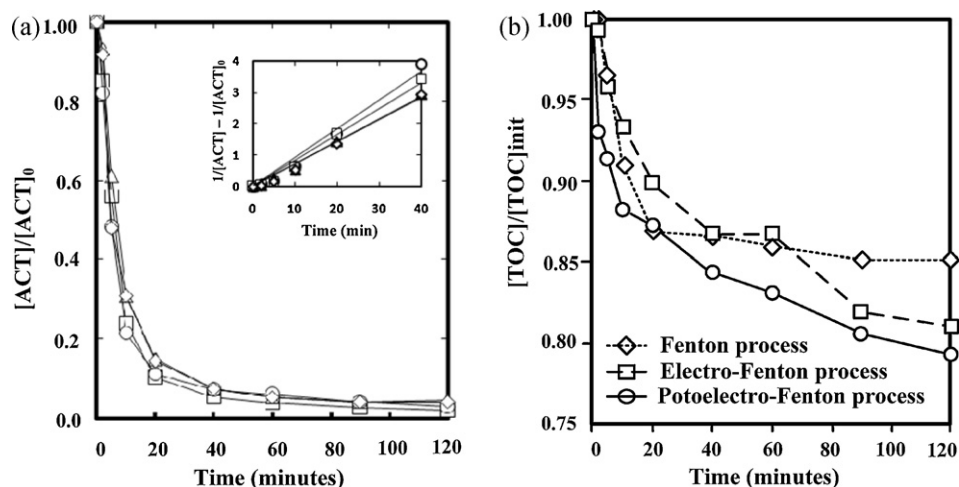
Fig. 2. (a) Acetaminophen removal and (b) TOC removal for different processes operated at optimum conditions (electro-Fenton process (□) and Fenton process (◇) operated at EF optimum: $[Fe^{2+}] = 0.087$ mM, $[H_2O_2] = 16.3$ mM, current density = 38 A/m^2; photoelectro-Fenton process (○): $[Fe^{2+}] = 0.08$ mM, $[H_2O_2] = 14.8$ mM, current density = 38 A/m^2).

Table 4
Comparison of H_2O_2 efficiency, current efficiency and energy cost for electro-Fenton and Photoelectro-Fenton processes.

Process	%H_2O_2 efficiency	%Current efficiency	Energy cost (kWh COD^{-1})
Electro-Fenton	134	408	3.53
Photoelectro-Fenton	149	413	3.56

higher degradation efficiencies were obtained for the PEF process even at lower initial Fe^{2+} concentration than the EF process. However, higher values of kinetic rate constants were recorded for the majority of the runs for electro-Fenton process when compared to the photoelectro-Fenton process. Thus, the effects of varying Fe^{2+} concentration are lower resulting to a lower correlation factor. The PEF process has a higher correlation factor on the ACT removal for both the initial H_2O_2 concentration and the applied current density than the EF process. In addition, the EF process has a higher correlation factor on the rate constant for the initial H_2O_2 concentration than PEF process. This phenomenon reveals that ACT degradation in the first 20 min was significantly affected by the H_2O_2 concentration.

3.2. Optimum points and validation of the model

An empirical correlation between the acetaminophen degradation efficiency, rate constant and the three factors were obtained using the Box–Behnken experimental design for both processes. A reduced cubic model was fitted for both processes having an r^2 value of 0.9999.

In the electro-Fenton process:

$$\begin{aligned} \text{ACT degradation} \ (\%) = {}& 6.21 + 930.07A + 0.22B + 68.46C \\ & + 75.32AB - 858.29AC - 0.74BC \\ & - 452.29A^2 - 5.44 \times 10^{-003}B^2 - 7.86C^2 \\ & - 330.63A^2B + 4552.33A^2C - 0.87AB^2 \end{aligned}$$

$$\begin{aligned} \text{Rate constant} = {}& -4.20841 \times 10^{-3} + 0.87485A + 9.62565 \times 10^{-4} \\ & - 0.012039C - 0.085723AB - 0.50141AC + 1.668 \\ & \times 10^{-3}BC - 9.67753A^2 + 4.53036 \times 10^{-5}B^2 \\ & + 0.022377C^2 + 1.89395A^2B + 2.19259A^2C \\ & - 2.86111 \times 10^{-4}AB^2 \end{aligned}$$

In the photoelectro-Fenton process:

$$\begin{aligned} \text{ACT degradation} \,(\%) = {}& 19.38 + 1287.88A - 1.70B + 76.18C \\ & + 72.82AB - 1221.21AC - 0.24BC \\ & - 10315.67A^2 + 0.06B^2 - 12.24C^2 \\ & - 88.88A^2B + 7406.28A^2C - 1.80AB^2 \end{aligned}$$

$$\begin{aligned} \text{Rate constant} = {}& -0.046408 + 0.28975A + 3.93604 \times 10^{-3}B \\ & + 0.052382C - 0.14566AB + 1.03167AC \\ & - 6.12000 \times 10^{-4}BC + 5.03469A^2 - 8.80058 \\ & \times 10^{-5}B^2 - 0.021829C^2 + 1.58198A^2B \\ & - 17.31111A^2C + 1.51833 \times 10^{-3}AB^2 \end{aligned}$$

These models can be used to predict the acetaminophen degradation for any values of the parameters with the initial Fe^{2+} (mol/m^3) and H_2O_2 (mol/m^3) concentrations and current density (A/m^2) being represented by *A*, *B* and *C*. These were obtained by correlating the response functions with the variations in the operating parameters using the Design Expert 7 software. The equation for ACT degradation (%) was used to examine the optimum conditions because rate constant of ACT degradation was only in response to the first 20 min reaction.

The optimum conditions were obtained using the optimization tool incorporated in the Design Expert 7 software for maximum removal of acetaminophen were 0.087 mol/m^3 Fe^{2+}, 16.3 mol/m^3 H_2O_2 and 38 A/m^2 for the electro-Fenton process and 0.08 mol/m^3 Fe^{2+}, 14.8 mol/m^3 H_2O_2 and 38 A/m^2 for the photoelectro-Fenton process. For this analysis, the response factor which is the acetaminophen degradation was set at maximum while the applied current and initial hydrogen peroxide concentration was set at minimum. This was done to ensure that maximum removal can be obtained at the least possible operating cost. However, the initial Fe^{2+} concentration being the most significant factor for the acetaminophen removal was set in range.

The electro-Fenton process has a higher requirement for both initial Fe^{2+} and H_2O_2 concentration compared to the photoelectro-Fenton process. This is mainly because the photoelectro-Fenton process has a higher efficiency in the regeneration of Fe^{2+} ions and hydroxyl radical formation due to the application of UV lights as shown in reactions (4) and (5). The same amount of current density at 38 A/m^2 was needed for both processes to obtain 100% removal. But if the amount of energy consumption for UV lights application is to be considered, the electro-Fenton process proves to be more energy efficient compared to the photoelectro-Fenton process. In order to validate the models used, both processes were run at optimum conditions. Table 3 shows the ACT degradation for each process. Another run was done at 50 mol/m^3 ACT using the same ratios of parameters at the optimum condition for the electro-Fenton process. This was done to investigate the applicability of the model for possible scale-up operations. As can be observed, the difference between the predicted and actual results for both processes is small. This only proves the reliability of the model used. The use of the same optimum conditions even at higher concentration yielded a 95% ACT removal which differed by 5% from the predicted results. The same trend was also observed for the COD removal for both low and high initial ACT concentration resulting to a 43% and 41%, respectively. The models obtained from this study are not restricted to the given initial ACT concentration it was proven that the model can be used to a wide range of ACT concentrations and can be applied for scale-up operations.

3.3. Process comparison

To determine the best process for the removal of acetaminophen containing wastewater, each process was run at optimum conditions. Two Fenton processes for each set of optimum conditions were also done. The results for ACT, COD and TOC removals efficiency, initial rate and rate constant are shown in Table 3. The differences between the degradation efficiencies of each processes run at the optimum conditions are negligible. The electro-Fenton process was able to degrade 98% while the photoelectro-Fenton process was able to obtain 97% degradation efficiency. Both Fenton processes were able to degrade about 96% of the total pollutant. A fast degradation of the target compound was observed in the first 40 min of the treatment time as shown in Fig. 2(a). The COD removal efficiencies obtained by the Fenton and the electrogenerated Fenton processes are quite different. The electro-Fenton process was able to remove 43% COD while the photoelectro-Fenton process was able to remove 42%. The Fenton process was
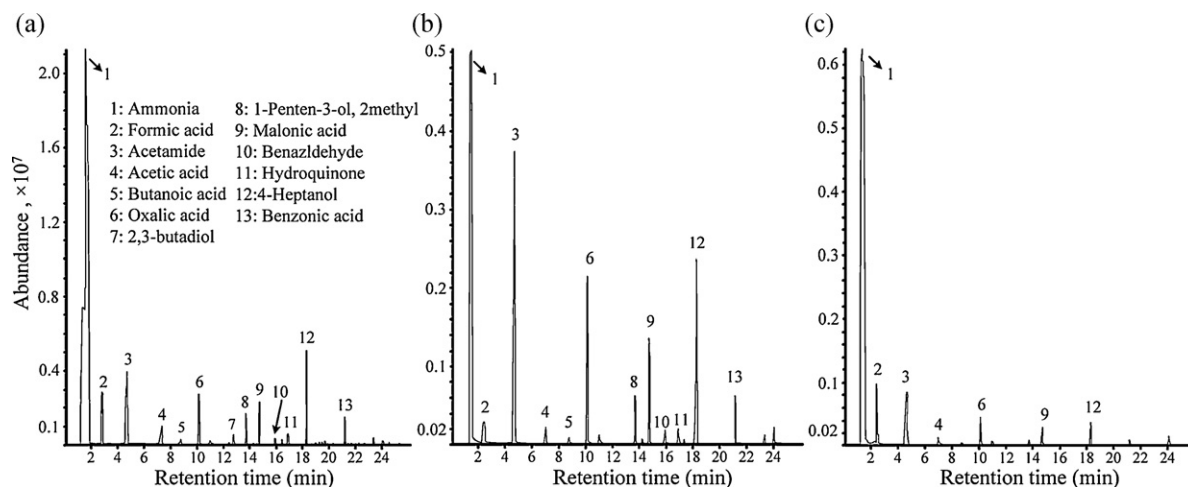
Fig. 3. GC/MS chromatogram for acetaminophen degradation at (a) 5 min, (b) 20 min and (c) 60 min.

able to obtain 28–29% COD even when operated at the same conditions. For TOC removal, Fenton process was able to remove 15% while removals for the electro-Fenton and photoelectro-Fenton processes were 19% and 21%, respectively. Although complete mineralization was impossible within the 2 h operating time, a continuous decrease in the TOC can still be observed for both the electro-Fenton and photoelectro-Fenton processes for the whole treatment period unlike the conventional Fenton process whose mineralization activity almost stopped after the 20 min operation as shown in Fig. 2(b). These results show that the electrochemically operated Fenton processes are superior to the Fenton process when it comes to COD and TOC removals. Formation of intermediates during the degradation process is one of the reasons of low removal efficiencies in the Fenton process. The production of intermediates such as oxalic acids which has the ability to form complexes with iron that leads to its precipitation [10]. As the treatment continues, less and less iron becomes available in the system thereby slowing the degradation process. The Fenton process does not have the capability to regenerate these complexes. With the aid of the current applied in the system, the complexes are able to regenerate back into Fe^{2+}. The UV lights also have the same effect as that of the applied current in the system [10]. This explains why of all the

Fenton technologies, the photoelectron-Fenton process had the highest TOC removal.

Almost complete removal of ACT was observed in the first 40 min. Hence, the data collected from the first 40 min of reaction were used to calculate the ACT removal rate. The estimative result shows that the ACT removal rate follows a second-order reaction, and a plot of $1/[ACT] - 1/[ACT]_0$ versus time should generate a straight line (the inset of Fig. 2(a)), with all correlation coefficients $r^2 > 0.98$. The initial rates were calculated for the first 2 min of operation. The electro-Fenton process had an initial rate of 0.39 mM min^{-1} and rate constant of 8.3×10^{-2} mM^{-1} min^{-1}. The application of the current was able to increase the initial oxidation rate of the system by 2.29 times than that of the conventional Fenton process. With the application of current in the system, faster reactions occurred due to more rapid regeneration of Fe^{2+} ions. The photoelectro-Fenton process was the fastest with an initial rate of 0.50 mM min^{-1} and rate constant of 9.1×10^{-2} mM^{-1} min^{-1}. It was 3.57 times faster than the conventional Fenton process and 1.28 times quicker than the electro-Fenton process during the initial 2 min. The same behavior can be deduced from the rate constants. The application of current alone was able to promote an efficiency of 1.15 while the application of both current and UVA lights during
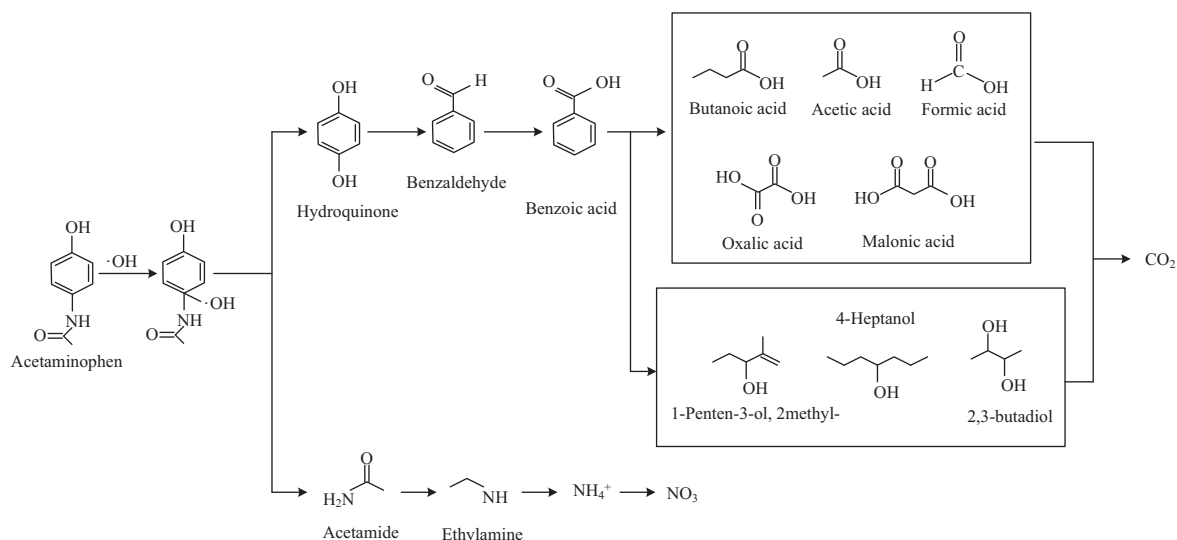

Fig. 4. Proposed acetaminophen degradation pathway.

the photoelectro-Fenton process was able to achieve a 1.28 promoted efficiency. As expected, the photoelectro-Fenton process exhibited the fastest rate of degradation among the three processes investigated. Even faster reactions are to be expected in the photoelectro-Fenton process due to the application of UV lights. However, the difference between the promoted efficiencies of the electro-Fenton and photoelectro-Fenton process was only 0.11 which amounts to a 9.5% increase in the promoted efficiency. Thus a small improvement was observed in the regeneration efficiency of Fe^{2+} with the additional application of UVA lights when compared to the application of current alone.

Since the differences between the treatment efficiencies of electro-Fenton and photoelectro-Fenton processes are not concrete, the use of energy-related parameters is utilized in these study as presented in Table 4. These are important parameters for comparison to see the viability of each process. The H_2O_2 efficiency, current efficiency and energy cost for both processes were calculated using Eqs. (8)–(10).

$$H_2O_2 \text{ efficiency} = \frac{\Delta COD(mg/L)}{available \ O_2(mg/L)} \times 100 \qquad (8)$$

$$Current \ efficiency = \frac{(\Delta COD)_t FV_s}{8It} \times 100 \qquad (9)$$

$$Energy \ efficiency = (\frac{kWh}{g \ COD}) = \frac{E_{cell}It}{(\Delta COD)_t V_s} \qquad (10)$$

The available oxygen is the theoretical amount of reactive oxygen in the hydrogen peroxide added. Other variables included in the equations are $(\Delta COD)_t$ which is the experimental COD decay $(g O_2/L)$ at time $t(s)$, F is the Faradays constant (96,487 C/mol), V_s is the volume of the solution (L), I is the current applied (A) and 8 is the oxygen equivalent mass (g/eq). E_{cell} is the average cell voltage (V) for the electrolysis time. The H_2O_2 efficiency can have a value greater than 100 since the COD removal is not only attributed to Fenton reaction alone. This scenario was also observed by Masomboon et al. [3]. In their study regarding the degradation of dimethyaniline, the photoelectro-Fenton process has a slightly higher H_2O_2 and current efficiencies than the electro-Fenton process. But in terms of energy consumption the electro-Fenton process requires lower energy since it does not need additional UVA irradiation for degradation making the electro-Fenton process more suitable and economical.

3.4. Acetaminophen degradation pathway

The main intermediate compounds of acetaminophen degradation were identified by standard compounds used and they are presented as GC chromatogram in Fig. 3. Thirteen different types of intermediates formed during the degradation process of acetaminophen were identified (Fig. 3(a)). As shown in Fig. 3(b) and (C), the peaks of large molecular and toxic compounds such as hydroquinone, benzaldehyde and benzoic acid disappeared with time, indicating acetaminophen could be transformed into harmless products. Carboxylic acids like acetic, formic, oxalic and malonic acids were also formed as what was found in previous studies. Hydroquinone and amide were also detected [12,19,26]. However, some alcohols which were not reported in previous studies were also identified such as 1-penten-3-ol,2-methyl, 4-heptanol and 2,3-butadiol. Benzaldehyde, benzoic acid, butanoic acid and ethylamine were also detected. Previous studies were not able to detect these intermediates. It is possible that due to the utilization of SPME method which is specific for different functional groups, the detection of more intermediates were promoted.

Fig. 4 presents the proposed degradation pathway for acetaminophen. The $\cdot$OH favored the attack in the para position with respect to the OH functional group. This attack produces

the hydroquinone and amide. The amide is further degraded into ethylamine and ammonium and finally turned into nitrates. The hydroquinone on the other hand is converted into benzaldehyde and the turned into benzoic acid. This substance is degraded further into either acids or alcohols. Complete mineralization turns these substances into CO_2. The pathway of acetaminophen degradation has also been proposed in the recent research [27,28]. Yang et al. [27] explored photocatalytic oxidation of acetaminophen and reported that more than 85% of TOC was mineralized at 450 min. Hence, in this study, some toxic intermediates were generated during the acetaminophen degradation should be transformed into harmless products.

4. Conclusion

The electro-Fenton process was proven to be more efficient in the treatment of acetaminophen containing wastewater than the photoelectro-Fenton method. Although the differences between the removal efficiencies of both processes are negligible, it is more energy efficient than the photoelectro-Fenton method. All parameters showed a positive effect on the degradation efficiency with the Fe^{2+} initial concentration being the most important parameter among the three for both processes. The Box–Behnken statistical design was proven to be an effective way of optimizing the given process. The optimum conditions were 0.087 mol/m^3 Fe^{2+} 16.3 mol/m^3 H_2O_2 and 38 A/m^2 for the electro-Fenton process and 0.08 mol/m^3 Fe^{2+}, 14.8 mol/m^3 H_2O_2 and 38 A/m^2 for the photoelectro-Fenton process. The models obtained were also not limited to the specific set of conditions employed during the study but can be used at a wider range of acetaminophen concentrations. Thirteen types of intermediates formed during the degradation process of acetaminophen were identified in this study. The $\cdot$OH was found to favor the attack in the para position with respect to the OH functional group. This attack produces the hydroquinone and amide. These are then degraded further into either acids or alcohols. Complete mineralization turns these substances into CO_2.

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