Chemical oxidation of 2,6-dimethylaniline by electrochemically generated Fenton's reagent

Nalinrut Masomboon [a], Chavalit Ratanatamskul [b], Ming-Chun Lu [c,*]

[a] Department of Interdisciplinary Programs in Environmental Science, Graduate School, Chulalongkorn University, Bangkok, Thailand
[b] Department of Environmental Engineering, Chulalongkorn University, Bangkok, Thailand
[c] Department of Environmental Resources Management, Chia-Nan University of Pharmacy and Science, Tainan 717, Taiwan
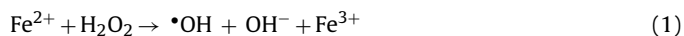
ARTICLE INFO

ABSTRACT

Oxidation of 2,6-dimethylaniline by electro-Fenton process in acidic solution at pH 2 was investigated. The effects of pH, Fe^{2+}, H_2O_2 and current density were assessed to determine the optimum operating parameters. The oxidation efficiency of 2,6-dimethylaniline was determined by the reduction of 2,6-dimethylaniline, COD and TOC in the solutions. Results reveal that 1 mM of 2,6-dimethylaniline can be completely degraded in 4 h with 1 mM of Fe^{2+} and 20 mM of H_2O_2 and current density of 15.89 A m^{-2} at pH 2. The highest COD and TOC removal were observed when 120 mM of hydrogen peroxide was applied. Consequently, the electro-Fenton process is a reliable alternative in the degradation of 2,6-dimethylaniline. 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid were detected during the degradation of 1 mM of 2,6-dimethylaniline solution by electro-Fenton method. A reaction pathway that includes these products is proposed for 2,6-dimethylaniline degradation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs) are commonly used processes for industrial effluent treatment when the contaminants are difficult to remove by the biological processes [1–2]. AOPs involve the generation of hydroxyl radicals ($^\bullet$OH), a strong oxidant with E^0 of 2.8 V, that can be used for the complete mineralization of many pollutants [3,4]. One of the AOPs is the Fenton process which uses hydrogen peroxide and ferrous ions to generate hydroxyl radicals that are able to efficiently degrade many kinds of pollutants into harmless compounds [5,6]. Fenton's reaction can be explained by the series of reactions below:

$$Fe^{2+} + H_2O_2 \rightarrow {}^\bullet OH + OH^- + Fe^{3+} \quad (1)$$

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

$${}^\bullet OH + organics \rightarrow products \quad (3)$$

$${}^\bullet OH + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (4)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow FeOOH^{2+} + H^+ \quad (5)$$

$$FeOOH^{2+} \rightarrow HO_2^\bullet + Fe^{2+} \quad (6)$$

$$HO_2^\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (7)$$

$$HO_2^\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \quad (8)$$

The major advantage of the Fenton process is the complete destruction of contaminants to carbon dioxide, water and inorganic salts [7]. Fenton's reagent (Fe^{2+} and H_2O_2) is commonly available, not difficult to operate and inexpensive. In addition, there is no need for special equipment like complex reaction vessels or ozone generators [8,9]. However, its application is limited due to the generation of ferric hydroxide sludge that requires additional separation processes and disposal [10,11]. Therefore, electro-Fenton process is developed to eliminate or minimize the disadvantages of the conventional Fenton process. The electrical current induced the reduction of ferric hydroxide sludge to form ferrous ions on the cathode side as shown in Eq. (9). Hence, it reduces the sludge disposal cost which is one of the major drawbacks of Fenton process and also enhances the degradation rate of target compounds [12,13].

$$Fe^{3+} + e^- \quad Fe^{2+} \quad (9)$$

$$H_2O + e^- \quad \frac{1}{2} H_2 + OH^- \quad (10)$$
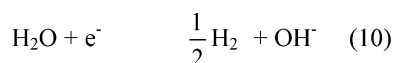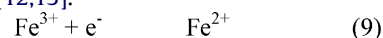
2,6-Dimethylaniline is a widely used chemical for the manufacture of pesticides, dyestuffs, antioxidants, pharmaceuticals and other products [14]. However, it is toxic and carcinogenic [15].

* Corresponding author. Tel.: +886 6 2660489; fax: +886 6 2663411.
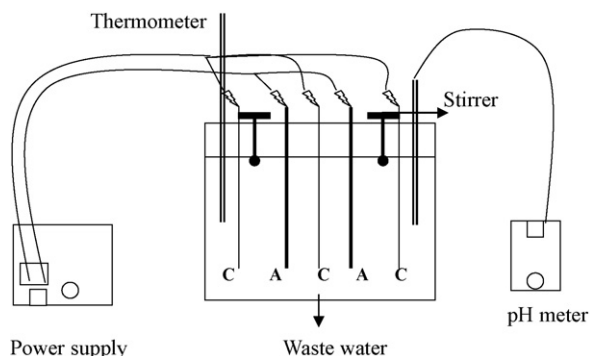*E-mail address:* mmclu@mail.chna.edu.tw (M.-C. Lu).

Fig. 1. The electro-Fenton reactor: C = cathode and A = anode.

These hazardous properties of 2,6-dimethylaniline necessitates the treatment of contaminated wastewater to prevent any deleterious effect to the environment. In this study, the effects of initial pH, ferrous ion concentration, hydrogen peroxide concentration and current density on the degradation of 2,6-dimethylaniline by electro-Fenton process were investigated. In addition, the degradation pathway of 2,6-dimethylaniline has been proposed.

2. Materials and methods

2.1. Chemicals and analytical method

All chemicals were prepared using de-ionized water from a Millipore system with a resistivity of 18.2 MΩ cm. 2,6-Dimethylaniline (>98%), perchloric acid (70–72%), ferrous sulfate (99.5–102%) and hydrogen peroxide (35–36.5%) were purchased from the MERCK company. COD was measured using closed-reflux titrimetric method based on the Standard methods (APHA). TOC was determined using an Elementar-liquid TOC (Germany) total organic carbon analyzer with high temperature combustion method. 2,6-Dimethylaniline was analyzed by a gas chromatograph (HP 4890II) equipped with flame ionization detector (FID) and a SUPELCO Equity^{TM}-5 Capillary Column (length: 15 m; id: 0.15 μm). Anions (oxalate, citric acid, formic acid, acetic acid) were determined by the Ion Chromatograph (Dionex DX-120) equipped with RFC-30 EGCII (KOH), IonPac®AG11 guard column (4 mm × 50 mm), IonPac®AS11 analytical column (4 mm × 250 mm), ASRS®-ULTRA II (4 mm) suppressor and conductivity detector. Other intermediates were examined by the GC–MS (Agilent 6890) with DB-5MS capillary column (30 mm × 0.25 mm i.d., 0.25 lm film, from J&W, USA).

2.2. Electro-Fenton reactor

The electro-Fenton reactor used in this study is presented in Fig. 1. This study was carried out using an acrylic reactor of 15 cm × 21 cm × 20 cm with a working volume of 5 L. The anodes and cathodes used were mesh-type titanium metal coated with IrO$_2$/RuO$_2$ and stainless steel, respectively. The working area on the cathode and anode were 900 and 600 cm^2, respectively. The electrodes were connected to a Topward 33010D power supply operated at the desired electric currents. In addition, two mixers were equipped to ensure appropriate agitation.

2.3. Electro-Fenton process

Firstly, synthetic wastewater containing 1 mM of 2,6-dimethylaniline was prepared in the reactor and agitated by two mixers. Then, the predetermined pH (1–4) was adjusted using perchloric acid. Afterwards, a calculated amount of catalytic
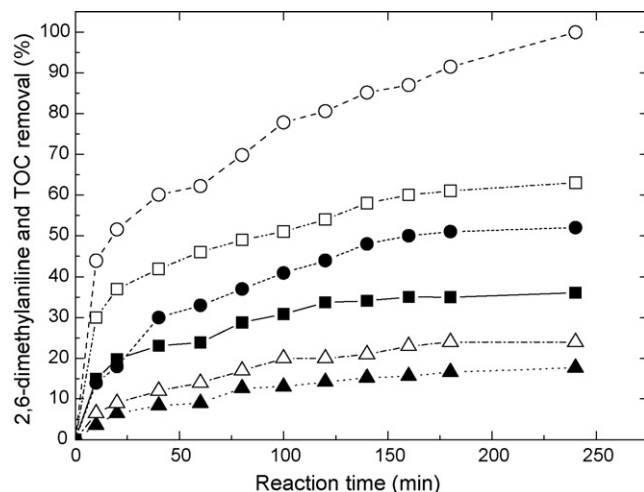

Fig. 2. 2,6-Dimethylaniline and TOC removal efficiency in various AOPs processes. When ($\bigcirc$) = 2,6-dimethylaniline removal by electro-Fenton, ($\bullet$) = TOC removal by electro-Fenton process, ($\square$) = 2,6-dimethylaniline removal by Fenton process, ($\blacksquare$) = TOC removal by Fenton process, ($\triangle$) = 2,6-dimethylaniline removal by electrolysis and ($\blacktriangle$) = TOC removal by electrolysis (electrolysis: I = 1.43 A, pH 2; Fenton process: [Fe^{2+}] = 1 mM, [H$_2$O$_2$] = 20 mM, pH 2; electro-Fenton process: [H$_2$O$_2$] = 20 mM, [Fe^{2+}] = 1 mM, I = 1.43 A, pH 2. All systems were using [2,6-dimethylaniline] = 1 mM).

ferrous sulfate (0.25–2.5 mM) was added as the source of Fe^{2+} in this experiment. The desired amount of H$_2$O$_2$ (5–150 mM) was then added into the reactor and the predetermined current density (5.56–66.67 A m^{-2}) or electrical current (0.5–6 A) was delivered through the experimental period. At selected time intervals, 1 mL of reaction mixture was taken and immediately injected into 0.1 N of NaOH to increase the pH to terminate the reaction [16]. The samples were filtered through 0.45 μm membrane filters to remove precipitates before analysis [17].

3. Results and discussion

3.1. 2,6-Dimethylaniline removal by different processes

To verify the effect of the electro-Fenton method, the control experiments were carried out for comparison. The degradation of 2,6-dimethylaniline at pH 2 by electrolysis, Fenton and electro-Fenton processes are shown in Fig. 2. Results indicate that the electrochemical method cannot remove 2,6-dimethylaniline efficiently; it is only 18% after 4 h of reaction. The same tendency can be found in the studies of Brillas et al. and Ting et al. [17,18]. Fenton process has higher degradation efficiency than the electrochemical method. The removal efficiency by Fenton process was 61% when using 1 mM of ferrous ion and 20 mM of hydrogen peroxide. This indicates that the destruction of 2,6-dimethylaniline is notably accelerated in the presence of ferrous ion and hydrogen peroxide only.

At the same conditions, however, 100% of removal efficiency was achieved by the electro-Fenton process. This could be ascribed to two different effects. Firstly, there was an increase in the ferrous ion concentration in the reactor due to the effect of the electric current on the regeneration of ferrous ion from ferric ion, which causes an increase in the rate of reaction (1) which then enhances the rate of reaction of 2,6-dimethylaniline with the hydroxyl radicals. Secondly, the increase of 2,6-dimethylaniline degradation was due to the effect of Fenton's reaction in the solution [16].

The effect of different processes on mineralization of 2,6-dimethyaniline was also investigated as shown in Fig. 2. The results follow the same trend as 2,6-dimethylaniline degradation. The elec-

Table 1
Effect of initial pH on 2,6-dimethylaniline removal, COD removal and initial degradation rate at the different initial pH ([2,6-dimethylaniline] = 1 mM, [H_2O_2] = 20 mM, Fe^{2+} = 1 mM, I = 1.43 A).

$pH_{initial}$	pH_{final}	2,6-DMA removal (%)	COD removal (%)	Initial degradation rate (mM min^{-1})
1	0.94	61.88	18.03	0.0157
1.5	1.38	79.20	25.93	0.0373
2	1.89	100.0	35.71	0.0468
2.5	2.46	82.19	25.02	0.0448
3	2.79	79.57	22.86	0.0351
3.5	3.25	73.86	29.00	0.0332
4	3.56	70.76	21.62	0.0265

trochemical method can remove only 15% TOC, while 36% of the TOC removal was found in the Fenton process. In the electro-Fenton process, 45% of the TOC was removed in 4 h. The final TOC removal by the electro-Fenton process was 10% higher than the conventional Fenton process. This indicates that the electro-Fenton process has a higher TOC removal efficiency. By Fenton and electro-Fenton processes, TOC removal was fast during the first 20 min, afterwards, the TOC removal was slowly decreased. This can be attributed to the depletion of ferrous ions in the solution. This information is similar to the electro-Fenton experiment that treated 4-nitrophenol [19]. Hydroxyl radicals produced from Fenton's reaction are the main species destroying aromatic products more rapidly, making the Fenton and electro-Fenton processes much more efficient than electrolysis. Consequently, electro-Fenton process was selected for degrading 2,6-dimethylaniline in this study.

3.2. Degradation of 2,6-dimethylaniline by electro-Fenton process

3.2.1. Effect of initial pH

It is well known that Fenton's reaction occur at low pH values. Normally, the Fenton reaction has the highest efficiency when the pH is around 2–4 [20]. To clarify the effect of pH, the 2,6-dimethylaniline solutions with initial pH of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 is investigated and the results are listed in Table 1. As seen from Table 1, the best 2,6-dimethylaniline removal efficiency (100%) and COD removal efficiency (36%) was observed at initial pH 2. The low 2,6-dimethylaniline and COD removal efficiencies were observed at the initial pH lower than 2. For initial pH 1.0 and 1.5, 2,6-dimethylaniline removal efficiencies were 62% and 79%, and the COD removal efficiencies were 18% and 26%, respectively.

For the tests at initial pH higher than 2, the 2,6-dimethylaniline and COD removal efficiencies decreased. The mineralization of 2,6-dimethylaniline can also be monitored by measuring the total organic carbon reduction during electro-Fenton reaction. TOC anal-

ysis was performed in order to know the amount of organic compounds that were depleted to carbon dioxide during the chemical oxidation [21]. The highest TOC removal by electro-Fenton process was around 45% at pH 2. The decrease of TOC can be attributed to the mineralization of 2,6-dimethylaniline by hydroxyl radicals from Fenton's reaction and from electrochemically generated ferrous ions from ferric ions via Eq. (9).

The initial degradation rate of 2,6-dimethylaniline at different initial pHs was also determined in this study. The highest initial rate (0.0468 mM min^{-1}) was achieved at pH 2. The initial rates are 0.0157, 0.0373, 0.0468, 0.0448, 0.0351, 0.0332 and 0.0265 mM min^{-1} when the initial pH was adjusted from 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0, respectively (as shown in Table 1). This phenomenon follows the same trend as 2,6-dimethylaniline removal, COD and TOC removal.

The decrease in 2,6-dimethylaniline degradation at low pH is probably due to the formation of $Fe(OH)^+$. $Fe(OH)^+$ formed at low pH and can compete with ferrous ion to react with hydrogen peroxide. However, $Fe(OH)^+$ reacts more slowly with hydrogen peroxide, therefore, produces less hydroxyl radicals. This reduces the degradation efficiency. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant at very low pH and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited [22]. On the contrary, ferrous ions are unstable at pH > 4.0 and they easily form ferric ions (Eqs. (2) and (7)), which have a tendency to produce ferric hydroxo complexes or ferric oxyhydroxides as shown in Eq. (5) [23]. At higher pH, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form $Fe(OH)_3$, which has a low activity and will not react with hydrogen peroxide. The ferric ions in the solution that can react with hydrogen peroxide are reduced via Eq. (5) with the rate constant 0.001–0.01 M^{-1} s^{-1} (7). Hydrogen peroxide is also unstable in basic solution and may decompose to give oxygen and water and lose its oxidation ability. Thus, hydrogen peroxide and ferrous ions have a difficulty in establishing an effective redox system and their degradation is also less

Table 2
Effect of initial hydrogen peroxide and ferrous ion concentration on 2,6-dimethylaniline removal, COD removal, initial degradation rate and H_2O_2 efficiency of 2,6-dimethylaniline and COD removal ([2,6-dimethylaniline] = 1 mM, I = 1.43 A, pH 2).

H_2O_2 (mM)	Fe^{2+} (mM)	[H_2O_2] [Fe^{2+}]	2,6-DMA removal (%)	COD removal (%)	Initial rate (mM min^{-1})	H_2O_2 efficiency (η)	
						2,6-DMA (%)	COD (%)
5	1	5	88.90	28.00	0.0275	63.42	137.7
20	1	20	100.0	35.71	0.0468	17.82	85.43
40	1	40	100.0	37.14	0.0559	8.91	31.97
60	1	60	100.0	37.16	0.0563	5.94	18.85
100	1	100	100.0	40.00	0.0572	3.56	17.62
120	1	120	100.0	42.57	0.0602	2.95	16.72
150	1	150	100.0	41.54	0.0589	2.22	9.04
20	0.10	200	60.15	18.21	0.0243	10.86	14.80
20	0.25	80	86.71	23.08	0.0313	15.45	30.30
20	0.50	40	94.03	30.00	0.0464	16.76	41.65
20	1.50	13.33	100.0	36.54	0.0482	17.32	71.61
20	2.00	10	100.0	38.23	0.0521	17.31	68.74
20	2.50	8	98.50	37.00	0.051	16.66	61.37

effective [24]. Hence, the optimum initial pH for this study should be 2.

3.2.2. Effect of hydrogen peroxide concentration

Hydrogen peroxide plays the role of an oxidizing agent in the Fenton reaction. Usually it has been observed that the percentage degradation of the pollutant increases with an increase in the concentration of hydrogen peroxide [22,25]. Increasing in the initial H_2O_2 concentration from 5 to 120 mM could promote the 2,6-dimethylaniline and COD removal efficiencies as illustrated in Table 2. The complete removal of 2,6-dimethylaniline was achieved when using an initial H_2O_2 concentration of 20–150 mM. The same trend was found for the COD removal. The COD removal increased from 28% to 42.57% as hydrogen peroxide dosage was increased from 5 to 120 mM. However, further increase to 150 mM showed a decrease in 2,6-dimethylaniline and COD removal efficiencies. This could be explained by the series of reaction mechanisms that might occur during the Fenton's reaction (5). Based on the Fenton's reactions, an increase in initial H_2O_2 concentration would also increase the production of hydroxyl radicals that could react with the organics in the solution via Eq. (3). Although, the 100% degradation of 2,6-dimethylaniline was achieved at 20 mM of H_2O_2, the COD removal was still low. This is probably due to the production of intermediates that are not as oxidizable as 2,6-dimethylaniline. Increasing the initial H_2O_2 concentration also increases the COD removal efficiency due to the formation of more hydroxyl radicals that could oxidize the by products of 2,6-dimethylaniline degradation.

The initial degradation rate of 2,6-dimethylaniline and the H_2O_2 efficiency of 2,6-dimethylaniline and COD removal were also investigated in this study. As seen from Table 2, the initial degradation rate followed the same trend as that of the COD removal efficiency, i.e. the initial degradation rate increased from 0.0275 to 0.0602 mM min^{-1} as the H_2O_2 concentration was increased from 5 to 120 mM but decreased to 0.0589 mM min^{-1} when H_2O_2 concentration was further increased to 150 mM. This increase in initial degradation rate was due to the presence of higher concentration of H_2O_2 forming non-hydroxyl radicals and hydroxyl radicals when reacted with Fe^{2+}. The higher $^\bullet OH$ concentration increases the degradation rate since there are more available $^\bullet OH$ to react with the organics in the solution. However, a high H_2O_2 concentration could also affect the degradation rate constant when the unreacted H_2O_2 might favor the side reactions that scavenged the $^\bullet OH$ to form hydroperoxyl radicals ($^\bullet OH_2$) via reaction (4). This has a rate constant of about $1.2–4.5 \times 10^7$ M^{-1} s^{-1} [2,26].

When increasing the initial H_2O_2 concentration from 5 to 150 mM, the H_2O_2 efficiencies of 2,6-DMA and COD decreased from 63.42 to 2.22 and from 137.7 to 9.04, respectively as listed in Table 2. H_2O_2 efficiencies higher than 100% were possible in this study since COD removal was not only attributed to Fenton's reaction. The efficiency of hydrogen peroxide for COD removal is defined by the equation below:

$$\eta = \left[\frac{\Delta COD\,(mg/l)}{available\,O_2\,(mg/l)} \right] \times 100 \tag{11}$$

where the available oxygen is the theoretical amount of reactive oxygen in the added hydrogen peroxide. COD could not be completely eliminated even though hydrogen peroxide dosage was higher than the theoretical dosage. A similar result was also found when landfill leachate was treated by electro-Fenton process [19]. When large quantities of hydrogen peroxide are present, it will acts as a scavenger for the generated hydroxyl radicals. At higher H_2O_2 concentrations, the $^\bullet OH$ produced might have followed other reaction pathways instead of Eq. (3) after 2,6-dimethylaniline was degraded. Higher H_2O_2 concentrations might have favored the side reactions that scavenged the hydroxyl radicals to form hydroper-

oxyl radicals ($^\bullet OH_2$). This could be supported by a decrease in the degradation rate constants from 0.0589 mM min^{-1} of the 150 mM initial H_2O_2 concentration compared with 0.0602 mM min^{-1} of 120 mM initial H_2O_2 concentration. The TOC removal was also determined in this study. The highest TOC removal was 52% when 120 mM of hydrogen peroxide was used. The low COD and TOC removals may indicate that, although 2,6-dimethylaniline might be highly oxidizable, some of its derivatives and intermediates might not be as readily oxidized.

3.2.3. Effect of ferrous ion concentration

The rate of degradation increases with an increase in the concentration of ferrous ions [6]. Table 2 shows that increasing the initial Fe^{2+} concentration from 0.1 to 2.5 mM enhanced both the 2,6-dimethylaniline and COD removal. One hundred percent of 2,6-dimethylaniline degradation was achieved when using 1 mM of Fe^{2+}. Though, the highest COD removal (38.23%) was observed when the initial Fe^{2+} concentration of 2 mM was added to the reactor. However, the COD removal efficiency started going down at concentrations higher than 2 mM. The initial degradation rate and the H_2O_2 efficiencies for both 2,6-DMA and COD also had the same trend, as listed in Table 2. The highest H_2O_2 efficiency for 2,6-dimethylaniline removal was about 17.82% and the COD removal was at 85.42% when an initial Fe^{2+} concentration of 2 mM was applied. The 2,6-dimethylaniline removal and COD removal decreased to 98.5% and 37%, respectively, when the initial Fe^{2+} concentration was increased to 2.5 mM. There was also a decrease in the initial degradation rate and the H_2O_2 efficiencies for both 2,6-DMA and COD removal at this high initial Fe^{2+} concentration.

The increase in the 2,6-dimethylaniline removal and COD removal may be explained by the rate constant of reaction (1) being 63 M^{-1} s^{-1}, while that for reaction (5) is only 0.01 M^{-1} s^{-1} [27]. This means that ferrous ions are consumed faster than they are produced. Accordingly, increasing in the initial Fe^{2+} concentration promoted the hydroxyl radical formation through reaction (1) and enhanced the 2,6-dimethylaniline removal and COD removal via reaction (3). An increase in initial Fe^{2+} concentration was needed to improve the organic compounds degradation and decomposition [13]. The low 2,6-dimethylaniline removal and COD removal at low initial Fe^{2+} concentration might due to the side reaction between H_2O_2 and $^\bullet OH$ through reaction (4), i.e. there was not enough Fe^{2+} to react with the available H_2O_2 such that the unreacted H_2O_2 reacted with the hydroxyl radical. Thus, the concentration of the hydroxyl radicals that could react with the organic compounds was reduced.

The decrease in initial rate, removal efficiencies and H_2O_2 efficiencies at high Fe^{2+} concentration may be attributed to the formation of iron complexes via reaction (5). Alternatively, it has been reported that an excess of ferrous ions would consume hydroxyl radicals through reaction (2) which has a rate constant of 3.2×10^8 M^{-1} s^{-1} [27–29]. The excess amount of ferrous ions may have a scavenging effect on the hydroxyl radical at the high initial Fe^{2+} concentration of 2.5 mM as indicated by the decreased of the initial rate. This resulted in a decrease of 2,6-dimethylaniline removal and COD removal as well as the H_2O_2 efficiencies for both 2,6-DMA removal and COD removal.

3.2.4. Effect of current density

Another important parameter of the electro-Fenton process is the amount of DC current applied to the electrodes. As the current applied to electrodes increases, the regeneration of ferrous ions from ferric ions becomes higher [30]. Results show that increasing the applied electric current from 0.5 to 4 A or current density from 5.56–44.44 A m^{-2} can promote the removal of 2,6-dimethylaniline from 93.12% to 100% as shown in Table 3. COD removal also increased when increasing the applied current density from 31.58% to 40.32%, indicating an enhancement of the degradation power.

Table 3
Effect of the applied electric current on 2,6-dimethylaniline removal, COD removal, rate constants, 2,6-dimethylaniline and COD removal efficiency and H_2O_2 efficiency ([2,6-dimethylaniline] = 1 mM, [H_2O_2] = 20 mM, [Fe^{2+}] = 1 mM, pH 2).

Current (A)	2,6-DMA removal (%)	2,6-DMA initial rate (mM min^{-1})	[Δ2,6-DMA] [ΔH_2O_2] (%)	Current impact E_{EF}/E_{CF}	COD removal (%)	[ΔCOD] [ΔH_2O_2] (%)	Current Impact E_{EF}/E_{CF}	Energy cost (kWh m^{-3})
0.00	42.55	0.0111	7.26	–	26.31	48.30	–	0
0.50	93.12	0.0421	16.59	2.29	31.58	72.82	1.51	1.77
1.00	99.53	0.0434	17.57	2.42	34.25	76.75	1.59	4.44
1.43	100.0	0.0468	17.82	2.46	35.71	85.42	1.77	6.41
2.00	100.0	0.0468	17.82	2.46	39.44	89.91	1.86	9.33
4.00	100.0	0.0473	17.82	2.46	40.32	93.60	1.94	23.81
6.00	96.25	0.0474	17.15	2.36	38.59	55.38	1.15	46.01

This observation was similar to the experiment on the removal of 4-nitrophenol by varying the electric current from 0.5 to 1 A [31]. In addition, the current impact at 44.44 A m^{-2} (4 A) was 2.46 for 2,6-dimethylaniline removal and 1.94 for COD removal as shown in Table 3. This means that electro-Fenton at 44.44 A m^{-2} is highly superior in 2,6-dimethylaniline degradation when it is compared to Fenton process operated at the same conditions. This was due to the higher electro-regeneration rate of ferrous ions from ferric ions with increased current which also increased the efficiency of the Fenton chain reactions. In this study, current impact was used to explain the important of electric current on the degradation of 2,6-dimethylaniline and COD. The current impact was calculated by comparing the removal efficiency of 2,6-dimethylaniline and COD of each electrical current applied with conventional Fenton process. We assumed that increasing electrical current will increased the current impact.

However, both 2,6-dimethylaniline and COD removal efficiencies decreased to 96.25% and 38.59%, respectively, when current density of 66.67 A m^{-2} (6 A) was applied. The same trend were also observed for the H_2O_2 efficiency of both 2,6-DMA and COD removal, and their corresponding current impacts as shown in Table 3. The TOC removal at 44.44 A m^{-2} was also found to be the highest and it is about 45%. The performance of the electro-Fenton process was evaluated by the instantaneous current impact. Since the current was kept constant, the amount of Fe^{2+} generated was proportional to the time of electrolysis. Current impact of 5.56, 15.89 and 44.44 A m^{-2} (0.5, 1.43 and 4 A) after 90 min were 2.29, 2.46 and 2.46, respectively. The initial degradation rate also increased when the current density increased. This is due to the increased regeneration of Fe^{2+} induced at the cathode via reaction (9) which promotes hydroxyl radical production through reaction (1). On the other hand, at a higher current density of 66.67 A m^{-2}, the competitive reactions such as the discharge of oxygen gas at the anode via reaction (12) and the evolution of hydrogen gas at the cathode via reaction (13) become more pronounced [31].

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (12)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (13)$$

Hence, the degradation rate constant decreased and H_2O_2 was not efficiently used. The energy cost for electro-Fenton process was also discussed. The equation applied for calculate the energy cost is [32]:

$$\text{Energy cost : } (\text{kWh/m}^3) = \left[\frac{V \times I \times t}{\text{volume}}\right] \times \left[\frac{COD_o}{\Delta COD_{exp.}}\right] \quad (14)$$

where V is the voltage applied until time t (Volt), I is the electric current (Ampere) used in the study, t is the given time (min), volume is the amount of organic solution used in the experiment (L), COD_o is the initial COD of the organic chemical and $\Delta COD_{exp.}$ is the difference between the initial COD and the final COD after treatment. By using Eq. (14), the energy cost increased when increasing the initial electric current and reaction time as shown in Table 3.

3.3. Identification of intermediates and proposed mechanism

The GC/MS and IC were applied to identify the intermediates that might occur from the degradation of 2,6-dimethylaniline by the electro-Fenton process. Several stable intermediates, such as 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid were detected during the degradation of 1 mM 2,6-dimethylaniline solution by the electro-Fenton method when current density of 15.89 A m^{-2} was applied.

The anions were examined by an Ion Chromatograph. The anions included lactic acid at 1.15 min, acetic acid at 2.9 min,
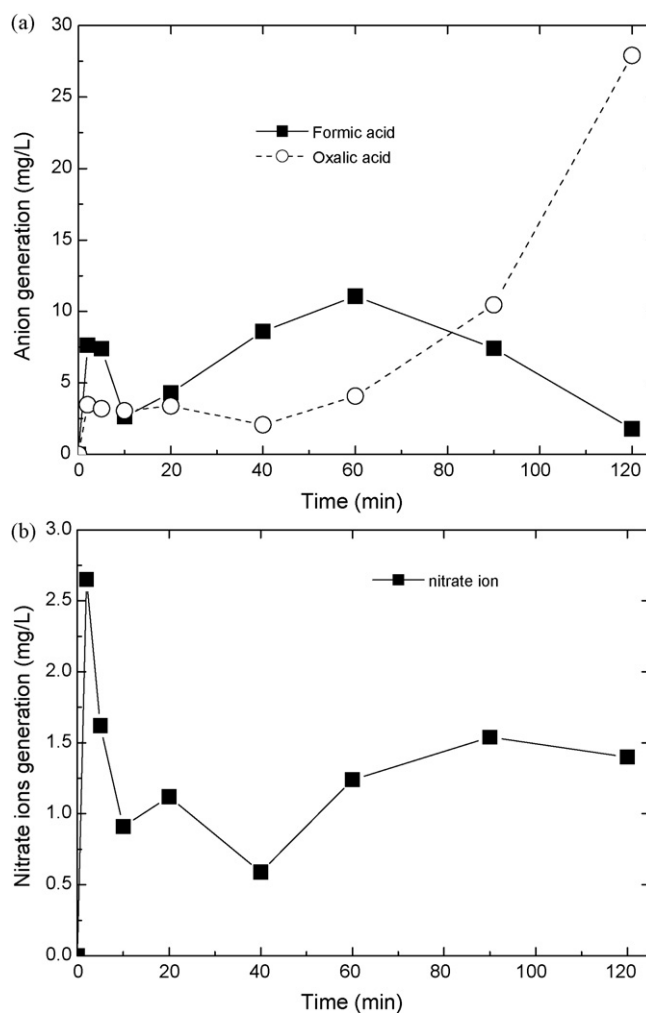

Fig. 3. Time-course of anions (a) and nitrate ions (b) concentration during the degradation of 2,6-dimethylaniline by electro-Fenton process ([2,6-DMA] = 1 mM; [Fe^{2+}] = 1 mM; [H_2O_2] = 20 mM; pH 2; I = 1.43 A).
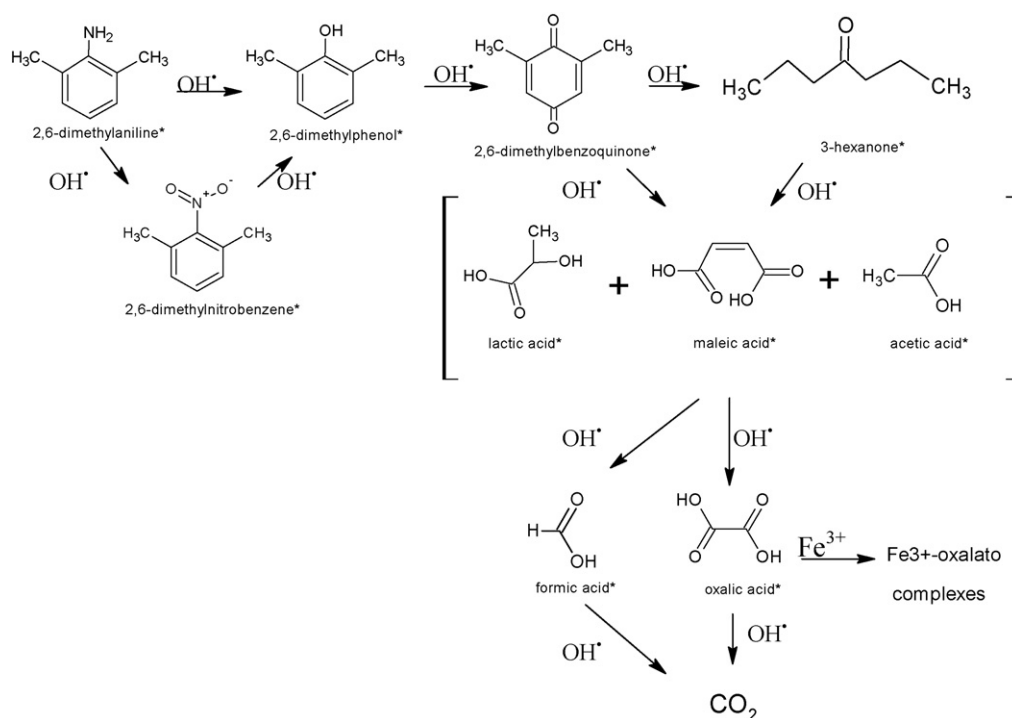
Fig. 4. Proposed reaction pathways for mineralization of 2,6-dimethylaniline at pH 2 by electro-Fenton process (*detected by GC–MS and IC).

maleic acid at 9.79 min, formic acid at 3.58 min and oxalic acid at 10.64 min. The formic acid was found after 2 min of the reaction time and its concentration increased with the increasing of time after 60 min the concentration of formic acid decreased. Oxalic acid was also found after 2 min. The concentration of oxalic acid increased as the time increased as shown in Fig. 3. Nitrate ions were also detected in the electrolyzed solutions. However, no nitrite ions were found in the solution. The nitrate ion generation profile is presented in Fig. 3. The nitrate ions were found due to the degradation of 2,6-dimethylaniline into other intermediates such as 2,6-dimethylphenol. Evolution of these species under electro-Fenton condition is presented in Fig. 4. 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, formic acid, acetic acid and maleic acid are practically eliminated in the experiment after 4 h of the reaction.

Based on this finding, a general pathway for degradation of 2,6-dimethylaniline at pH 2 with the electro-Fenton process was proposed. The proposed pathway is shown in Fig. 4. In electro-Fenton oxidation, the main oxidizing species is the hydroxyl radical. It is known that $^\bullet$OH radicals are nonselective and strong electrophilic oxidizing species [33]. The degradation process can be initiated either by the attack of $^\bullet$OH on 2,6-dimethylaniline that yields 2,6-dimethylnitrobenzene or by the direct hydroxylation of 2,6-dimethylaniline's N-position to give 2,6-dimethylphenol. 2,6-dimethylbenzoquinone is also formed from $^\bullet$OH attack on 2,6-dimethylphenol which further breaks into 3-hexanone. In Fenton reactions, $^\bullet$OH addition to the aromatic substrates to give mono- or multihydroxyl intermediates or products (hydroquinone/quinone analogues) has been firmly established [34]. The further degradation of 2,6-benzoquinone and 3-hexanone leads to a mixture of lactic acid, maleic acid and acetic acid. The three acids are transformed into formic acid and oxalic acid. The formic acid is directly mineralized to carbon dioxide. The ultimate carboxylic acid, oxalic acid, is very slowly converted into CO_2 by $^\bullet$OH since it forms very stable Fe^{3+}-oxalato complexes under the electro-Fenton process. It can be easily established that 2,6-dimethylaniline is degraded to 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone and probably other nitrogen-free organic derivatives. As far as we know, the proposed degradation pathways of 2,6-dimethylaniline using the electro-Fenton process at pH 2 has not yet been reported in the literature.

4. Conclusions

This study employed electro-Fenton process to oxidize 2,6-dimethylaniline. Results show that pH, Fe^{2+}, H_2O_2 and current density have a significant effect on the degradation of 2,6-dimethylaniline. Results obtained from the experiments revealed that 1 mM of 2,6-dimethylaniline can be completely degraded in 4 h when it is in the presence of 1 mM Fe^{2+} and 20 mM H_2O_2 and using a current of 15.89 A m^{-2} at pH 2. However, the highest COD and TOC removal were achieved when 120 mM of hydrogen peroxide was applied. 2,6-dimethylaniline cannot completely mineralize to carbon dioxide and water but rather transform into some other intermediates. The most important intermediates that can find in electro-Fenton process were 2,6-dimethylphenol, 2,6-dimethylnitrobenzene, 2,6-dimethylbenzoquinone, 3-hexanone, lactic acid, oxalic acid, acetic acid, maleic acid and formic acid.

References

[1] F. Mijangos, F. Varona, N. Villota, Changes in solution color during phenol oxidation by Fenton reagent, Environ. Sci. Technol. 40 (2006) 5538–5543.
[2] J.H. Sun, S.P. Sun, M.H. Fan, H.Q. Guo, L.P. Qiao, R.Z. Sun, A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process, J. Hazard. Mater. 148 (2007) 172–177.

[3] M.M. Ballesteros Martín, J.A. Sánchez Pérez, J.L. Csas López, I. Oller, S. Malato Rodríguez, Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation, Water Res. 43 (2009) 653–660.

[4] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

[5] C.P. Huang, C. Dong, Z. Tang, Advanced chemical oxidation: its present role and potential future in hazardous waste treatment, Waste Manage. 13 (1993) 361–377.

[6] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[7] E. Neyen, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33–50.

[8] C. Walling, Fenton's reagent revised, Acc. Chem. Res. 8 (1975) 125–131.

[9] S.M. Arnold, W.J. Hickey, R.F. Harris, Degradation of atrazine by Fenton's reagent: condition optimization and product quantification, Environ. Sci. Technol. 29 (1995) 2083–2089.

[10] P.H. Chang, Treatment of non-biodegradable wastewater by electro-Fenton method, Water Sci. Technol. 49 (4) (2004) 213–218.

[11] A. Özcan, M.A. Oturan, N. Oturan, Y. Şahin, Removal of acid orange 7 from water by electrochemically generated Fenton's reagent, J. Hazard. Mater. 163 (2009) 1213–1220.

[12] M. Gnann, C.H. Gregor, S. Schelle, Chemical oxidation process for purifying highly contaminated wastewater, WO patent 93/08129, Period-Chemie CmbH, DE (1993).

[13] J. Anotai, M.C. Lu, P. Chewpreecha, Kinetics of aniline degradation by Fenton and electro-Fenton processes, Water Res. 40 (2006) 1841–1847.

[14] U. John, K.P.R. Nair, Liquid phase overtone spectral investigations of 2,6-dimethylaniline and 2,4-dimethylaniline-evidence for steric nature of the ortho effect and the consequent base weakening, Spectrochim. Acta A 60 (10) (2004) 2337–2341.

[15] E. Oliveros, O. Legrini, M. Hohl, T. Müller, M. Braun, Industrial wastewater treatment: large scale development of a light-enhanced Fenton reaction, Chem. Eng. Process. 36 (1997) 397–405.

[16] M.C. Lu, Y.F. Chang, I.M. Chen, Y.Y. Huang, Effect of chloride ions on the oxidation of aniline by Fenton's reagent, Environ. Manage. 75 (2005) 177–182.

[17] W.P. Ting, M.C. Lu, Y.H. Huang, Kinetics of 2,6-dimethylaniline degradation by electro-Fenton process, J. Hazard. Mater. 161 (2009) 1484–1490.

[18] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectron-Fenton processes, Appl. Catal. B 16 (1998) 31–42.

[19] H. Zhang, D. Zhang, J. Zhou, Removal of COD from landfill leachate by electro-Fenton method, J. Hazard. Mater. B135 (2006) 106–111.

[20] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater. 125 (2005) 166–174.

[21] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, Water Res. 35 (2001) 1047–1051.

[22] J.J. Pignatello, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[23] S. Wang, A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes Pigments 76 (3) (2008) 714–720.

[24] W.G. Kuo, Decolorizing dye waste-water with Fenton reagent, Water Res. 26 (1992) 881–886.

[25] S.H. Lin, C.M. Lin, H.G. Leu, Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, Water Res. 33 (7) (1999) 1735–1741.

[26] R. Watts, A. Teel, Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations-CHP) for in situ soil and groundwater remediation, J. Environ. Eng. 131 (4) (2005) 612–622.

[27] N. Kang, D.S. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, Chemosphere 47 (2002) 915–924.

[28] M. Zhou, Q. Yu, L. Lei, The preparation and characterization of a graphite PTFE cathode system for the decolorization of C.I. Acid Red 2, Dyes Pigments 77 (2008) 129–136.

[29] M. Panizza, G. Cerisola, Electro-Fenton degradation of synthetic dyes, Water Res. 43 (2009) 339–344.

[30] E. Atmaca, Treatment of landfill leachate by using electro-Fenton method, J. Hazard. Mater. 163 (2009) 109–114.

[31] H. Zhang, C. Fei, D. Zhang, F. Tang, Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method, J. Hazard. Mater. 145 (2007) 227–232.

[32] E. Brillas, J. Casado, Aniline degradation by electro-Fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment, Chemosphere 47 (2002) 241–248.

[33] L.A. Pérez-estrada, S. Malato, W. Gernjak, A. Agüera, E.M. Thurman, I. Ferrer, A.R. Fernández-alba, Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway, Environ. Sci. Technol. 39 (2005) 8300–8306.

[34] R. Chen, J.J. Pignatello, Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds, Environ. Sci. Technol. 31 (1997) 2399–2406.