



Kinetics of 2,6-dimethylaniline oxidation by various Fenton processes

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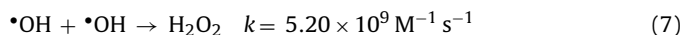
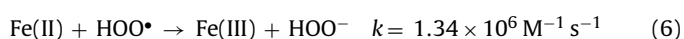
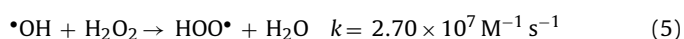
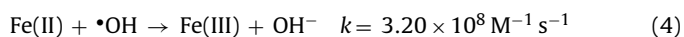
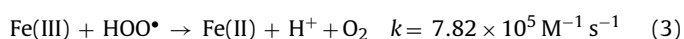
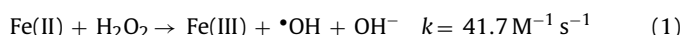
ABSTRACT

The kinetics of 2,6-dimethylaniline degradation by Fenton process, electro-Fenton process and photoelectro-Fenton process was investigated. This study attempted to eliminate the potential interferences from intermediates by making a kinetics comparison of Fenton, electro-Fenton and photoelectro-Fenton methods through use initial rate techniques during the first 10 min of the reaction. Exactly how the initial concentration of 2,6-dimethylaniline, ferrous ions and hydrogen peroxide affects 2,6-dimethylaniline degradation was also examined. Experimental results indicate that the 2,6-dimethylaniline degradation in the photoelectro-Fenton process is superior to the ordinary Fenton and electro-Fenton processes. Additionally, for 100% removal of 1 mM 2,6-dimethylaniline, the supplementation of 1 mM of ferrous ion, 20 mM of hydrogen peroxide, current density at 15.89 A m⁻² and 12 UVA lamps at pH 2 was necessary. The overall rate equations for 2,6-dimethylaniline degradation by Fenton, electro-Fenton and photoelectro-Fenton processes were proposed as well.

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1. Introduction

Having received considerable attention, advanced oxidation processes (AOPs) are promising alternatives for destroying toxic and biorefractory organic compounds [1–3]. The Fenton process is an AOP known for more than a century and considered as a successful treatment for industrial wastewater [4]. This process involves the production of hydroxyl radicals (OH•), which is a highly reactive oxidant that can oxidize and mineralize nearly all organic pollutants [5–7]. As an aqueous mixture of ferrous ions and hydrogen peroxide, Fenton's reagent has a rapid oxidation rate, is relatively inexpensive and is easy to operate and maintain [8]. First described in 1894, Fenton's reagent generally occurs in acidic medium between pH 2 and 4 [9,10] and may involve the following steps [11,12]:



The Fenton process completely destroys contaminants and breaks them down into harmless compounds, such as carbon dioxide, water and inorganic salts [13]. However, its applications are limited due to the generation of excessive amounts of ferric hydroxide sludge that requires additional separation processes and disposal [14]. The electro-Fenton (EF) process was subsequently developed to eliminate or minimize the limitations of the conventional Fenton process. As an electrochemical process, the electro-Fenton process can be generally divided into many groups, depending on the objective of the current supply. In this study, an electrical current is used to induce the reduction of ferric ions to form ferrous ions on the cathode side (Eq. (8)), subsequently reducing sludge disposal costs which represent a major limitation of the conventional Fenton method [1,15].

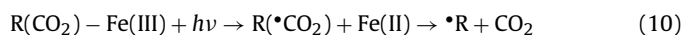


Regenerated ferrous ions react with hydrogen peroxide and produce more hydroxyl radicals that can destroy target compounds. In principle, although ferric ion can reduce to ferrous ion at the cathode during the electro-Fenton process, the ferrous ion regeneration is slow—even when the optimum electric current is applied. Both the current density and current efficiency diminish rapidly above pH ~ 2.5 [16]. Therefore, in this study, the proposed method can promote the ferrous ion regeneration by using ultraviolet (UV)-radiation to increase the efficiency of pollutant removal and reduce the amount of ferric hydroxide sludge.

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The photoelectro-Fenton process (PEF) involves additional irradiation of the solution with UVA light. The photoelectro-Fenton process refers to the generation of additional hydroxyl radicals from the regeneration of ferrous ion and the reaction of hydrogen peroxide that reacted with UV light [17–19]. Under UV–vis irradiation, overall efficiency of the process is increased, due mainly to the regeneration of ferrous ions and formation of additional hydroxyl radicals. UVA light can favor (a) the regeneration of ferrous ion with production of additional hydroxyl radicals from photoreduction of $\text{Fe}(\text{OH})^{2+}$ (Eq. (9)), which is the predominant ferric ion species in an acid medium [20] and (b) the photodecomposition of complexes of ferric ion with generated carboxylic acids (Eq. (10)) [18].



Given that the maximum adsorption wavelength of $\text{Fe}(\text{OH})^{2+}$ species is lower than 360 nm, visible irradiation may not drive the reaction of Eq. (9). An interesting and potentially useful modification of the photoreduction reaction takes advantage of the photo-ability of $\text{Fe}(\text{III})$ -oxalate complexes, which is efficient up to 500 nm [21].

2,6-Dimethylaniline was used as a target pollutant owing to its toxicity which can be found in wastewaters generated from many sources. This pollutant is widely used as a chemical intermediate to manufacture pesticides, dyestuffs, antioxidants, pharmaceuticals and other products [22]. However, a previous study demonstrated the carcinogenic nature of 2,6-dimethylaniline [23]. Such hazardous properties necessitate the treatment of contaminated wastewater to prevent its deleterious environmental effects. The literature review revealed that the Fenton, electro-Fenton and photoelectro-Fenton processes on 2,6-dimethylaniline degradation, have not been compared. In particular, their kinetics have not yet been elucidated. Therefore, this investigation compares the kinetics of 2,6-dimethylaniline degradation with those of Fenton, electro-Fenton and photoelectro-Fenton processes using initial rate techniques that cannot be found in the literature. The effect of ferrous ions and hydrogen peroxide on the degradation of 2,6-dimethylaniline by the three processes of interest was also discussed. The overall reaction rate equation for 2,6-dimethylaniline degradation by the three Fenton processes were proposed and r_F , r_{EF} and r_{PEF} the overall rate constants for Fenton, electro-Fenton and photoelectro-Fenton processes, respectively, were obtained. Finally, the 2,6-dimethylaniline removal efficiency and initial degradation rates were determined.

2. Materials and methods

All chemicals that were used in this study were prepared using de-ionized water from a Millipore system with a resistivity of 18.2 M Ω cm. 2,6-Dimethylaniline (2,6-xylydine) (>98%), perchloric acid (70–72%), ferrous sulfate (99.5–102%) and hydrogen peroxide (35–36.5%) were purchased from MERCK. Sodium hydroxide (99%) was purchased from Riedel-da Haën. All of the preparations and experiments were conducted at room temperature.

All experiments were carried out in batch mode using an acrylic reactor with dimensions of 15 cm \times 21 cm \times 20 cm and a working volume of 5 L. The two anodes and three cathodes were mesh-type titanium metal, coated with $\text{IrO}_2/\text{RuO}_2$ and stainless steel, respectively. The working areas of the cathode and anode were 900 and 600 cm², respectively. The electrodes were connected to a Topward 33010D power supply that was operated at the desired electric current. The reactor was also equipped with two mixers to ensure appropriate effective agitation. UVA lights were turned on to initiate the reaction. The irradiation source was a set of 0.06 W/UVA lamps (Sunbeamtech.com) that were fixed inside a

cylindrical Pyrex tube (which could be penetrated by $\lambda > 320$). In addition to all of the experimental conditions mentioned above, the inside of the reactor was irradiated with UVA light with a maximum wavelength of 360 nm from 12 UVA lamps, supplying a photoionization energy to the solution at a maximum power of 0.72 W.

Synthetic wastewater that contained 0.5, 1 and 5 mM of 2,6-dimethylaniline was prepared with de-ionized water and then adjusted to pH 2 with perchloric acid. After the pH adjustment, a calculated amount of catalytic ferrous sulfate was added as a source of Fe^{2+} , and then H_2O_2 was added to the reactor. The electrical current and UVA lights were delivered throughout the experimental period. The samples that were taken at predetermined time intervals were immediately injected into tubes that contained sodium hydroxide solution to quench the reaction by increasing the pH to 11 [1,24,25]. The samples were filtered through 0.45 μm membrane filters to remove the precipitates formed. 2,6-Dimethylaniline was analyzed by a gas chromatogram (HP 4890II) that was equipped with a flame ionization detector (FID) and a SUPELCO EquityTM-5 Capillary Column (length: 15 m; id: 0.15 μm). The solution pH was monitored using a SUNTEX pH/mV/TEMP (SP-701) meter. All experiments were performed in duplicate.

3. Results and discussion

The following sections will separately discuss the effects of 2,6-dimethylaniline, ferrous ion and hydrogen peroxide concentrations on the kinetics of 2,6-dimethylaniline degradation.

3.1. Effect of 2,6-dimethylaniline concentration

The pollutant concentration is one of the important factors in Fenton, electro-Fenton and photoelectro-Fenton methods. Fig. 1(a)–(c) plots the effect of 2,6-dimethylaniline concentration on the removal efficiency of 2,6-dimethylaniline by Fenton, electro-Fenton and photoelectro-Fenton processes. The figures clearly reveal that, in all processes, increasing the 2,6-dimethylaniline concentration reduces the removal efficiency of 2,6-dimethylaniline. The experiments of Muruganandham and Swaminathan [5] on the decolorization of dye by Fenton and photo-Fenton processes yielded the same results. They found that increasing the dye concentration decreased the removal efficiency and also the removal rate. The main reason for this phenomenon is the formation of hydroxyl radicals. Increasing the 2,6-dimethylaniline concentration increases the number of 2,6-dimethylaniline molecules but not the hydroxyl radical concentration, so the removal efficiency decreases. This study shows that the 2,6-dimethylaniline degradation kinetics under the given test conditions varied among conventional Fenton process, electro-Fenton process and photoelectro-Fenton processes. The kinetics of the Fenton, electro-Fenton and photoelectro-Fenton methods were compared using initial rate techniques (during the first 10 min of the reaction) to eliminate interference from intermediates that might have occurred later in the study period. Normally, the rate constant specifies the rate of degradation of the organic compound over the entire reaction. However, the degradation of 2,6-dimethylaniline in Fenton processes was a two-stage reaction, mainly because Fe^{2+} reacted very rapidly with H_2O_2 , generating a large amount of OH^\bullet , as described by Eq. (1) with a reaction rate constant of 42 M⁻¹ s⁻¹. The OH^\bullet in Eq. (1) rapidly reacted with 2,6-dimethylaniline, and therefore in the first stage, the degradation of 2,6-dimethylaniline was faster than that in the second stage. The first stage of the reaction took 10 min. The Fe^{3+} that is produced according to Eq. (1) reacts with the available hydrogen peroxide, producing HO_2^\bullet , according to Eqs. (2) and (3). Both OH^\bullet and HO_2^\bullet in the reactor can degrade 2,6-dimethylaniline. However, the rate constant of

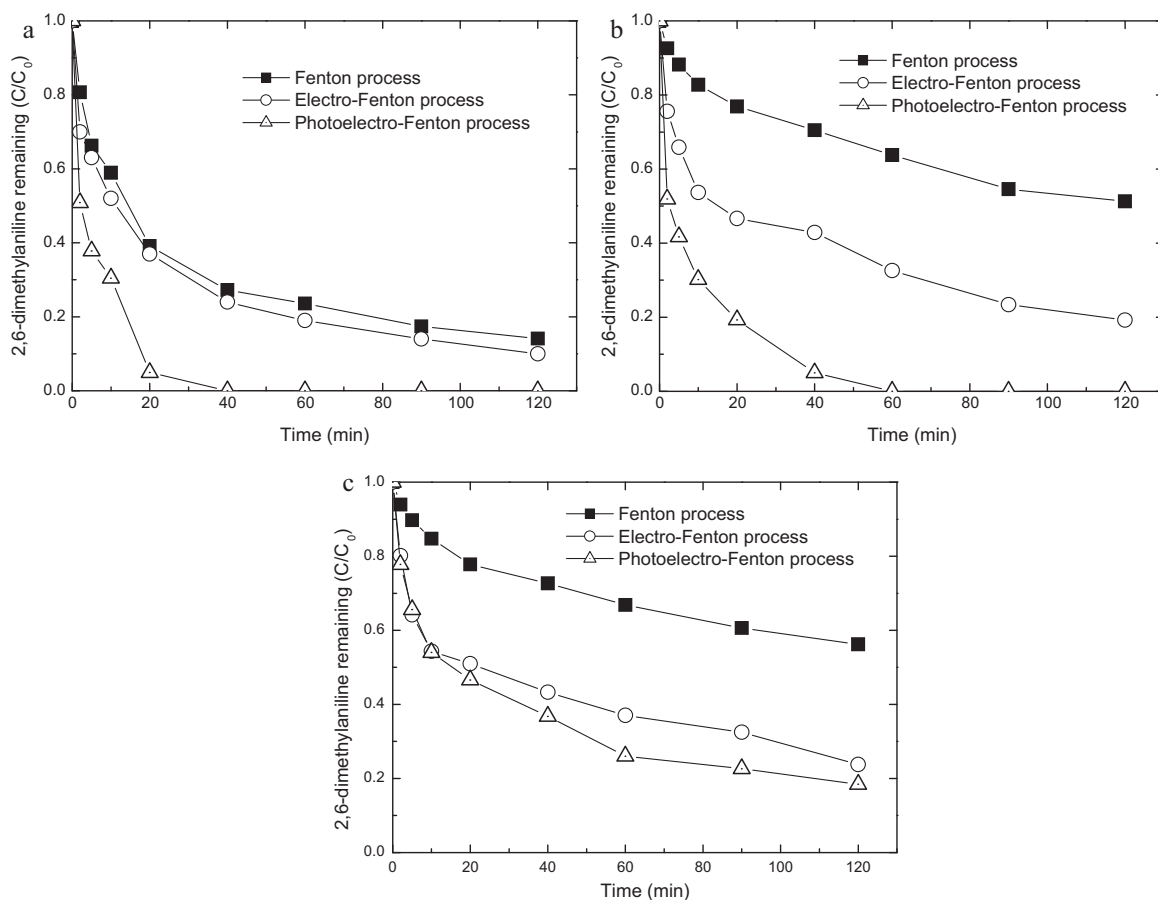


Fig. 1. Effect of 2,6-dimethylaniline concentration on the removal efficiency of 2,6-dimethylaniline (a) 2,6-DMA 0.5 mM, (b) 2,6-DMA 1.0 mM and (c) 2,6-DMA 5.0 mM ($[\text{Fe}^{2+}] = 1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 20 \text{ mM}$, $I = 15.89 \text{ A m}^{-2}$, pH 2, UVA = 12 lamps).

the reaction of Fe^{3+} with hydrogen peroxide to form Fe^{2+} is only $7.82 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ to $2.00 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Thus, the reaction of Fe^{2+} with H_2O_2 is faster than that Fe^{3+} with H_2O_2 . Therefore, in the rate of OH^\bullet production is higher in the first stage reaction than in the second stage reaction. In this study, the second stage began at 10 min. The degradation of 2,6-dimethylaniline was slower in the second stage, and involved a reaction of ferric ions with hydrogen peroxide. Fe^{3+} has a lower catalytic activity than Fe^{2+} and may complex with target organic substrates or their degradation intermediates. Another reason that the second stage of the reaction was slower may be the generation of fewer ferrous ions from ferric ions and perhaps the complexation of ferric ions and the degradation intermediates. To minimize the error of degradation rate of the intermediate and in the second stage, the initial degradation rate (in the first stage only) is used in this research [26]. The initial degradation rate was calculated using the data obtained at reactions times from 0 min to 10 min.

The results in Table 1 indicate that as the 2,6-dimethylaniline concentration increased from 0.5 to 5 mM, the initial degradation rate increased in all processes. The initial degradation rate was high at a high concentration of 2,6-dimethylaniline probably because the excess 2,6-dimethylaniline reacted with hydroxyl radicals that were produced from hydrogen peroxide and ferrous ions that destroyed 2,6-dimethylaniline. These results were also similar to those of a study of *p*-nitroaniline (PNA) degradation by Fenton oxidation process by Sun et al. [6]. They found that the amount of *p*-nitroaniline removed decreased as the initial *p*-nitroaniline concentration increased, but the initial degradation rate increased with the PNA concentration [6] and the removal of nitroaromatic explosives with Fenton's reagent [27].

The plot of the initial rate versus 2,6-dimethylaniline concentration on a log–log scale yielded a straight line with a slope of 0.16 for the Fenton process, 0.33 for the electro-Fenton process and 0.42 for the photoelectro-Fenton process. Therefore, the reaction rate equations are,

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{Fenton}} = r_{F,2,6\text{-DMA}}[2,6\text{-DMA}]^{0.16} \quad (11)$$

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{electro-Fenton}} = r_{\text{EF},2,6\text{-DMA}}[2,6\text{-DMA}]^{0.33} \quad (12)$$

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{photoelectro-Fenton}} = r_{\text{PEF},2,6\text{-DMA}}[2,6\text{-DMA}]^{0.42} \quad (13)$$

where 2,6-DMA is 2,6-dimethylaniline, and $r_{F,2,6\text{-DMA}}$, $r_{\text{EF},2,6\text{-DMA}}$ and $r_{\text{PEF},2,6\text{-DMA}}$ are the rate constants for the Fenton, electro-Fenton and photoelectro-Fenton processes with respect to 2,6-dimethylaniline degradation, respectively. The kinetics of degradation by the Fenton process in Eq. (11) approached zero-order with respect to 2,6-dimethylaniline concentration. However, the kinetics of degradation by the photoelectro-Fenton process approached half-order.

3.2. Effect of ferrous ion concentration

Normally, the rate of degradation increases with the concentration of ferrous ions. The effect of ferrous ion concentration on the kinetics of 2,6-dimethylaniline degradation was studied by varying the ferrous ion concentration from 0.25 to 2 mM and under

Table 1
Initial degradation rate of 2,6-dimethylaniline by Fenton, electro-Fenton and photoelectro-Fenton processes.

[2,6-DMA] (mM)	[Fe ²⁺] (mM)	[H ₂ O ₂] (mM)	Initial degradation rate		
			Fenton (mM s ⁻¹)	EF (mM s ⁻¹)	PEF (mM s ⁻¹)
0.5	1.00	20	3 × 10 ⁻⁴	4.5 × 10 ⁻⁴	5 × 10 ⁻⁴
1.0	1.00	20	3 × 10 ⁻⁴	8 × 10 ⁻⁴	10 × 10 ⁻⁴
5.0	1.00	20	10 × 10 ⁻⁴	20 × 10 ⁻⁴	25 × 10 ⁻⁴
1.0	0.25	20	2 × 10 ⁻⁴	7 × 10 ⁻⁴	9 × 10 ⁻⁴
1.0	2.00	20	5 × 10 ⁻⁴	11 × 10 ⁻⁴	13 × 10 ⁻⁴
1.0	1.00	5	1 × 10 ⁻⁴	5 × 10 ⁻⁴	9 × 10 ⁻⁴
1.0	1.00	100	3 × 10 ⁻⁴	7 × 10 ⁻⁴	8 × 10 ⁻⁴

the experimental conditions of an initial concentration of 2,6-dimethylaniline of 1 mM, a hydrogen peroxide concentration of 20 mM, pH 2 and a current density of 15.89 A m⁻² for the electro-Fenton process and 12 UVA lamps in the photoelectro-Fenton process. The results reveal that the removal efficiency by the Fenton, electro-Fenton and photoelectro-Fenton methods increased with the ferrous ion concentration from 0.25 to 2 mM, as shown in Fig. 2(a)–(c) [28]. In the Fenton process, the removal efficiency increased from 25 to 90% as the ferrous ion concentration. The same trend was exhibited in removal by the electro-Fenton process, and the removal efficiency increased from 87 to 100%. The photoelectro-Fenton process had a removal efficiency of 100% after 2 h for all initial ferrous ion concentrations. Additionally, in the first 60 min of reactions, the removal efficiency increased from 88% to 100% as the initial ferrous ion concentration was increased.

The initial rate of degradation by the Fenton process of 2,6-dimethylaniline increased with the initial ferrous ion concentration from 2 × 10⁻⁴ to 5 × 10⁻⁴ mM s⁻¹; that by the electro-Fenton process increased from 7 × 10⁻⁴ to 11 × 10⁻⁴ mM s⁻¹ and that by the photoelectro-Fenton process increased from 9 × 10⁻⁴ to 13 × 10⁻⁴, respectively, as listed in Table 1. The ratio of the ferrous ion concentration to the hydrogen peroxide concentration in this study was less than one. Therefore, some scavenging reactions may have occurred (Eq. (5)).

Usually, as the initial ferrous ion concentration is increased, the generation rate of hydroxyl radicals is increased. Moreover, the ferric ion in Eq. (1) can reduce to the ferrous ion according to Eq. (8) for the electro-Fenton process and Eq. (9) for the photoelectro-Fenton process, accelerating the degradation of 2,6-dimethylaniline. For this reason, these two processes yielded similar results. The addition of hydrogen peroxide throughout the experiment may improve

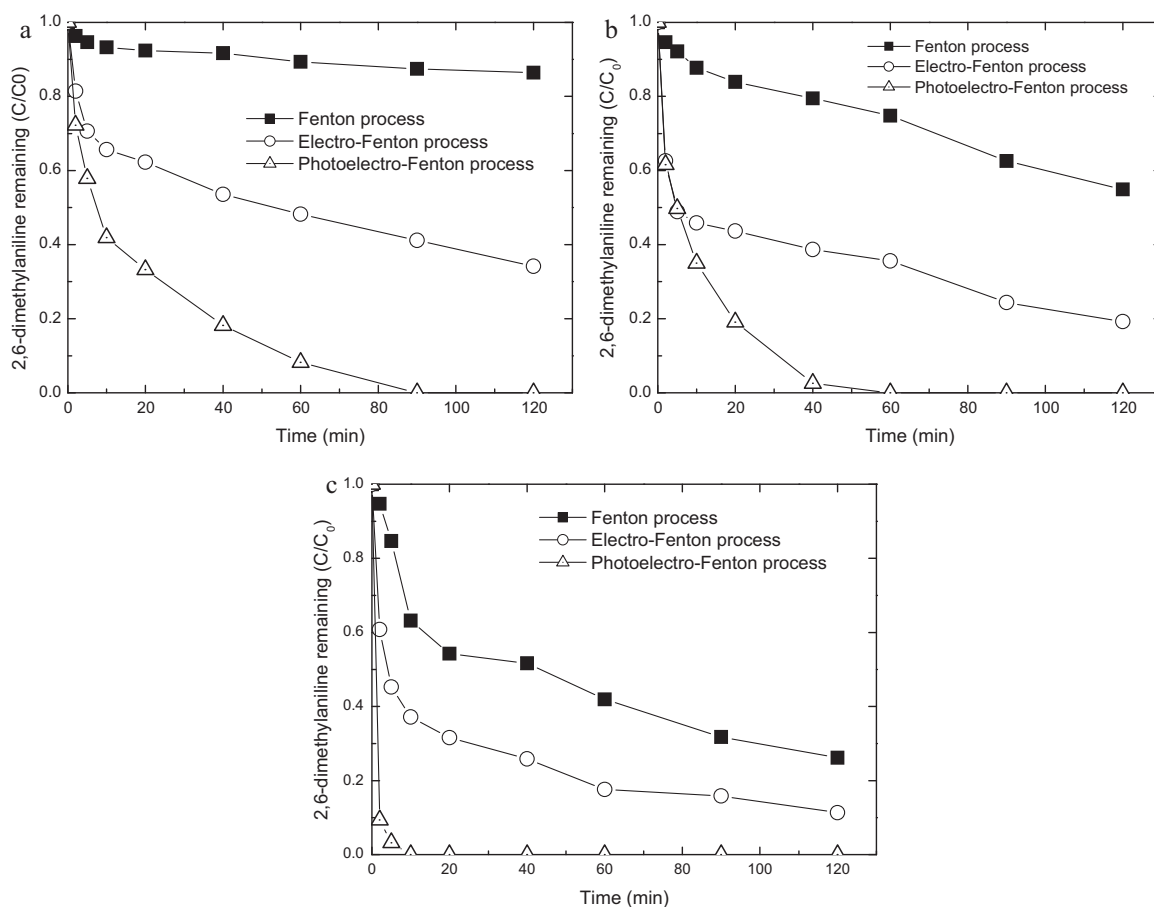


Fig. 2. Effect of initial ferrous ion concentration on the removal efficiency of 2,6-dimethylaniline (a) Fe²⁺ 0.25 mM, (b) Fe²⁺ 1.00 mM and (c) Fe²⁺ 2.00 mM ([2,6-DMA] = 1 mM, [H₂O₂] = 20 mM, *I* = 15.89 A m⁻², pH 2, UVA = 12 lamps).

the removal efficiency by ferrous ions as it may lead to more regeneration of ferrous ions from ferric ions, as described in Eqs. (8) and (9). Therefore, the total amount of generated hydroxyl radicals and removal efficiency increase with the ferrous ion concentration.

The initial rate and removal efficiency of 2,6-dimethylaniline in the electro-Fenton process were similar to those by the Fenton process. The electrons that were supplied by the electrical current rapidly regenerate ferrous ions and so can react with hydrogen peroxide as long as hydrogen peroxide is still available in the reactor. For that reason, the degradation of 2,6-dimethylaniline continued without the addition of ferrous ions to the solution, increasing the efficiency of hydroxyl radical production. The initial degradation rate and removal efficiency of 2,6-dimethylaniline in the photoelectron-Fenton process were similar to those in the Fenton and electro-Fenton processes.

The photoelectro-Fenton process combined all of the advantages of Fenton's reaction in the formation of hydroxyl radicals, the reduction of ferric ions to ferrous ions at the cathode in the electro-Fenton system and the photoreduction of ferric ions to ferrous ions in photoelectro-Fenton system. This combination made the efficiency of the photoelectro-Fenton process higher than those of both the Fenton process and the electro-Fenton process. The 2,6-dimethylaniline degradation kinetics under the given test conditions were the same in the electro-Fenton and photoelectro-Fenton processes. The results indicate that the rate of 2,6-dimethylaniline degradation increased with ferrous ion concentration.

The relationships between the initial rate of degradation and ferrous ion concentration for the Fenton, electro-Fenton and photoelectro-Fenton processes were determined. The calculation reveals that the initial rates were linearly proportional to the concentration of added ferrous ions, with slopes of 0.17, 0.23 and 0.23 on a log-log scale for Fenton, electro-Fenton and photoelectro-Fenton processes, respectively. Thus, the effect of ferrous ion concentration on the kinetics of 2,6-dimethylaniline degradation can be described by the following equations.

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{Fenton}} = r_{\text{F,Fe}^{2+}} [\text{Fe}^{2+}]^{0.17} \quad (14)$$

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{electro-Fenton}} = r_{\text{EF,Fe}^{2+}} [\text{Fe}^{2+}]^{0.23} \quad (15)$$

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{photoelectro-Fenton}} = r_{\text{PEF,Fe}^{2+}} [\text{Fe}^{2+}]^{0.23} \quad (16)$$

where $r_{\text{F,Fe}^{2+}}$, $r_{\text{EF,Fe}^{2+}}$ and $r_{\text{PEF,Fe}^{2+}}$ are the rate constants for the Fenton, electro-Fenton and photoelectro-Fenton processes, respectively, with respect to ferrous ions. As in the previous section, the rate of degradation by the Fenton process, corresponding to Eq. (14), approached zero-order with respect to Fe^{2+} concentration. The decomposition of 2,6-dimethylaniline by the electro-Fenton and photoelectro-Fenton processes also approached zero-order with respect to Fe^{2+} . The results indicate that ferrous ion play an important role in the degradation of 2,6-dimethylaniline by reacting with hydrogen peroxide to generate hydroxyl radicals. However, increasing the concentration of supplementary ferrous ions using the Fenton, electro-Fenton and photoelectro-Fenton processes is not recommended because of the formation of a large amount of ferric hydroxide sludge, which requires further separation and disposal, making the overall process uneconomical.

3.3. Effect of hydrogen peroxide concentration

Hydrogen peroxide is an oxidizing agent in the Fenton reaction. The percentage degradation of the pollutant increases with the concentration of hydrogen peroxide [25]. The effect of initial hydrogen peroxide concentration on the removal efficiency

and rate of 2,6-dimethylaniline degradation was investigated by varying the initial hydrogen peroxide concentration from 5 to 100 mM.

The experimental results indicate that the removal efficiencies of Fenton, electro-Fenton and photoelectro-Fenton processes increased with the initial concentration of hydrogen peroxide, as plotted in Fig. 3(a)–(c) [29]. The removal efficiency in the Fenton process increased from 49% to 77% as the hydrogen peroxide concentration increased from 5 to 100 mM. The same trend was found in the electro-Fenton process, in which the removal efficiency increased from 89 to 100%, as shown in Fig. 3(b). In the photoelectro-Fenton process all (100%) of the 2,6-dimethylaniline was removed after 2 h.

Table 1 shows that the initial rate of 2,6-dimethylaniline degradation increased with hydrogen peroxide concentration from 5 to 20 mM. This increase in initial rate was caused by the availability of hydrogen peroxide to react with ferrous ions in the solution. However, increasing the initial concentration of hydrogen peroxide to 100 mM led reduced initial rate—from 8×10^{-4} to $7 \times 10^{-4} \text{ mM s}^{-1}$ in the electro-Fenton process and from 10×10^{-4} to $8 \times 10^{-4} \text{ mM s}^{-1}$ in the photoelectro-Fenton process. However, the initial rate in the Fenton process remained constant. This phenomenon was probably associated with the scavenging of hydroxyl radicals by hydrogen peroxide, as described by Eq. (5) [26]. The accumulation of hydroperoxyl radicals also consumed hydroxyl radicals [6,30]. Hydrogen peroxide might have been consumed in the scavenging reaction and by some intermediates [25]. The relationship between the initial rate of the reaction and the initial concentration of hydrogen was linear with slopes on a log-log scale of 0.0014, 0.001 and -0.0015 for the Fenton, electro-Fenton and photoelectro-Fenton processes, respectively. Therefore,

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{Fenton}} = r_{\text{F,H}_2\text{O}_2} [\text{H}_2\text{O}_2]^{0.0014} \quad (17)$$

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{electro-Fenton}} = r_{\text{EF,H}_2\text{O}_2} [\text{H}_2\text{O}_2]^{0.001} \quad (18)$$

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{photoelectro-Fenton}} = r_{\text{PEF,H}_2\text{O}_2} [\text{H}_2\text{O}_2]^{-0.0015} \quad (19)$$

where $r_{\text{F,H}_2\text{O}_2}$, $r_{\text{EF,H}_2\text{O}_2}$ and $r_{\text{PEF,H}_2\text{O}_2}$ are rate constants for the Fenton, electro-Fenton and photoelectro-Fenton processes, respectively, with respect to hydrogen peroxide. In fact, the decomposition of 2,6-dimethylaniline by all of these processes approached zero-order with respect to H_2O_2 concentration.

3.4. Overall reaction rate equation for 2,6-dimethylaniline degradation

The concentrations of 2,6-dimethylaniline, ferrous ion and hydrogen peroxide affected the reaction rate equations for the degradation of 2,6-dimethylaniline by the Fenton, electro-Fenton and photoelectro-Fenton processes. The overall kinetics of degradation of 2,6-dimethylaniline by these three methods are summarized below.

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{Fenton}} = r_{\text{F}} [2, 6\text{-DMA}]^{0.16} [\text{Fe}^{2+}]^{0.17} [\text{H}_2\text{O}_2]^{0.0014} \quad (20)$$

$$-\left(\frac{d[2, 6\text{-DMA}]}{dt}\right)_{\text{electro-Fenton}} = r_{\text{EF}} [2, 6\text{-DMA}]^{0.33} [\text{Fe}^{2+}]^{0.23} [\text{H}_2\text{O}_2]^{0.001} \quad (21)$$

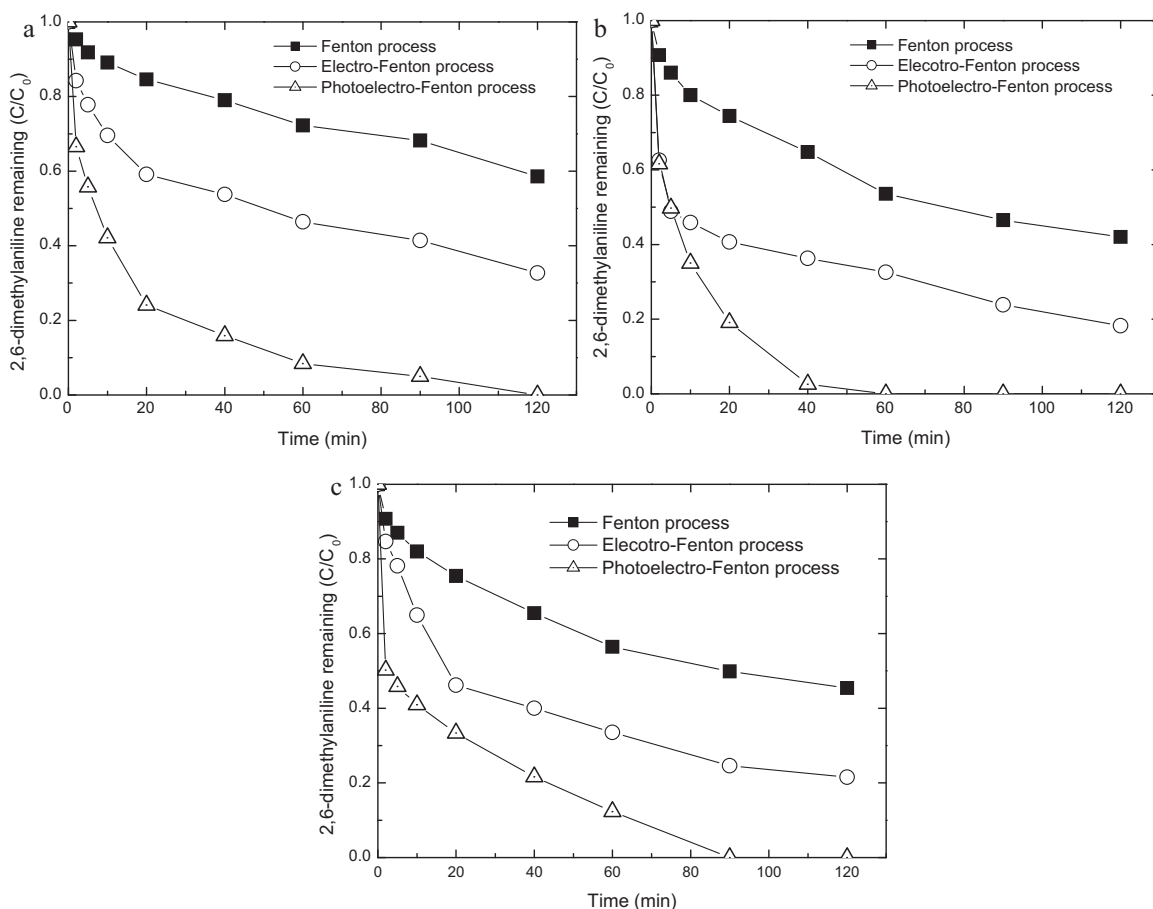


Fig. 3. Effect of initial hydrogen peroxide concentration on the removal efficiency of 2,6-dimethylaniline (a) H_2O_2 5 mM, (b) H_2O_2 20 mM and (c) H_2O_2 100 mM ([2,6-DMA] = 1 mM, $[\text{Fe}^{2+}] = 1$ mM, $I = 15.89 \text{ A m}^{-2}$, pH 2, UVA = 12 lamps).

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{photoelectro-Fenton}} = r_{\text{PEF}}[2,6\text{-DMA}]^{0.42}[\text{Fe}^{2+}]^{0.23}[\text{H}_2\text{O}_2]^{-0.0015} \quad (22)$$

where r_F , r_{EF} and r_{PEF} are the overall rate constants for the Fenton, electro-Fenton and photoelectro-Fenton processes, respectively. From Eqs. (20) and (21), the degradation rate of 2,6-dimethylaniline by the Fenton process and the electro-Fenton process depended on both ferrous ion and hydrogen peroxide (Fenton's reagent). However, Eq. (22) reveals that the degradation rate of 2,6-dimethylaniline is independent of the concentration of H_2O_2 when an electrical current and UVA are applied. Nevertheless, the ferrous ions remain an important chemical species for the degradation of 2,6-dimethylaniline. Therefore, Fenton's reagent is still important for this process. The r_F , r_{EF} and r_{PEF} , from Eqs. (20)–(22), can be calculated using a non-linear least squares method, which minimizes the sum of the squares of errors between the observed initial rates and the calculated initial rates. Accordingly, the r_F , r_{EF} and r_{PEF} could be determined from the concentrations of 2,6-dimethylaniline, ferrous ion and hydrogen peroxide in millimolar (mM) to be 6.72×10^{-4} , 3.69×10^{-3} and 6.88×10^{-3} , respectively. Therefore, the final reaction rate equations are,

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{Fenton}} = 6.72 \times 10^{-4}[2,6\text{-DMA}]^{0.16}[\text{Fe}^{2+}]^{0.17}[\text{H}_2\text{O}_2]^{0.0014} \quad (23)$$

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{electro-Fenton}} = 3.69 \times 10^{-3}[2,6\text{-DMA}]^{0.33}[\text{Fe}^{2+}]^{0.23}[\text{H}_2\text{O}_2]^{0.001} \quad (24)$$

$$-\left(\frac{d[2,6\text{-DMA}]}{dt}\right)_{\text{photoelectro-Fenton}} = 6.88 \times 10^{-3}[2,6\text{-DMA}]^{0.42}[\text{Fe}^{2+}]^{0.23}[\text{H}_2\text{O}_2]^{-0.0015} \quad (25)$$

Based on this kinetic study, the presence of Fenton's reagent, electricity and a UVA lamp can all increase the removal efficiency and rate of degradation of 2,6-dimethylaniline. Within the range of concentrations of Fenton's reagent that were used in this study, the initial ferrous ion concentration was the most important parameter that affected the removal efficiency and initial degradation rate. Thus, the use of electro-Fenton and photoelectro-Fenton methods to accelerate the regeneration of ferrous ions from ferric ions could significantly improve both the removal efficiency and the initial degradation rate of 2,6-dimethylaniline. Based on the results, the overall rate equations for the degradation of 2,6-dimethylaniline by Fenton, electro-Fenton and photoelectron-Fenton process indicate that Fenton's reagent significantly affects the degradation of 2,6-dimethylaniline.

4. Conclusions

In this study Fenton, electro-Fenton and photoelectro-Fenton processes were used to oxidize 2,6-dimethylaniline. The results indicate that all three processes degraded the target compound. However, the photoelectro-Fenton process was superior to the Fenton and electro-Fenton processes. 1 mM 2,6-dimethylaniline was completely degraded under conditions of 1 mM of ferrous ions, 20 mM of hydrogen peroxide, 12 UVA lamps, 1.43 A and pH 2.

The experimentally established kinetics were mathematically analyzed by considering the three important parameters, which were the concentrations of 2,6-dimethylaniline, ferrous ions and hydrogen peroxide. The initial degradation rate of 2,6-dimethylaniline (1) decreased as the concentration of 2,6-dimethylaniline increased in the range 0.5–5 mM; (2) it increased with initial ferrous ion concentration in the range 0.25–2 mM, and (3) it also increased with the hydrogen peroxide in the Fenton process. However, the initial rate decreased as the initial hydrogen peroxide concentration was increased further. The results also indicate that the concentrations of 2,6-dimethylaniline, ferrous ions and hydrogen peroxide strongly influenced the kinetic rate constant for 2,6-dimethylaniline degradation.

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