Journal of Hazardous Materials

Oxidative degradation of diethyl phthalate by photochemically-enhanced Fenton reaction

Gui-Peng Yang [a,b,*], Xue-Kun Zhao [a,c], Xiao-Jing Sun [a], Xiao-Lan Lu [a]

[a] *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266003, PR China*
[b] *Department of Biology (Québec-Océan), Pavillon Vachon, Local 2078, Laval University, Québec, P.Q., Canada G1K 7P4*
[c] *Administrative Committee of High & New Technology Industries Development Zone of Weifang Ocean Chemical Engineering, Weifang 262737, PR China*

Abstract

A kinetic investigation into the photo-degradation of aqueous diethyl phthalate by Fenton reagent was conducted in this study. The obtained results showed the enhancement of diethyl phthalate (DEP) decomposition by UV irradiation with the Fenton reaction. It was found that H_2O_2 concentration, Fe^{2+} concentration, and aqueous pH value were the three main factors that could significantly influence the degradation rates of DEP. The highest degradation percentage (75.8%) of DEP was observed within 120 min at pH 3 in the $UV/H_2O_2/Fe^{2+}$ system, with original H_2O_2 and Fe^{2+} concentrations of 5.00×10^{-4} and 1.67×10^{-4} mol L^{-1}, respectively. The present study provides an effective approach to the treatment of wastewater containing DEP.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Phthalate acid esters (PAEs) are a class of organic compounds most widely used in the industrial production and mainly serve as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating (about 85% of the whole production) [1]. In addition, minor applications are in cosmetics, insect repellent, insecticide carries and propellants [2]. At present, the worldwide production of phthalate acid esters has reached 2.7 million metric tons per year [3]. Owing to the large production and utilization, these compounds are leached out by water thus turning into ubiquitous aqueous persistent organic pollutant in environment [4]. Some of the PAEs, especially the long chained esters, have been recognized as cancer suspect agents and are therefore considered as 'priority pollutants' [4].
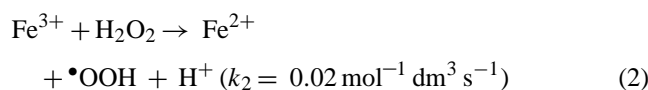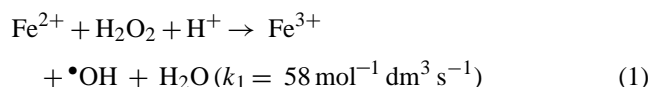
The short-chained esters such as diethyl phthalate, which mainly come from the discharge of wastewater, and leaching and volatilization from plastic products during their usage and after disposal [3,5], are among the most frequently identified PAEs in diverse environmental samples including surface marine waters [6–10], freshwaters [1,10–12] and sediments [6,10,13]. Furthermore, the esters are found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base food chain in both marine and fresh water environments [5]. Since phthalate esters are becoming a class of concerning water pollutants, which are difficult to biologically and photo-chemically degrade [5], there is a strong need to look for effective treatment processes for such pollutants.

Mainly due to the inability of biological processes to treat highly contaminated and toxic wastewater with organic pollutants (especially persistent organic pollutants (POPs)), various photochemically advanced oxidation processes (AOPs) such as O_3/UV [14], UV/H_2O_2 [14,15],

* Corresponding author. Tel.: +86 532 2032686; fax: +86 532 2032483.
  E-mail address: gpyang@mail.ouc.edu.cn (G.-P. Yang).

TiO$_2$/UV [16–18] and Fenton/UV [14–16,18–26], have been successfully utilized to degrade most of the organic compounds present in polluted water. In photochemically AOPs, the hydroxyl radicals are generated in solution and are responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide [15,27].

The Fenton reaction is recognized as one of the most powerful oxidizing reaction available, with a demonstrated capacity for large-scale decomposition of the refractory synthesized or natural organic compounds. The primary reactions in representative Fenton process are [28–30]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+}$$
$$+ {}^{\bullet}OH + H_2O \, (k_1 = 58 \, mol^{-1} \, dm^3 \, s^{-1}) \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+}$$
$$+ {}^{\bullet}OOH + H^+ \, (k_2 = 0.02 \, mol^{-1} \, dm^3 \, s^{-1}) \tag{2}$$

where ${}^{\bullet}OH$ is the hydroxyl radical and ${}^{\bullet}OOH$ is the superoxide radical. If the concentration of hydroxyl radicals generated in the Fenton system is sufficient, almost all the organic substances can be oxidized and mineralized to carbon dioxide and water [6,14,15,17,19–25,28–33]. Thus, Fenton treatment has attracted much interest for the destruction of toxic organic compounds in wastewater. In recent years, many studies have shown that the decomposition of various organic pollutants using hydrogen peroxide as an oxidants under UV illumination have been proven to be very effective [14,15,17,19–24]. Phenol [14], p-chlorophenol [15], polyvinyl alcohol [17], dichloroacetic acid [19], 2,4-dichlorophenol [19], malachite green [20], benzothiazole [21], diclofenac [22], nitrobenzene [23], nitrophenols [24], fenitrothion [26] and many other aromatic compounds are degraded much more rapidly under the UV illumination of the Fe^{2+}/H$_2$O$_2$ or Fe^{3+}/H$_2$O$_2$ systems than in the dark reactions.

Considering the toxicity of PAEs and their inability of biological degradation, we have first undertaken a detailed kinetic study on the degradation of dimethyl phthalate (DMP) by Fenton/UV system [34]. The previous research results showed that the photo-degradation percentage of dimethyl phthalate within 120 min was as high as 81% under the optimum conditions. As a series of researches, in this paper we choose another representative phthalate ester, diethyl phthalate (DEP), to investigate its decomposition behavior under UV irradiation with the Fenton reaction. The experiments were conducted under a variety of reaction conditions using hydrogen peroxide and ferrous ion (Fenton reagent) as oxidant with artificial UV light (high pressure Hg lamp). The obtained data indicated that the Fenton degradation of DEP could be greatly accelerated by UV irradiation.

2. Experimental

2.1. Reagents

Diethyl phthalate, hydrogen peroxide (30% w/w), FeSO$_4$·7H$_2$O and Na$_2$SO$_3$, purchased from Shanghai Chemical Reagent Co., China, were of analytical grade and used without further purification. Deionized water was used throughout the study. The initial concentration of DEP in all the experiments was 10 mg L^{-1}. The stock solutions of high concentrations of hydrogen peroxide (10.00 mol L^{-1}) and iron (5.00 mol L^{-1}) were prepared according to the previous literatures [25,27–30]. The high concentration of H$_2$O$_2$ was determined by a potassium permanganate method.

2.2. Methods

The degradation reaction of DEP in aqueous solution during the Fenton/UV-treatment was performed in a SGY1 Model Multifunction Photochemistry Reactor (Nanjing Sidongke Instrument Co. Ltd., China). The reactor was a cylindrical quartz glass vessel with a diameter of 8 cm and a capacity of 1.0 L. A 160 W high pressure Hg lamp (Institute of Electric Light Source of Beijing, China) as a UV light source was set within the cylindrical quartz vessel. A water circulation system placed between the reactor and Hg lamp was used to cool the lamp. The reaction chamber was filled with the reaction mixture and was approximately 4 cm away from the UV lamp. The emission spectrum of the UV lamp used in this study was between 230 and 700 nm, with most part of energy focusing on 290–450 nm. This wavelength range could penetrate into the irradiated solution with a permeation ratio of >80%.

For each experiment, synthetic aqueous solution of 10 mg L^{-1} DEP was prepared in deionized water. Then 300 mL solution of 10 mg L^{-1} DEP was poured into the reactor. Subsequently, a series of different volumes (0–0.03 mL) of high concentration of H$_2$O$_2$ or Fe^{2+} solution were added into the reactor to examine the effects of the concentration on the degradation reaction. Because the volume of the standard stock solution added was minimal, no dilution effect would produce on DEP solution. The pH value of the solution was 3.0 (if not mentioned differently), which was adjusted using NaOH and H$_2$SO$_4$ solution. The change in the pH of the reaction solution was within 0.2 during the irradiation. Therefore, no pH buffer solution was used in the experimental processes. The time at which the lamp was turned on was considered as time zero or the beginning of the experiment, which was taking place simultaneously with the addition of H$_2$O$_2$ and Fe^{2+}. Subsamples (20 mL) were periodically taken out from the reactor during the course of the reaction. The dark reaction was conducted by wrapping the tubes with aluminum foil to prevent exposure to light. One drop of 10% aqueous solution of Na$_2$SO$_3$ was added to each sample to quench the reaction between ${}^{\bullet}OH$ and DEP [24]. The total reaction time was 120 min. All experiments were carried out at 25 ± 1 °C.

2.3. Analysis

At given irradiation time intervals, subsamples were taken out and analyzed by HPLC experiments. The HPLC experiments were carried out on both devices: a Hewlett-Packard, series 1050 with UV detection at 202 nm and a Waters chromatograph 540 with a Waters photodiode array detector 990. The chromatographic column used was a kromasil C-18, 5 μm, 100 Å, 150 mm × 4.6 mm Touzart and Matignon column. The mixture of acetonitrile with H_2O (ACN/H_2O 40/60 v/v) was utilized as a mobile phase with a flow rate of 1 mL min^{-1}. Changes in DEP concentrations with irradiation time and the degradation percentage of DEP were determined. All samples were immediately analyzed to avoid further reactions. Relative standard deviation for the sample analyses was typically within 5%.

3. Results and discussion

3.1. Effect of UV-Fenton system on the degradation of DEP

The degradation trends and percentages of DEP (10 mg L^{-1}) at pH 3.0 under different conditions were shown in Fig. 1 and Table 1, respectively. As shown in Fig. 1, the degradation of DEP could not occur in aqueous solution only irradiated under high pressure Hg lamp (curve a of Fig. 1). Even under UV irradiation with Fe^{2+} or H_2O_2, the concen-
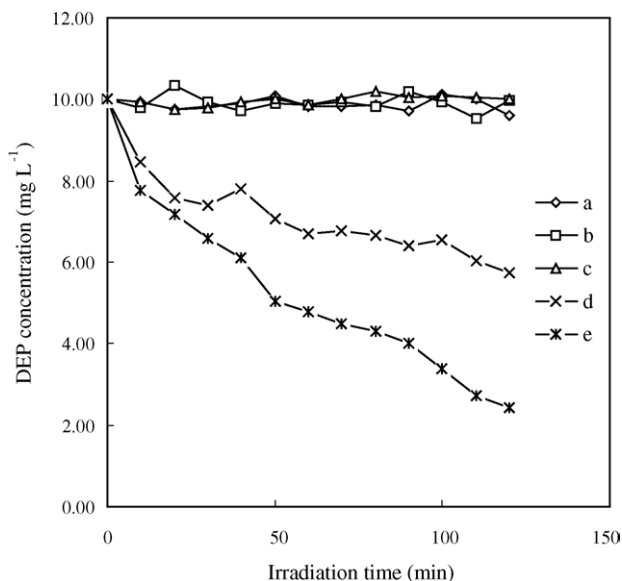

Fig. 1. The degradation of DEP (10 mg L^{-1}) at pH 3.0 under different conditions. (a) Solution without Fe^{2+} and H_2O_2 under UV light irradiation; (b) solution with Fe^{2+} (1.67 × 10^{-4} mol L^{-1}) under UV light irradiation; (c) solution with H_2O_2 (5.00 × 10^{-4} mol L^{-1}) under UV light irradiation; (d) solution with H_2O_2 (5.00 × 10^{-4} mol L^{-1}) and Fe^{2+} (1.67 × 10^{-4} mol L^{-1}) in dark; (e) solution with H_2O_2 (5.00 × 10^{-4} mol L^{-1}) and Fe^{2+} (1.67 × 10^{-4} mol L^{-1}) under UV light irradiation.

trations of DEP were almost constant in aqueous solution (curves b and c of Fig. 1). Although hydroxyl radical could be formed in H_2O_2 solution under the irradiation according to Eq. (3) [33] and had high oxidation potential ($E_0 = 2.80$ V) [31],

$$H_2O_2 + h\nu \rightarrow\ 2^{\bullet}OH \tag{3}$$
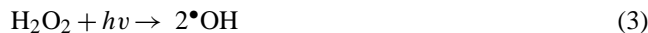
the degradation of DEP still did not occur (curve c of Fig. 1). This might be resulted from the fact that the amount of $^{\bullet}$OH formed from Eq. (3) was not enough to oxidize DEP in virtue of highly inert characteristics of DEP itself.

However, Fig. 1 shows that the degradation of DEP occurred in the solution with Fe^{2+} and H_2O_2 (i.e. Fenton reagent) in dark (curve d of Fig. 1). This was mainly caused by the reaction between H_2O_2 and ferrous salt. From Eqs. (1) and (2), it is apparent that the decomposition of H_2O_2 by iron ions is through the interaction between Fe^{2+} and Fe^{3+}. Because the reaction rate of Eq. (1) was faster than that of Eq. (2), Fe^{2+} was rapidly oxidized to Fe^{3+} in the reaction process. Therefore, the concentration of hydroxyl radical in the solution rapidly increased and could oxidize DEP. In addition, from Eq. (2) it could be seen that Fe^{2+} could be re-generated from the reduction of Fe^{3+}, leading to the continuous generation of hydroxyl radical.

Additionally, from Fig. 1 it can be seen that the rate of degradation of DEP in the H_2O_2/Fe^{2+}/UV system (curve e of Fig. 1) was much faster than that in the H_2O_2/Fe^{2+}/dark system (curve d of Fig. 1). Simultaneously, the degradation percentage of DEP in the H_2O_2/Fe^{2+}/UV system within 120 min was about two-fold that of DEP in the H_2O_2/Fe^{2+}/dark system (Table 1). This observation could be related to two factors. On one hand, in combination of thermal process and UV irradiation, the oxidation power of Fenton reagent was significantly increased due mainly to the photo-reduction of Fe(III) to Fe(II), which could react with H_2O_2 establishing a cycle mechanism of generating additional hydroxyl radials (Eq. (4)) [29,35,36].

$$Fe^{3+} + H_2O + h\nu \rightarrow\ ^{\bullet}OH\ +\ Fe^{2+} + H^+ \tag{4}$$
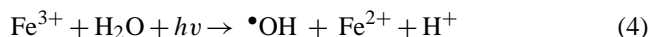
On the other hand, the influence of UV light was also attributed to the direct hydroxyl radical formation and regeneration of Fe^{2+} from the photolysis of the complex Fe(OH)$^{2+}$ in solution. It was known that the exiting form of ferrous iron was connected with the acidity of solution. At about pH 3.00, a part of ferrous iron would exist as the form of Fe(OH)$^{2+}$, whose photolysis under UV irradiation could directly produce $^{\bullet}$OH radical and Fe^{2+}, as indicated below [37]:.

$$Fe(OH)^{2+} + h\nu \rightarrow\ ^{\bullet}OH\ +\ Fe^{2+} \tag{5}$$

Therefore, higher degradation rate and percentage of DEP was reasonably expected in the Fenton-UV system.

Table 1 also lists the degradation result of DMP under the same conditions as DEP, which was obtained in our previous study [34]. The comparison showed that the degradation percentage of DEP in the H_2O_2/Fe^{2+}/dark system was apparently

Table 1
The degradation percentage of DEP at pH 3.0 under different conditions within 120 min

Conditions	UV	Fe^{2+}/UV	H$_2$O$_2$/UV	Fe^{2+}/H$_2$O$_2$/dark	Fe^{2+}/H$_2$O$_2$/UV
Degradation percentage of DEP (%)	0	0	0	42.7	75.8
Degradation percentage of DMP (%) [34]	0	0	0	30	81

higher than that of DMP. On the contrary, the degradation percentage of DEP in the H$_2$O$_2$/Fe^{2+}/UV system was slightly lower than that of DMP. Our results clearly indicated that some difference appeared between the degradation percentages of DEP and DMP in the H$_2$O$_2$/Fe^{2+}/UV system, though these two compounds belong to the same phthalate series and have only little difference in the chemical and physical properties.

3.2. Effect of original H$_2$O concentration on the degradation of DEP

Since the primary factor contributing to the chemical costs of Fenton reagent is the cost of H$_2$O$_2$, it is important to minimize the amount of H$_2$O$_2$ required, especially for treating large volumes of wastewater with pollutants such as DEP. Therefore, the impact of the change in H$_2$O$_2$ concentration on Fenton oxidation of DEP was investigated. In these experiments, the original concentration of H$_2$O$_2$ was changed from 0 to 10.00×10^{-4} mol L^{-1}, but the concentration of Fe^{2+} remained constant. The degradation states of diethyl phthalate under different original concentrations of H$_2$O$_2$ were illustrated in Fig. 2 and the degradation percentages during 120 min were presented in Table 2.
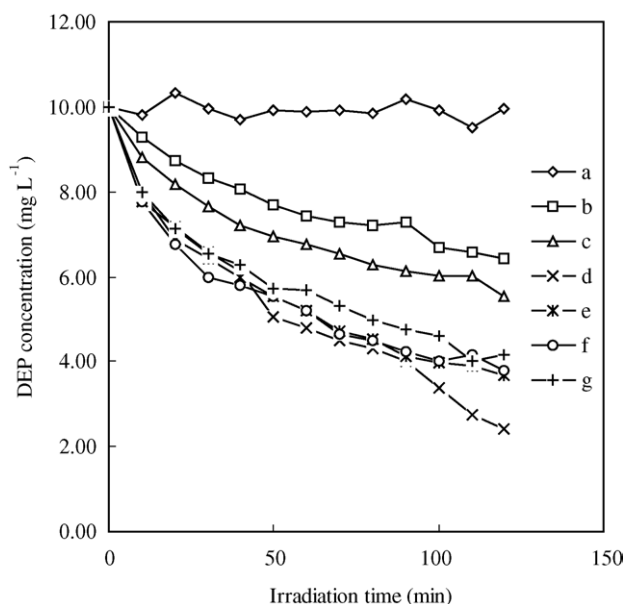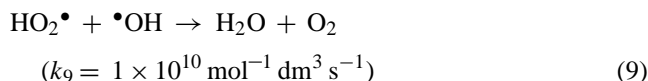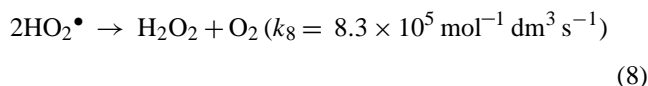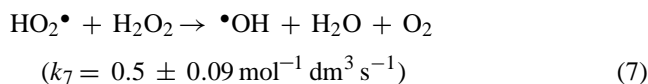

Fig. 2. The degradation of DEP (10 mg L^{-1}) in the solution with Fe^{2+} (1.67×10^{-4} mol L^{-1}) at pH 3.0 under UV light irradiation at different original H$_2$O$_2$ concentrations. (a) 0 mol L^{-1}; (b) 1.67×10^{-4} mol L^{-1}; (c) 3.33×10^{-4} mol L^{-1}; (d) 5.00×10^{-4} mol L^{-1}; (e) 6.67×10^{-4} mol L^{-1}; (f) 8.33×10^{-4} mol L^{-1}; (g) 10.00×10^{-4} mol L^{-1}.

Table 2
The degradation of DEP in solution with Fe^{2+} (1.67×10^{-4} mol L^{-1}) at pH 3.0 under UV light irradiation at different original H$_2$O$_2$ concentrations within 120 min

H$_2$O$_2$ concentration (10^{-4} mol L^{-1})	Degradation percentage (%)
0	0
1.67	35.8
3.33	44.8
5.00	75.8
6.67	63.4
8.33	62.2
10.00	58.4

Fig. 2 showed that degradation of DEP did not occur in the absence of H$_2$O$_2$, but by the addition of H$_2$O$_2$, DEP began to be degraded and the photo-degradation rate increased with increasing H$_2$O$_2$ concentration. In addition, Table 2 showed that the photo-degradation percentage of DEP varied from 0 to 75.8% when the concentration of H$_2$O$_2$ varied from 0 to 5.00×10^{-4} mol L^{-1}. This point proved that the effect of increasing H$_2$O$_2$ concentration was first positive for the degradation of DEP because the oxidation power of Fenton reagent was improved with increasing hydroxyl radical amount in solution from the decomposition of increasing H$_2$O$_2$. However, with the continuous increase in the original concentration of H$_2$O$_2$, especially beyond 5.00×10^{-4} mol L^{-1}, the photo-degradation rate of diethyl phthalate began to decrease. In the oxidation process of Fenton reagent, hydroxyl radicals were mainly responsible for the degradation of DEP. However, in the excess of hydrogen peroxide and hydroxyl radicals, competitive reactions take place. Hydroxyl radicals are prone to recombination or to reaction according to the following schemes [38–41].

$$^{\bullet}\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^{\bullet} + \text{H}_2\text{O}$$
$$(k_6 = 2.7 \times 10^7 \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}) \tag{6}$$

$$\text{HO}_2^{\bullet} + \text{H}_2\text{O}_2 \rightarrow {}^{\bullet}\text{OH} + \text{H}_2\text{O} + \text{O}_2$$
$$(k_7 = 0.5 \pm 0.09 \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}) \tag{7}$$

$$2\text{HO}_2^{\bullet} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \, (k_8 = 8.3 \times 10^5 \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1})$$
$$\tag{8}$$

$$\text{HO}_2^{\bullet} + {}^{\bullet}\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$$
$$(k_9 = 1 \times 10^{10} \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}) \tag{9}$$

$$2\,{}^{\bullet}\text{OH} \rightarrow H_2O_2 \ (k_{10} = 4.2 \times 10^9 \, \text{mol}^{-1} \, \text{dm}^3 \, \text{s}^{-1}) \qquad (10)$$
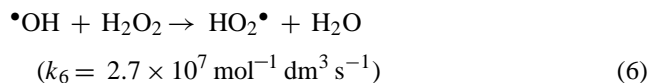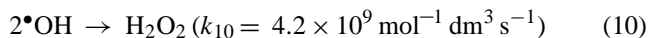
From Eqs. (6), (9) and (10), it can be found that a part of hydroxyl radicals would be consumed before oxidizing DEP. Therefore, an inhibitory effect for the degradation was produced and the DEP degradation rate and percentage decreased when the concentration of H_2O_2 was higher than $5.00 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$.

The results of Fig. 2 and Table 2 point out the negative effect of an excess of H_2O_2 on the degradation of DEP. The concentration of the reagent must be enough for the formation of a considerable amount of hydroxyl radicals, but a high concentration is detrimental.

3.3. Effect of original Fe^{2+} concentration on the degradation of DEP

From Eq. (1), it is apparent that Fe^{2+} initiates the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. Fe^{2+} plays an important role in the degradation reaction of organic pollutants and the original concentration of Fe^{2+} can influence the degradation rate and percentage of organic pollutants. In this study, various original concentrations of Fe^{2+} were investigated to obtain an optimal original concentration of Fe^{2+} for the degradation of DEP. The degradation trends and percentages of DEP with various Fe^{2+} concentrations were showed in Fig. 3 and Table 3, respectively.

From Fig. 3 and Table 3, there is a negative effect on the degradation of DEP when the initial concentration of Fe^{2+} was beyond or under $1.67 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$. It can
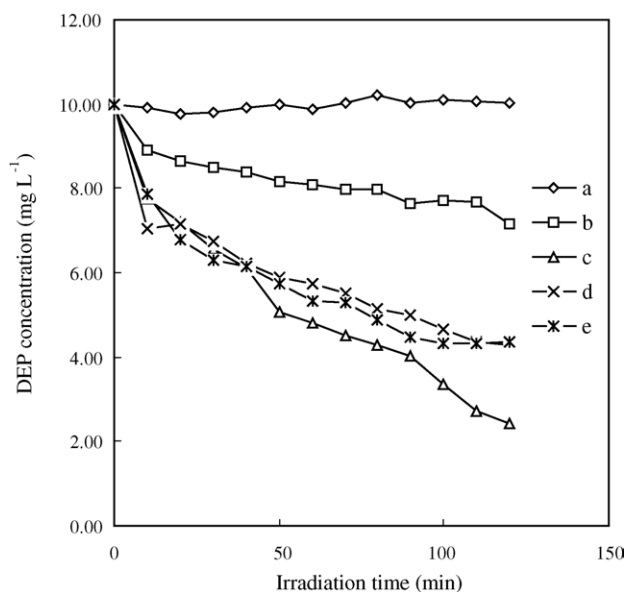
Table 3
The degradation of DEP in the solution with H_2O_2 ($5.00 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$) at pH 3.0 under UV light irradiation at different original Fe^{2+} concentrations within 120 min

Fe^{2+} concentration ($10^{-4} \, \text{mol} \, \text{L}^{-1}$)	Degradation percentage (%)
0	0
0.83	28.5
1.67	75.8
2.50	57.2
3.33	56.6

also be seen that maximum degradation rate and percentage (75.8%) of DEP appeared as the concentration of Fe^{2+} was $1.67 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$. As mentioned above, hydroxyl radicals was mainly responsible for the degradation of organic pollutants, therefore, this phenomena was because the decomposing effect of Fe^{2+} was influenced by concentration of itself in aqueous solution. On one hand, when Fe^{2+} concentration increased from 0 to $0.83 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$, the decomposing effect accordingly increased and the amount of hydroxyl radicals from decomposition of H_2O_2 would increase. Consequently, the degradation percentage of DEP naturally increased. On the other hand, when the concentration of Fe^{2+} became higher and especially was beyond $1.67 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$, a great amount of Fe^{3+} from the process of H_2O_2 decomposition by Fe^{2+} was easy to exit in the form of $Fe(OH)^{2+}$ in acidic environment. Because $Fe(OH)^{2+}$ at higher concentration had a strong absorption for UV light between 290 and 400 nm, the strength of UV light would decrease [42] and this would produce unfavorable effects on the reactions of Eqs. (3), (4) and (5). Moreover, the production rate of OH with $Fe(OH)^{2+}$ photolysis (Eq. (5)) may be lower than other radical production rates (Eqs. (1)–(4)) and this may be another reason for the decrease in degradation rate of DEP. Besides, ${}^{\bullet}$OH could be eliminated because of the reaction between Fe^{2+} and ${}^{\bullet}$OH ($3.2 \times 10^8 \, \text{mol}^{-1} \, \text{dm}^3 \, \text{s}^{-1}$) [43]. Then these factors directly led to a decrease in the amount of hydroxyl radicals formed from Eqs. (3), (4) and (5) in solution. In addition to the above reasons, the effect of sulfate ion with increasing iron concentration on the decomposition rate of DEP was also possible. Therefore, the decrease in the degradation rate and percentage of diethyl phthalate would occur.

3.4. Effect of pH on the degradation of diethyl phthalate

Fenton reactions are usually more effective in oxidation of organic compounds under acidic conditions than under neutral conditions. However, it is still not clear how the acidity of solution affects the degradation of DEP. For this reason we studied the effect of pH on the degradation of DEP and the experimental results were showed in Fig. 4 and Table 4.

In homogeneous solutions of H_2O_2 and Fe^{2+}, the acidity has a direct effect on the decomposition of hydrogen peroxides. Thus pH value can indirectly affect the oxidation efficiency of organic matter through directly influencing the

Fig. 3. The degradation of DEP (10 mg L^{-1}) in the solution with H_2O_2 ($5.00 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$) at pH 3.0 under UV light irradiation at different original Fe^{2+} concentrations. (a) 0 mol L^{-1}; (b) $0.83 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$; (c) $1.67 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$; (d) $2.50 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$; (e) $3.33 \times 10^{-4} \, \text{mol} \, \text{L}^{-1}$.
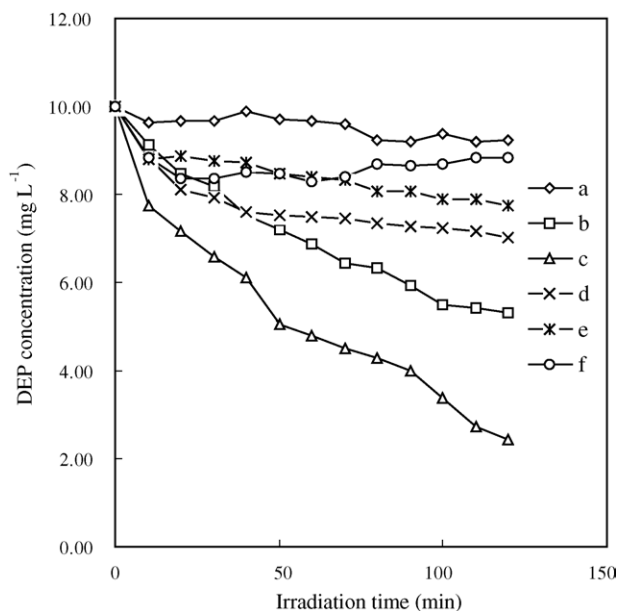
Fig. 4. The degradation of DEP $(10\,mg\,L^{-1})$ with Fe^{2+} $(1.67 \times 10^{-4}\,mol\,L^{-1})$ and H_2O_2 $(5.00 \times 10^{-4}\,mol\,L^{-1})$ under UV light irradiation at different pH values. (a) 1.0; (b) 2.0; (c) 3.0; (d) 4.0; (e) 5.0; (f) 6.0.

generation of hydroxyl radicals. From Fig. 4 and Table 4, a maximum degradation of 75.8% within 120 min was obtained in the $UV/H_2O_2/Fe^{2+}$ system at pH 3.0. Beyond pH 3.0 or under pH 3.0, the acidity produced a negative effect on the degradation of DEP. The degradation declined at pH > 3.0, because iron started to precipitate as hydroxide, leading to a reduction in the transmission of the radiation [44]. Obviously, the results obtained in the experiment at different pH could be due to the speciation of Fe(III) as a function of pH. Additionally, the oxidation potential of hydroxyl radical was known to decrease with increasing pH [45]. Consequently, the degradation of DEP at pH 6.0 was below 1/7 of that at pH 3.0 (Table 4). At pH 1.0, DEP was degraded very slowly by Fenton/UV system (curve a of Fig. 4) and the degradation percentage was only 1/10 of that at pH 3.0 (Table 4). At low pH, hydrogen peroxide can stay stable, probably because it solvates a proton to form an oxonium ion $(H_3O_2^{+})$. An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [44]. Therefore, amount of hydroxyl

radicals formed from Eq. (1) would decrease below pH 3 and thus low degradation rate and percentage of DEP appeared. In addition, there may be another possibility that the competition of sulfate ion (that was used to reduce pH) with DEP for reacting with $^{\bullet}OH$ radical might have caused the decrease in DEP degradation rate. Further research will be required.

According to the previous investigation, the wavelength of light also appeared to have an important impact on the degradation of organic matter using UV-Fenton reaction. For example, Feng et al. [46] reported that the UV light with a shorter wavelength exhibited a higher efficiency in the removal of organic matter than that with a longer wavelength. This is because the UV light wavelength can significantly influence the direct formation of $^{\bullet}OH$ radical as well as photo-reduction rate of Fe^{3+} to Fe^{2+}. Therefore, some caution should be exerted when preparing our experimental results with those produced from different light sources.

4. Conclusions

In this paper, an advanced oxidation process, Fenton/UV was utilized to degrade aqueous DEP, which was among persistent organic pollutants in environment. The optimal concentrations of reagents such as hydrogen peroxide and iron and pH in the photo-Fenton reaction were examined. The maximum degradation percentage (75.8%) of DEP was observed within 120 min at pH 3 in the $UV/H_2O_2/Fe^{2+}$ system, with original H_2O_2 and Fe^{2+} concentrations of 5.00×10^{-4} and $1.67 \times 10^{-4}\,mol\,L^{-1}$, respectively. Our experimental results clearly indicated that the photo-Fenton process was an effective process in wastewater treatment and could produce a high degradation percentage of DEP under acidic condition during a very short radiation time.

Table 4
The degradation of DEP in the solution with Fe^{2+} $(1.67 \times 10^{-4}\,mol\,L^{-1})$ and H_2O_2 $(5.00 \times 10^{-4}\,mol\,L^{-1})$ under UV light irradiation at different pH values within 120 min

pH	Degradation percentage (%)
1.0	7.6
2.0	46.9
3.0	75.8
4.0	29.8
5.0	22.6
6.0	10.6

References

[1] M. Vitali, M. Guidotti, G. Macilenti, C. Cremisini, Phthalates esters in freshwaters as markers of contamination sources-a site study in Italy, Environ. Int. 23 (1997) 337–347.

[2] D.B. Peakall, Phthalate esters: occurrence and biological effects, Residue Rev. 54 (1975) 1–41.

[3] M.J. Bauer, R. Hermann, Estimation of the environmental contamination by phthalic esters leaching from household waters, Sci. Total Environ. 208 (1997) 49–57.

[4] L.H. Keith, W.A. Telliard, Priority pollutants, Environ. Sci. Technol. 13 (1979) 416–419.

[5] C.A. Staples, D.R. Peterson, T.F. Parkarton, W.J. Adams, The environmental fate of phthalate esters: a literature review, Chemosphere 35 (1997) 667–749.

[6] G.H. Tan, Residues levels of phthalates esters in water and sediments sands from the Klang River Basin, Bull. Environ. Contam. Toxicol. 54 (1995) 171–176.

[7] O.S. Fatoki, F. Vernon, Phthalates in rivers of the Great Manchest area, UK, Sci. Total Environ. 95 (1990) 227–232.

[8] F.L. Mayer, D.L. Stalling, J.L. Johnson, Phthalate esters as environmental contaminants, Nature 238 (1972) 411–413.

[9] C.S. Giam, H.S. Chan, G.S. Nett, E.L. Atlas, Phthalates esters plasticizers: a new class of marine pollutant, Science 199 (1978) 419–421.

[10] W.E. Gledhill, R.G. Kaley, W.J. Adams, O. Hicks, P.R. Michael, V.W. Saeger, G.A. LeBlanc, An environmental safety assessment of butyl benzyl phthalate, Environ. Sci. Technol. 14 (1980) 301–305.

[11] C.A. Staples, T.F. Parkerton, D.R. Peterson, A risk assessment of selected phthalate esters in North American and western European surface waters, Chemosphere 40 (2000) 885–891.

[12] H.E. Schwartz, C.J.M. Anzion, H.P.M. van Vliet, J.M. Lopius Peereboom, U.A.Th. Brinkman, Analysis of phthalate esters in sediments from Dutch rivers by means of high performance liquid chromatography, Int. J. Environ. Anal. Chem. 6 (1979) 133–144.

[13] A. Thuren, Determination of phthalates in aquatic environments, Bull. Environ. Contam. Toxicol. 36 (1986) 33–40.

[14] S. Esplugas, J. Giménez, S. Contreras, E. Pasual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Wat. Res. 36 (2002) 1034–1042.

[15] M.Y. Ghaly, G. Härtel, R. Mayer, R. Haseneder, Photochemical oxidation of *p*-chlorophenol by UV/H_2O_2 and photo-Fenton process. A comparative study, Waste Manag. 21 (2001) 41–47.

[16] R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, P. Maletzky, The photo-Fenton reaction and the TiO_2/UV process for waste water treatment-novel developments, Catal. Today 53 (1999) 131–144.

[17] A. Nedoloujko, J. Kiwi, TiO_2 speciation precluding mineralization of 4-tert-butylpyridine: accelerated mineralization via Fenton photoassisted reaction, Wat. Res. 34 (2000) 3277–3284.

[18] M. Muneer, J. Theurich, D. Bahnemann, Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate, J. Photochem. Photobiol. A: Chem. 143 (2001) 213–219.

[19] R.F.P. Nogueira, A.G. Trovó, D.F. Modé, Solar photodegradation of dichloroacetic acid and 2,4-dichlorophenol using an enchanced photo-Fenton process, Chemosphere 48 (2002) 385–391.

[20] K.Q. Wu, Y.D. Xie, J.C. Zhao, H. Hidaka, Photo-Fenton degradation of a dye under visible light irradiation, J. Mol. Catal. A: Chem. 144 (1999) 77–84.

[21] R. Andreozz, A. D'Apuzzo, R. Marotta, A kinetic model for the degradation of benzothiale by Fe^{3+}-photo-assisted Fenton process in a completely mixed batch reactor, J. Hazard. Mater B80 (2000) 241–257.

[22] M. Ravina, L. Campanella, J. Kiwi, Accelerated mineralization of the drug Diclofenac via Fenton reactions in a concentration photoreactor, Wat. Res. 36 (2002) 3553–3560.

[23] Z.M. Li, P.J. Shea, S.D. Comfort, Nitrotoluene destruction by UV-catalyzed Fenton oxidation, Chemosphere 36 (1998) 1849–1865.

[24] A. Goi, M. Trapido, Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study, Chemosphere 46 (2002) 913–922.

[25] T. Turan-Ertas, M.D. Gurol, Oxidation of diethylene glycol with ozone and modified Fenton processes, Chemosphere 47 (2002) 293–301.

[26] A.S. Derbalah, N. Nakatani, H. Sakugawa, Photocatalytic removal of fenitrothion in pure and natural waters by photo-Fenton reaction, Chemosphere 57 (2004) 635–644.

[27] L.C. Lei, X.J. Hu, P.L. Yue, S.H. Bossmann, S. Göb, A.M. Braun, Oxidative degradation of polyvinyl alcohol by the photochemically enhanced Fenton reaction, J. Photochem. Photobiol. A: Chem. 116 (1998) 159–166.

[28] J. Bandara, C. Marrison, J. Kiwi, C. Pulgarin, P. Peringer, Degradation/decoloration of concentrated solutions of Orange II. Kinetics and quantum yield for sunlight induced reactions via Fenton type reagents, J. Photochem. Photobiol. A: Chem. 99 (1996) 57–66.

[29] J.J. Pignatello, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 439–444.

[30] R.G. Zepp, B.C. Faust, J. Hoigné, Hydroxyl radicals formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton, Environ. Sci. Technol. 26 (1992) 313–319.

[31] J.H. Carey, An introduction to advanced oxidation processes (AOP) for destruction of organics in wastewater, Wat. Poll. Res. J. Can. 27 (1992) 1–21.

[32] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.

[33] A.M. Braun, L. Jakob, E. Oliveros, Advanced oxidation processes-concepts of reactor design, J. Wat. SRT-Aqua. 42 (1993) 166–173.

[34] X.K. Zhao, G.P. Yang, Y.J. Wang, X.C. Gao, Photochemical degradation of dimethyl phthalate by Fenton reagent, J. Photochem. Photobio. A: Chem. 161 (2004) 215–220.

[35] Z.M. Li, S.D. Comfort, P.J. Shea, Destruction of 2,4,6-trinitroluene by Fenton oxidation, J. Environ. Technol. 26 (1997) 480–487.

[36] E. Lipczynska-Kochany, Degradation of nitrobenzene and nitrophenols in homogenous aqueous solution: direct photolysis versus photolysis in presence of hydrogen peroxide and the Fenton reagent, Wat. Poll. Res. J. Can. 27 (1992) 97–122.

[37] B.C. Faust, J. Hoigne, Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain, Atmos. Environ. 24A (1990) 79–89.

[38] H. Christensen, K. Sehested, H. Corfiten, Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures, J. Phys. Chem. 86 (1982) 1588–1590.

[39] K. Sehested, E. Bjergbakke, O.L. Rasmussen, Reactions of H_2O_2 in the pulse-irradiated Fe(II)-O_2 system, J. Chem. Phys. 51 (1969) 3159–3166.

[40] R.L. Cisneros, A.G. Espinoza, M.I. Litter, Photodegradation of an azo dye of the textile industry, Chemosphere 48 (2002) 393–399.

[41] J.H. Baxendale, J.A. Wilson, Photolysis of hydrogen peroxide at high intensities, Trans. Faraday Soc. 53 (1957) 344–356.

[42] R.Z. Chen, J.J. Pignatello, Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidation of aromatic compounds, Environ. Sci. Technol. 31 (1997) 2345–2349.

[43] Z. Stuglik, Z.P. Zagoski, Pulse-radiolysis of neutral iron(II) solutions-oxidation of ferrous-ions by OH radicals, Radiat. Phys. Chem. 17 (1981) 229–233.

[44] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of *p*-chlorophenol oxidation by Fenton's reagent, Wat. Res. 33 (1999) 210–218.

[45] H.R. Eisenhauser, Oxidation of phenolic wastes, J. Wat. Pollut. Control Fed. 36 (1964) 1116–1128.

[46] J.-Y. Feng, X.-J. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Discoloration and mineralization of Reactive Red HE-3B byheterogeneous photo-Fenton reaction, Wat. Res. 37 (2003) 3776–3784.