

Photochemical degradation of diethyl phthalate with UV/H₂O₂

Bin Xu^a, Nai-Yun Gao^{a,*}, Xiao-Feng Sun^a, Sheng-Ji Xia^a, Min Rui^a,
Marie-Odile Simonnot^b, Christel Causserand^c, Jian-Fu Zhao^a

^a State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering,
Tongji University, Shanghai 200092, PR China

^b Laboratory of Chemical Engineering Science, CNRS-INPL, 1 rue Grandville, BP451, F-54001 Nancy Cedex, France

^c Laboratory of Chemical Engineering, UMR 5503 CNRS INP, Université Paul Sabatier, 31062 Toulouse Cedex 9, France

Received 22 March 2006; received in revised form 2 June 2006; accepted 6 June 2006

Available online 15 June 2006

Abstract

The decomposition of diethyl phthalate (DEP) in water using UV–H₂O₂ process was investigated in this paper. DEP cannot be effectively removed by UV radiation and H₂O₂ oxidation alone, while UV–H₂O₂ combination process proved to be effective and could degrade this compound completely. With initial concentration about 1.0 mg/L, more than 98.6% of DEP can be removed at time of 60 min under intensity of UV radiation of 133.9 μW/cm² and H₂O₂ dosage of 20 mg/L. The effects of applied H₂O₂ dose, UV radiation intensity, water temperature and initial concentration of DEP on the degradation of DEP have been examined in this study. Degradation mechanisms of DEP with hydroxyl radicals oxidation also have been discussed. Removal rate of DEP was sensitive to the operational parameters. A simple kinetic model is proposed which confirms to pseudo-first order reaction. There is a linear relationship between rate constant *k* and UV intensity and H₂O₂ concentration.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Diethyl phthalate; UV–H₂O₂ process; Hydroxyl radical; Reaction kinetics; Photochemical degradation

1. Introduction

Phthalate esters (PAEs), commonly known as phthalates, are produced all over the world in large quantities. Commonly, PAEs are used primarily as plasticizers for plastics, dope and paint industry, and also in manufacture of insecticide carriers and propellants. These chemicals have been reported with heavily tendency to bioconcentrate in animal fat [1]. Moreover, it has been demonstrated that most chemicals of PAEs can act as endocrine disruptors and lead to adverse effects on organisms even in a low concentration; for example the occurrence of reproductive and developmental disruptions in snails, fish, piscivorous birds, alligators, and sea animals [2,3]. Furthermore, they can also induce various etiological diseases of human, such as disorders of male reproductive tract, breast and testicular cancers, dysfunction of neuroendocrine system and so on [4,5]. Due to their wide application and high toxicity, some of the compounds belong to the chemicals list of endocrine disruptors

issued by USEPA, World Wildlife Funds, and other agencies, as well as the priority control pollutants in USA, China and so on either [6].

Commonly, these compounds are stable liquid in ambient temperature, with high molar mass and low volatility. Nowadays, along with the boom of industry production, PAEs are widely distributed in the global environment and readily leachable with water. These contaminants are susceptible to interact during the process of their transport and in filtration of leachate from the solid waste into groundwater [7]. In recent years, there also have lots of investigations show PAEs is widely distributed in aquatic environment of the whole world and the range concentrations in ng/L to μg/L. Such as, eight kind of PAEs including diethyl phthalate (DEP), di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), dipropyl phthalate (DPP), diphenyl phthalate (DPhP), benzylbutyl phthalate (BBP), dihexyl phthalate (DHP), and dicyclohexyl phthalate (DCP), were detected in surface water of Taiwan with concentrations ranged from ND to 18.5 ng/L [8]. Wu [9] detected DBP of 3–33 μg/L in raw water with samples collected from Hangzhou, China. Yu et al. [10] did an investigation of phthalates in waterworks, North China and reported that the PAEs cannot be

* Corresponding author. Tel.: +86 21 65982691.

E-mail address: gaonaiyun@mail.tongji.edu.cn (N.-Y. Gao).

removed effectively by conventional water treatment processes as coagulation, sedimentation, filtration and disinfection.

Diethyl phthalate (DEP) is one of the most frequently identified phthalates with high water solubility and short-chain in diverse environmental samples including surface water, drinking water, sea water and so on. Since DEP is difficult to biologically and photo-chemically degrade [8], there is a strong need to look for effective treatment processes for such pollutants.

Homogeneous advanced oxidation process (AOP) employing hydrogen peroxide with UV-light has been found to be very effective in the degradation of endocrine disruptors [11,12]. In UV–H₂O₂ process the photolysis of hydrogen peroxide generates effective oxidizing species hydroxyl radical ($\cdot\text{OH}$), which can oxidize a broad range of organic pollutants quickly and non-selectively [13]. There have some investigations on DEP degradation by Fe(III)-solar process [14], Fenton reaction [15] and biological process [16], however, few report on DEP removal by combination of UV radiation and H₂O₂ oxidation could be found.

The purpose of the present study was to investigate the oxidation behavior of DEP by UV–H₂O₂ process and thus the possibility of removal from waters polluted by DEP. The results of effects, influencing factors, degradation mechanism and also theoretically perform a kinetic on the degradation of DEP were presented in this paper.

2. Experimental

2.1. Material and analysis

DEP, chromatographical purity, obtained from Sigma Chemical Company (purity >99%). The physical and chemical properties of DEP are shown in Table 1. H₂O₂ (30%, w/w) was obtained from Sinopharm Chemical Reagent Co. Ltd., China. AR grade NaOH and HCl were used to adjust the pH value. The double distilled water was used to prepare experimental solution. The ionic strength was not controlled.

A high performance liquid chromatograph (HPLC 2010 AHT, Shimadzu, Japan) was used to analyze DEP. The HPLC system consisted of an SIL-auto-injector auto-sampler with the volume injection set to 10 μL , Shimadzu VP-ODS column

Table 1
Chemical and physical characteristic of DEP

Parameters	Value
CAS number	84-66-2
Molecular weight (g/mol)	222.24
Molecular formula	C ₁₂ H ₁₄ O ₄
Water solubility at 25 °C (mg/L)	1000
Log <i>K</i> _{ow}	2.47
Henry's law constant (kPa)	7.9×10^{-5}

Chemical structure

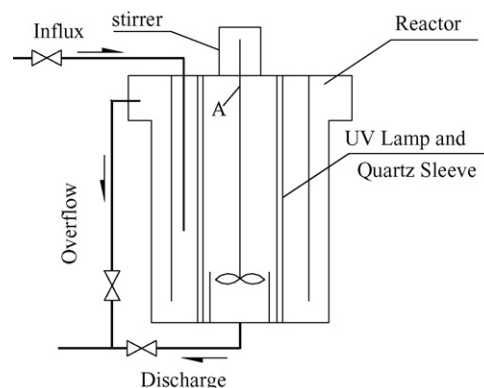
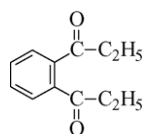


Fig. 1. Schematic diagram of experiment system.

(150 mm \times 4.6 mm), UV detector at 224 nm. The mobile phase consisted of methanol (Fisher, USA) and Milli-Q water (Millipore, Molsheim, France), methanol/H₂O = 50/50% and the applied flow rate was 1 mL/min. A UV–vis spectrophotometer UV2550 (Shimadzu) was used to scan the spectrum of DEP at 0.1 nm intervals.

The intermediate products during photochemical degradation of DEP were extracted by the solid phase extraction (Supelco C18 disk, 500 mg). Dichloromethane was used to elute the intermediate products. This solution was concentrated under nitrogen flow for the analysis of the by-products. A GC–MS (Shimadzu GC–MS QP 2010S) was used for separation and detection of the intermediate products. The GC equipped with an HP-5 capillary column (30 m \times 0.25 mm, i.d.) in helium carrier gas was used at the following chromatographic conditions: injector temperature 270 °C, column temperature program 60 °C (2 min), 60–280 °C (4 °C/min) and 280 °C (3 min). Helium was used as the carrier gas at 1.5 mL/min. The interface was kept at 280 °C. Qualitative analyses were performed in the electron-impact (EI) mode, at 70 eV using the full scan mode.

2.2. Photoreactor

The irradiation set-up was a completely mixed batch reactor (CMB, made of stainless steel, volume of irradiated solution = 140 L, *D* = 35 cm, *H* = 150 cm). The schematic diagram of experiment system was shown in Fig. 1. Ten UV lamps (emitting wavelength = 253.7 nm, 30 W) with quartz sleeves were fixed in circularity in the reactor. Meanwhile, the UV light intensity (A point in Fig. 1), controlled by turning on or off the lamps, was monitored by light intensity meter and the value had been shown in Table 2. In order to homogenize the solution, a mechanical stirrer was provided at the centre. All the reactions were carried out at room controlled temperature.

3. Results and discussions

The experiment was carried out under the following conditions: (1) self photolysis of DEP solution with different initial concentrations and UV radiations; (2) H₂O₂ oxidation alone with DEP solution in dark; (3) DEP solution oxidation with UV-light and H₂O₂; (4) effects of different impact factors in UV–H₂O₂ process.

Table 2
Values of the intensity of UV radiation

UV lamps	Intensity ($\mu\text{W}/\text{cm}^2$)
1	15.5
2	21.2
3	42.3
4	51.0
5	68.0
6	77.2
7	85.7
8	107.6
10	133.9

With the maximum intensity of UV radiation about intensity as $133.9 \mu\text{W}/\text{cm}^2$, Fig. 2 shows concentration of DEP versus reaction time for experiments carried out with UV radiation only and different initial concentrations of DEP. DEP is resistant to direct UV-photolysis and decreased slightly along with reaction time under different initial concentration. The removal rate was found to be as low as 25.52% after 90 min with the initial concentration DEP 1.851 mg/L.

To investigate the performance of DEP oxidation by H_2O_2 , the solution of DEP with concentration of 1 mg/L and H_2O_2 (35 mg/L) were added to the reactor simultaneously without UV radiation and then mixed by a mechanical stirrer. It could be found that DEP concentration after 3 h reaction was not changed, which implied that DEP is extremely inert and difficult to be degraded by H_2O_2 oxidation alone.

3.1. Effect of addition of H_2O_2

The effect of addition of H_2O_2 (2.5–30 mg/L) on the photochemical degradation has been investigated. The results are shown in Fig. 3. As it can be seen, the removal rate of DEP increases with increasing H_2O_2 concentration, the addition of 2.5–30 mg/L increases the degradation from 16.8% to 99.8% at time of 40 min. Moreover, the increment is also very limited above 20 mg/L. The degradation of DEP in UV– H_2O_2 process can be explained by the reaction of hydroxyl radicals generated upon photolysis of hydrogen peroxide. The reaction process can

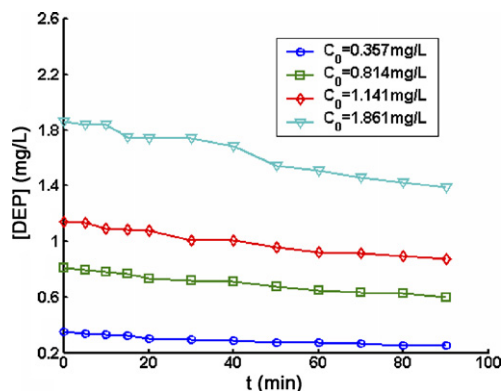


Fig. 2. Effect of UV radiation in DEP degradation with different $[\text{DEP}]_0$. $I_0 = 133.9 \mu\text{W}/\text{cm}^2$.

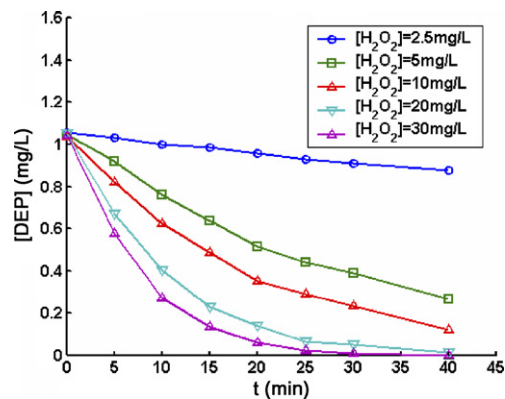
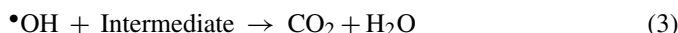


Fig. 3. Effect of initial concentration of H_2O_2 in DEP degradation. $I_0 = 133.9 \mu\text{W}/\text{cm}^2$ and $[\text{DEP}]_0 = 1 \text{ mg/L}$.

be expressed as the following equations:



The enhancement of degradation by addition of H_2O_2 is due to the increase in the hydroxyl radical concentration. At low concentration H_2O_2 cannot generate enough hydroxyl radical and the removal rate is limited. However, it was reported that high concentration of H_2O_2 could restrain the reaction [17]. This phenomenon did not happen in our experiment for the reason that the dosage did not reach the restrain point.

3.2. Effect of UV radiation intensity

The impact of UV radiation intensity on the degradation of DEP has been investigated by varying the UV radiation intensities from 21.2 to $133.9 \mu\text{W}/\text{cm}^2$. The results are shown in Fig. 4. The figure clearly shows that the removal rate steadily increased with increasing UV radiation intensity with the value from 51.6% to 98.6% at the time of 40 min. It can be deduced that the enhancement of removal rate is also due

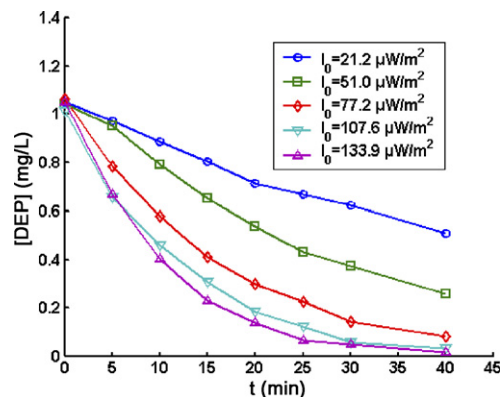


Fig. 4. Effect of UV intensity in degradation of DEP. $[\text{H}_2\text{O}_2]_0 = 20 \text{ mg/L}$ and $[\text{DEP}]_0 = 1 \text{ mg/L}$.

to the increase of hydroxyl radical concentration. According to Eq. (1), the rate of photolysis of H_2O_2 depends directly on the UV intensity. At low UV intensity the photolysis of H_2O_2 is limited. At high UV intensity more hydroxyl radicals are formed, which directly results in the high removal rate of DEP.

3.3. Effect of initial DEP concentration

Concerning contamination of DEP from different water varies from locations. It is important to investigate the impact of different initial DEP concentrations in oxidation process. With the same initial concentration of H_2O_2 and UV intensity, the processes with different initial DEP concentrations were carried out from 0.5 to 1.8 mg/L in the experiments. The results are shown in Fig. 5. As shown in the figure, photooxidation efficiency decreased as initial concentration of DEP is increased with the value from 82.6% to 81.5% at the time of 40 min. It can be explained that by considering that both the DEP and H_2O_2 absorb UV radiation in the range emitted by the lamp. An increase in DEP concentration induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation. By this way, hydrogen peroxide can only be irradiated by a smaller portion of UV light to form lower free radicals and the degradation rate decrease [18].

3.4. Effect of water temperature

It is well known that photocatalytic oxidation is not affected by minor changes in temperature [19]. In our experiments temperatures has been selected to simulate the operating condition at ambient room temperature from 15 to 31 °C. The effect of various initial water temperatures on the photochemical degradation has been investigated. The results are shown in Fig. 6. According to the results, increase of water temperature from 288 to 304 K, the removal rate keeps from 76.2% to 80.5% at the time of 40 min. It is apparent that the results indicate little effect of the temperature on the photo catalytic degradation of DEP at this range.

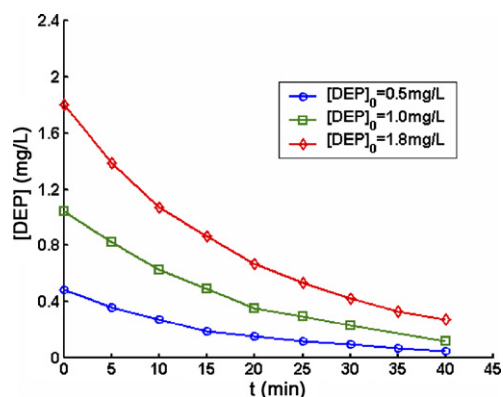


Fig. 5. Effect of initial concentration of DEP in chemical oxidation degradation. $I_0 = 133.9 \mu\text{W}/\text{cm}^2$ and $[\text{H}_2\text{O}_2]_0 = 10 \text{ mg/L}$.

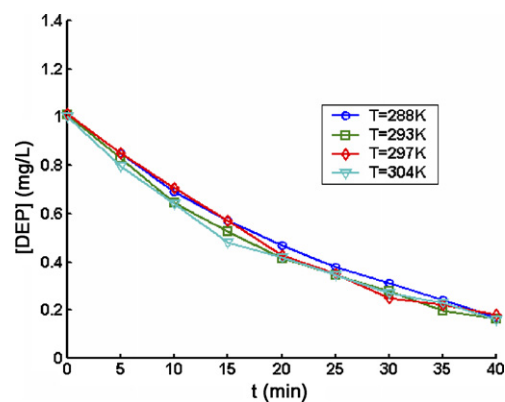


Fig. 6. Effect of water temperature in degradation of DEP. $I_0 = 85.7 \mu\text{W}/\text{cm}^2$, $[\text{H}_2\text{O}_2]_0 = 20 \text{ mg/L}$, and $[\text{DEP}]_0 = 1 \text{ mg/L}$.

3.5. Spectral changes of DEP and degradation pathways during photooxidation

3.5.1. UV absorption spectra analysis

The UV spectra of DEP solutions prepared with distilled water were examined during UV– H_2O_2 process. Fig. 7 shows the changes in the optical densities of DEP at different degradation time.

According to Fig. 7, the disappearance of 230 nm absorption bands was observed with increasing degradation time. However, absorbance at 245–310 nm of the solution after the reaction increased comparing with that before the reaction. All reagents such as H_2O_2 did not exist the absorption band around the wavelength. Furthermore, DEP solution before the reaction included H_2O_2 . Therefore, the increase of absorbance might be due to the presence of intermediate products derived from DEP. This consideration would be supported by the absorption spectrum of DEP after the reaction of 40 min, in which the absorbance at 278 nm decreased compared with that before the reaction. Consequently, it was confirmed that UV– H_2O_2 was effective photochemical process for the decomposition of DEP.

3.5.2. HPLC spectra analysis

From the results obtained from the HPLC analysis (Fig. 8), at least three peaks from degradation intermediates (designated as

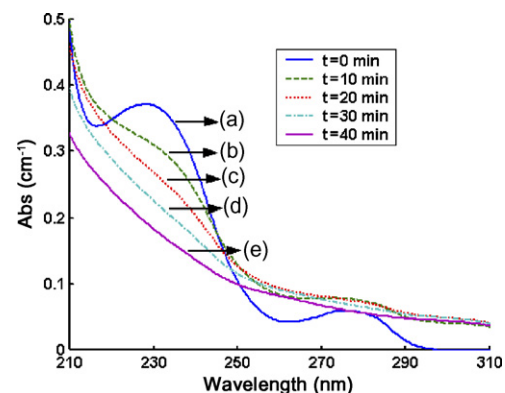


Fig. 7. UV spectral changes of DEP during photooxidation with UV-light and H_2O_2 . $I_0 = 85.7 \mu\text{W}/\text{cm}^2$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mg/L}$, and $[\text{DEP}]_0 = 10 \text{ mg/L}$.

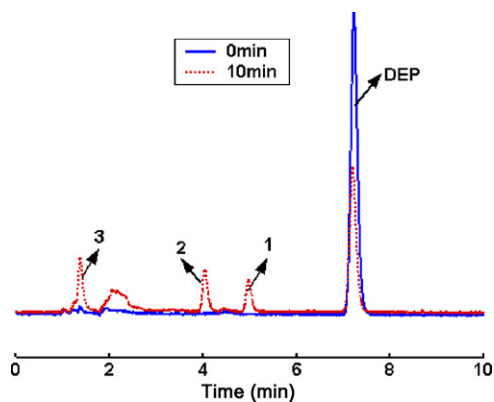


Fig. 8. HPLC spectral changes of DEP during photooxidation with UV-light and H_2O_2 . $I_0 = 85.7 \mu\text{W}/\text{cm}^2$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mg}/\text{L}$, and $[\text{DEP}]_0 = 10 \text{ mg}/\text{L}$.

1, 2, 3) formed from the photooxidation. In addition, intermediates have more hydrophilic structure than DEP since it was eluted out from the column prior to DEP. This is consistent with reported results in the literature that degradation products produced from a photochemical oxidation usually have more hydroxylated structures than the parent molecule [20].

3.5.3. Degradation pathways analysis

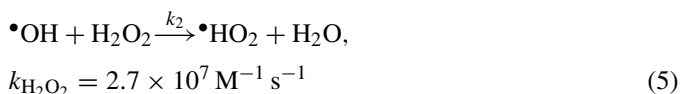
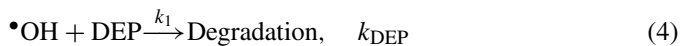
The intermediate products formed in the photochemical degradation of DEP in the solution for 10 min were investigated by GC–MS analysis. Only three products were identified by the molecular ion and mass fragment peak and also through comparison with GC/MS NIST library data. Table 3 lists main fragments (m/z) obtained and relative abundance (%) for the intermediate products. The similarities of these two intermediate products to the NIST library data were 89% and 92%, respectively.

It was deduced that the photolytic degradation of DEP mainly occurred via the aliphatic chain cracked rather than the aromatic ring decomposition firstly. Muneera et al. [21] also reported that in the photocatalytic degradation of DEP in aqueous suspensions of titanium dioxide, phthalic acid was detected as one of intermediate products. It believed that either ethyl or ester chain scissions of the aliphatic part of DEP was the dominant degradation mechanism of the process [22], with the aromatic ring

remaining intact. Therefore, the present experimental data and literature reports suggest the photochemical degradation pathway of DEP in water as illustrated in Fig. 9.

3.6. Kinetic study

It is well known that the UV irradiation of hydrogen peroxide in aqueous solution leads to the production of $\bullet\text{OH}$ radicals. In the presence of DEP, hydroxyl radicals react either with DEP, intermediates S_i and excess H_2O_2 :



The corresponding kinetic equations for DEP and hydroxyl radical can be expressed as:

$$\frac{d[\text{DEP}]}{dt} = -k_1[\text{DEP}][\bullet\text{OH}] \quad (7)$$

$$\frac{d[\bullet\text{OH}]}{dt} = \phi^{\text{pri}} I_{\text{a}, \text{H}_2\text{O}_2} - k_1[\bullet\text{OH}][\text{DEP}] - \sum_i k_i[\bullet\text{OH}][S_i] - k_2[\bullet\text{OH}][\text{H}_2\text{O}_2] \quad (8)$$

where ϕ^{pri} is the initial quantum yield of hydrogen peroxide disappearance, equal to 0.5, $I_{\text{a}, \text{H}_2\text{O}_2}$, the rate of light absorption of hydrogen peroxide. Other reaction with DEP was not taken into consideration due to much lower reactivity than that of hydroxyl radical [23].

Under the steady-state concentration of hydroxyl radical, the value of $d[\bullet\text{OH}]/dt$ equals to zero, and $[\bullet\text{OH}]_s$ can be got by

Table 3
GC–MS–EI retention time, mass fragment ions (m/z) and relative abundance (%) of intermediate products and DEP

Retention time (min)	Detected ions m/z (% abundance)	Molecular weight	Molecular structure
13.5	105 (100), 77 (50), 51 (25), 122 (25)	150	
27.6	149 (100), 177 (21), 76 (14), 105 (10)	222	
29.8	120 (100), 165 (38), 92 (22), 65 (10)	166	

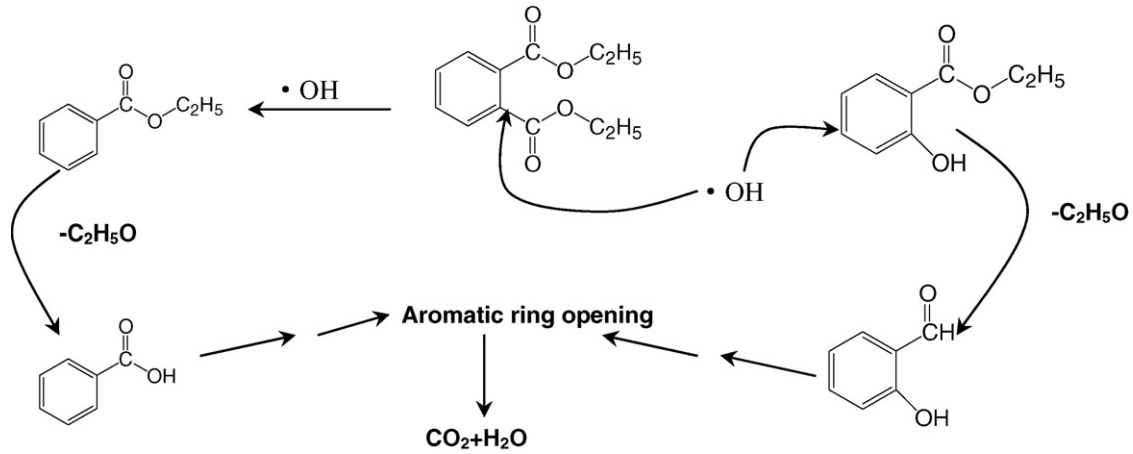


Fig. 9. The degradation mechanism of DEP with hydroxyl radicals.

solving Eq. (8):

$$[\bullet\text{OH}]_s = \frac{\phi^{\text{pri}} I_{a,\text{H}_2\text{O}_2}}{k_1[\text{DEP}] + \sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]} \quad (9)$$

Since H_2O_2 only absorbs UV light ranging from 200 to 300 nm, the fraction of light absorbed by H_2O_2 ($I_{a,\text{H}_2\text{O}_2}$) can be calculated from Eq. (10) with respect to the lower and upper limits of 200 and 300 nm on the wavelength:

$$I_{a,\text{H}_2\text{O}_2} = \frac{\sum_{200}^{300} f E_\lambda Q_{\text{H}_2\text{O}_2}}{\sum_{200}^{300} E_\lambda} = I_0 f Q_{\text{H}_2\text{O}_2} \quad (10)$$

where f is the total fraction of light absorbed by DEP and H_2O_2 are certain wavelength, E_λ is the known incident photoflux of lamp for the given wavelength, I_0 represent the incident UV-light intensity, and $Q_{\text{H}_2\text{O}_2}$ is the fraction of absorbance of H_2O_2 (A) at the give wavelength. f and $Q_{\text{H}_2\text{O}_2}$ can be calculated as follows [23]:

$$f = 1 - 10^{-(\epsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + \epsilon_{\text{DEP}}[\text{DEP}])} \quad (11)$$

$$Q_{\text{H}_2\text{O}_2} = \frac{A_{\text{H}_2\text{O}_2}}{A_{\text{H}_2\text{O}_2} + A_{\text{DEP}}} \quad (12)$$

$\epsilon_{\text{H}_2\text{O}_2}$ and ϵ_{DEP} are the molar extinction coefficients for H_2O_2 and DEP, respectively. For the process condition, $[\bullet\text{OH}]$ can be simplified as:

$$[\bullet\text{OH}]_s = \frac{\phi^{\text{pri}} I_0 Q_{\text{H}_2\text{O}_2}}{k_1[\text{DEP}] + \sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]} \quad (13)$$

and then Eq. (7) can be changed into Eq. (14):

$$\frac{d[\text{DEP}]}{dt} = -k_1[\text{DEP}] \frac{\phi^{\text{pri}} I_0 Q_{\text{H}_2\text{O}_2}}{k_1[\text{DEP}] + \sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]} \quad (14)$$

In the present study the concentration of DEP is much lower than that of H_2O_2 , hence $k_1[\text{DEP}] \ll \sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]$, Eq. (14) can be simplified as:

$$\frac{d[\text{DEP}]}{dt} = -\frac{k_1 \phi^{\text{pri}} I_0 Q_{\text{H}_2\text{O}_2}}{\sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]} [\text{DEP}] = k[\text{DEP}] \quad (15)$$

It can be seen that above equation corresponds to a pseudo-first order kinetics model and the integrated form is Eq. (16).

$$-\ln \frac{[\text{DEP}]_t}{[\text{DEP}]_0} = \frac{k_1 \phi^{\text{pri}} I_0 Q_{\text{H}_2\text{O}_2}}{\sum_i k_i[S_i] + k_2[\text{H}_2\text{O}_2]} t = kt \quad (16)$$

Take the prime operational parameters (initial H_2O_2 concentration and UV intensity) into consideration, the kinetics of elimination for DEP can be shown in Figs. 10 and 12 as examples.

As shown in Fig. 10, in agreement with Eq. (16), straight lines are obtained meaning that pseudo-first order kinetics model is verified. The values are shown in Table 4. According to Fig. 11, the apparent reaction rate constant (k) for degradation of DEP is a function of H_2O_2 concentration. The results also reveal that k increases with increasing the amount of H_2O_2 . A linear relation exists between pseudo-first order reaction rate and initial H_2O_2 concentration, which indicated that employed H_2O_2 dosage in this study are in the low range.

Concerning the effect of UV intensity on DEP degradation, the linear method by the kinetics model also is used to analysis the relationship between the pseudo-first order reaction rate and UV intensity. The results are shown in Fig. 12 and Table 4. It

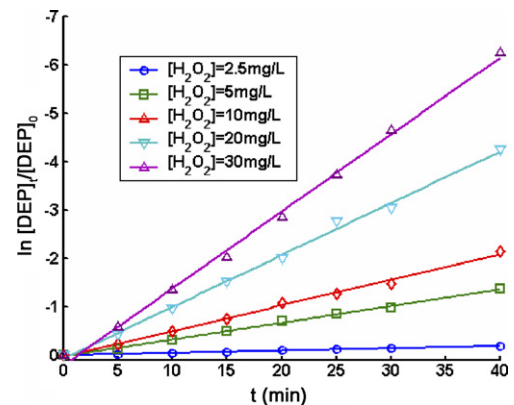


Fig. 10. Pseudo-first order decay curves of DEP degradation with different initial concentration of H_2O_2 .

Table 4
Pseudo-first order rate constants for degradation of DEP under different operational condition

Number	Initial DEP concentration (mg/L)	UV intensity ($\mu\text{W}/\text{cm}^2$)	Initial H_2O_2 concentration (mg/L)	k (min^{-1})	R^2
1	1.06	133.9	2.5	0.0048	0.9919
2	1.05	133.9	5	0.0345	0.9978
3	1.04	133.9	10	0.0530	0.9962
4	1.05	133.9	20	0.1071	0.9964
5	1.04	133.9	30	0.1588	0.9968
6	1.05	21.2	20	0.0182	0.9971
7	1.04	51.0	20	0.0361	0.9960
8	1.07	77.2	20	0.0646	0.9985
9	1.02	107.6	20	0.0898	0.9904
10	0.50	133.9	10	0.0553	0.9965
11	1.02	133.9	10	0.0530	0.9962
12	1.80	133.9	10	0.0473	0.9993

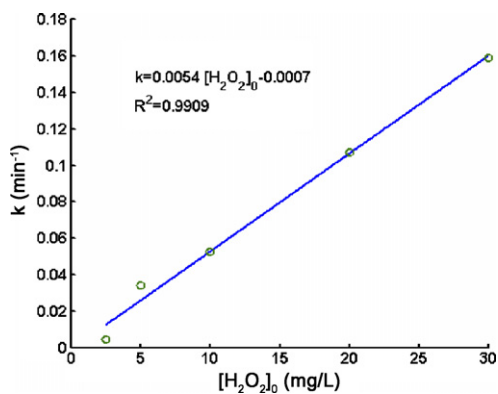


Fig. 11. Relation between pseudo-first order reaction rate constant with different initial concentration of H_2O_2 .

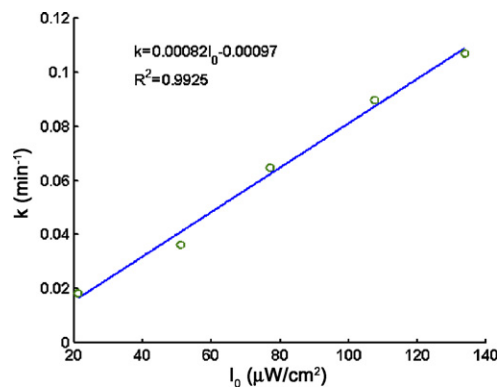


Fig. 13. Relation between pseudo-first order reaction rate constant with UV intensity.

appears that with increasing the light intensity the degradation rate increase and also in a good agreement with kinetic model. As shown in Fig. 13, there also have linear relationship between k value and UV intensity, which shows higher UV intensity can be used to improve the removal effect of DEP. As seen in Table 4, pseudo-rate constant k decreases as the initial concentration of DEP increase, which has the same law with the removal effect in Section 3.3.

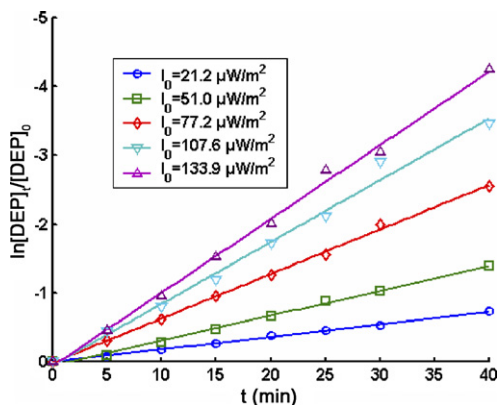


Fig. 12. Pseudo-first order decay curves of DEP degradation with different UV intensity.

4. Conclusion

The results obtained in this study clearly indicate that single UV radiation process and H_2O_2 oxidation process can hardly remove DEP from water and the UV– H_2O_2 process is very promising for complete removal of DEP from contaminated water. The degradation rate and removal efficiency of DEP can be affected by intensity of UV radiation, initial H_2O_2 and DEP concentration and so on. Two oxidation intermediate products were detected by HPLC and GC–MS during DEP degradations. The degradation follow pseudo-first order kinetics. Pseudo-rate constant (k) is affected with varying UV intensity, H_2O_2 concentration and initial concentration of DEP. There have linear relationship between rate constant k and UV intensity and H_2O_2 concentration, which indicated higher removal capacity can be achieved by improvement of both factors.

Acknowledgments

This study was supported in part by Basic Science Research Program (no. 05JC14059) in Shanghai and High Technology Research and Development (863) Program (no. 2002AA601130) in China. This work belongs to the open program of State Key Laboratory of Pollution Control and Resources Reuse (PCRRF05007). The authors also thank Mr.

Ruo-Yu Li and Ms. Dan-Dan Zhao of College of Environmental Science and Engineering, Tongji University.

References

- [1] S. Jobling, T. Reynolds, R. White, M.G. Parker, J.P. Sumpter, A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic, *Environ. Health Perspect.* 103 (1995) 582–587.
- [2] W.-L. Chen, H.-H. Sung, The toxic effect of phthalate esters on immune responses of giant freshwater prawn (*Macrobrachium rosenbergii*) via oral treatment, *Aquat. Toxicol.* 74 (2005) 160–171.
- [3] H.-H. Sung, W.-Y. Kao, Y.-J. Su, Effects and toxicity of phthalate esters to hemocytes of giant freshwater prawn, *Macrobrachium rosenbergii*, *Aquat. Toxicol.* 64 (2003) 25–37.
- [4] T.F. Parkerton, W.J. Konkel, Application of quantitative structure–activity relationship for assessing the aquatic toxicity phthalate esters, *Ecotoxicol. Environ. Saf.* 45 (2001) 61–78.
- [5] S. Takeuchi, M. Iida, S. Kobayashi, et al., Differential effects of phthalate esters on transcriptional activities via human estrogen receptors α and β , and androgen receptor, *Toxicology* 210 (2005) 223–233.
- [6] T.A. Thomsen, C.L. Gand, et al., SAR/QSAR approaches to solubility, partitioning and sorption of phthalate, *Chemosphere* 38 (1999) 2613–2624.
- [7] M. Ahel, N. Mikac, B. Cosovic, E. Prohic, V. Soukup, The impact of contamination from a municipal solid waste landfill (Zagreb, Croatia) on underlying soil, *Water Sci. Technol.* 37 (1998) 203–210.
- [8] S.Y. Yuan, C. Liu, C.S. Liao, B.V. Chang, Occurrence and microbial degradation of phthalate esters in Taiwan river sediments, *Chemosphere* 49 (2002) 1295–1299.
- [9] P.-G. Wu, G.-G. Han, H.-H. Wang, Investigation of PAEs in drinking water, *J. Environ. Health* 16 (1999) 338–339.
- [10] H. Yu, J.-Y. Hu, X.-H. Jin, Monitoring of phthalates in raw water and treatment process of a waterworks in north China, *Water Wastewater Eng.* 31 (2005) 20–22.
- [11] W. Chu, Modeling the quantum yields of herbicide 2,4-D decay in UV/H₂O₂ process, *Chemosphere* 44 (2001) 935–941.
- [12] A.M. Fares, S. Carmen, E. Santiago, A comparative study of the advanced oxidation of 2,4-dichlorophenol, *J. Hazard. Mater.* 107 (2004) 123–129.
- [13] O.M. Alfano, R.J. Brandi, A.E. Cassano, Degradation kinetics of 2,4-D in water employing hydrogen peroxide and UV radiation, *Chem. Eng. J.* 82 (2001) 209–218.
- [14] G. Mailhot, M. Sarakha, B. Lavedrine, et al., Fe(III)-solar light induced degradation of diethyl phthalate (DEP) in aqueous solutions, *Chemosphere* 49 (2002) 525–532.
- [15] G.-P. Yang, X.-K. Zhao, X.-J. Sun, X.-L. Lu, Oxidative degradation of diethyl phthalate by photochemically-enhanced Fenton reaction, *J. Hazard. Mater.* 126 (2005) 112–118.
- [16] B.V. Chang, C.S. Liao, S.Y. Yuan, Anaerobic degradation of diethyl phthalate, di-*n*-butyl phthalate, and di-(2-ethylhexyl) phthalate from river sediment in Taiwan, *Chemosphere* 58 (2005) 1601–1607.
- [17] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV–H₂O₂ process, *Dyes Pigments* 62 (2004) 269–275.
- [18] A. Aleboyeh, Y. Moussa, H. Aleboyeh, The effect of operational parameters on UV/H₂O₂ decolourisation of Acid Blue 74, *Dyes Pigments* 66 (2005) 129–134.
- [19] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.* 93 (1993) 341–357.
- [20] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Photocatalytic degradation and mineralization of bisphenol A by TiO₂ and platinumized TiO₂, *Appl. Catal. A: Gen.* 261 (2004) 225–237.
- [21] M. Muneera, J. Theurichb, D. Bahnemannb, Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate, *J. Photochem. Photobiol. A: Chem.* 143 (2001) 213–219.
- [22] T.K. Lau, W. Chu, N. Graham, The degradation of endocrine disruptor di-*n*-butyl phthalate by UV irradiation: a photolysis and product study., *Chemosphere* 60 (2005) 1045–1053.
- [23] P. Mazellier, A. Rachel, V. Mambo, Kinetics of benzenesulfonates elimination by UV and UV/H₂O₂, *J. Photochem. Photobiol. A: Chem.* 163 (2004) 389–393.