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Degradation of di-*n*-butyl phthalate in aqueous solution by the O_3/UV process

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ABSTRACT

The degradation of di-*n*-butyl phthalate (DBP), which is a pollutant of concern in an aqueous environment, was investigated using the combination of ozonation with ultraviolet irradiation (O_3/UV) in this study. Compared with either ozonation or UV irradiation, the hybrid system stimulated the O_3 molecule photolysis and the hydroxyl radical (·OH) generation; therefore, the DBP degradation through the pathway of ·OH attack was markedly reinforced. Since ·OH was a more vigorous oxidant than O_3, both the kinetics of the DBP removal and the mineralization were increased. With the aqueous O_3 fed rate of 4.03 mg/(L min), the spiked DBP molecules almost completely disappeared in 60 min, approximately 70% of which were converted into H_2O and CO_2. The effects of DBP concentration, aqueous O_3 fed rate, and solution pH on the DBP degradation were also investigated. Pseudo-first-order kinetics model was able to depict the experimental data under different conditions. Eight intermediates were identified, and the DBP degradation by the O_3/UV process was supposed to be mainly started with the ·OH attack to the aliphatic chains. Since the combination of O_3 with UV benefits the complete decomposition of DBP and reduces the possible toxicity of the treated water, it is a promising process for DBP removal from an aqueous solution.

Keywords: Di-*n*-butyl phthalate (DBP); Hydroxyl radical (·OH); Mineralization; Ozonation; Ultraviolet (UV)

1. Introduction

Phthalate esters (PAEs) are important chemicals with wide industrial, agricultural, and domestic uses. One of the most well-known uses is as plasticizers to improve the flexibility and workability of polymeric materials, for example, polyvinyle chloride resin and cellulose film [1]. However, during the manufacturing, usage, and disposal of the plastic products, PAEs may

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release into the ecosystem via wastewater effluent, leaching, and volatilization. Because most PAEs are endocrine disrupting compounds, PAEs have been reported to be related to several human diseases even at very low concentrations, for example, disorders of the male reproductive tract, breast and testicular cancers, disruptors of the neuroendocrine system, and skeletal effects [2,3]. As a result, the US Environmental Protection Agency, the European Union, and China National Environmental Monitoring Center classify PAEs as a kind of top priority pollutants and mandate the reduction and control of the PAEs pollution [4].

One of the most common PAEs is di-*n*-butyl phthalate (DBP), an important additive in special paints and adhesives with an annual production of over 4.54×10^5 kg in the USA [5]. It also draws great attention because it acts as a weak estrogen receptor agonist and exhibits an antiandrogenic effect, which affects the male development [6]. Unfortunately, DBP has been detected in groundwater, river, soil, lake, and marine sediments, and other environmental components [7]. Extremely high DBP concentrations were also reported in rivers of Venda region in South Africa and in sediments of Yangtze River in China, which were 3.08–10.17 mg/L and 11.7–246.0 mg/kg-dw, respectively [8,9]. Since the aqueous hydrolysis and atmospheric photo-oxidation are very slow and insignificant, DBP accumulates in the environment and poisons a variety of aquatic organisms, which would enter the food chain of human beings [10]. Besides, its toxicity would be much more severe considering its high bioaccumulation rate (from 100 to 3,000) in organisms [10].

In view of this situation, many studies focus on the degradation of DBP, especially from an aqueous environment. The biodegradation of DBP generally requires a rather long hydration retention time in a range of several days up to a few months; therefore, it is less effective. In addition, the produced wastewater sludge needs an appropriate treatment during the anaerobic digestion in order to avoid the secondary pollution [11]. Both adsorption and coagulation have also been investigated for the DBP removal [12–14]. However, since the removed DBP in these processes remained intact, the risk of pollution transfer increases in the disposal of the exhausted adsorbents and the produced floc. The best available technologies for the PAEs removal should be able to mineralize these refractory organic pollutants into inorganic matters, that is, CO_2 and H_2O. Therefore, several advanced oxidation processes (AOPs) based on the strong oxidation of hydroxyl radicals ($^{\cdot}OH$) are proposed in recent years, including TiO_2/UV [15–17], H_2O_2/UV [18], H_2O_2/Fe(II) [19], Fe(III)/UV [20], electrolysis with boron-doped diamond anode [21], and so on.

Compared with the conventional AOPs, ozonation is more typical of the conditions in the existing water treatment plants. It is a versatile process in drinking water and wastewater treatment and has been used for disinfection and the removal of various organic pollutants [22–24]. The mechanism of ozonation in water was supposed to be either direct oxidation by molecular O_3 or indirect oxidation by $^{\cdot}OH$ formed during the O_3 decomposition [25]. Since $^{\cdot}OH$ is a much stronger oxidant than molecular O_3, the introduction of proper measures to make the ozonation dominated by the $^{\cdot}OH$ attack would significantly benefit the complete destruction of organic pollutants and improve the O_3 utilization efficiency as well.

In this study, the combination of ozonation with UV irradiation (O_3/UV) was proposed for the DBP removal. The purpose of this hybrid process was to enhance the production of more $^{\cdot}OH$ radicals for a stronger oxidation of DBP. The effects of DBP concentration, aqueous O_3 fed rate, and solution pH on the DBP degradation kinetics were investigated. Based on the intermediates identified using gas chromatograph-mass spectrometry (GC-MS) and liquid chromatograph-mass spectrometry (LC-MS), the primary DBP degradation pathway in the O_3/UV process was also discussed.

2. Materials and methods

2.1. Materials

Analytical grade DBP (purity > 99.5%) used in this study was purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. The DBP solutions were prepared in ultrapure water with a resistivity higher than 18 MΩ cm. The organic reagents used for GC-MS and LC-MS analysis, namely hexane, methanol, ethyl acetate, dichloromethane, and acetonitrile, were all of HPLC grade and purchased from CNW Technologies GmbH, Germany. NaOH solution (1 mol/L) and H_2SO_4 solution (1 mol/L) were used for pH adjustment.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. All the tests were carried out in the mineral glass reactor with an effective volume of 10 L. O_3 was produced by an ozone generator (Tianning Purification Equipment Manufactory, China) using pure oxygen as the gas source. The UV lamp (wavelength = 253.7 nm, 15 W,

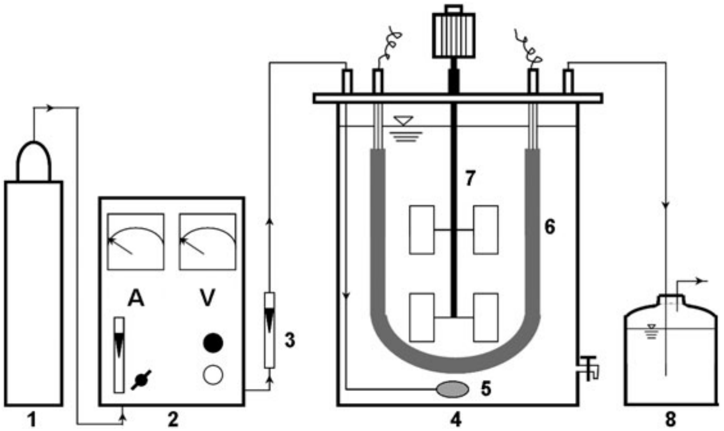


Fig. 1. Schematic diagram of the experimental setup: (1) oxygen cylinder; (2) ozone generator; (3) flow meter; (4) reactor; (5) diffuser; (6) UV lamp; (7) mechanical stirrer; (8) KI solution.

Tianjing Zijing Special Light Source Co., Ltd. China) was equipped with a quartz sleeve and fixed in the center of the reactor. The solution in the reactor was able to immerse the whole lamp. A mechanic stirrer at 200 rpm was used to mix the solution during the reaction. The discharged gas was absorbed by 2% KI solution before its emitting into the air.

The experiments were conducted in a batch mode in an air-conditioned laboratory (20–25℃). After a test solution containing a predetermined concentration of DBP was filled into the reactor, O_3 was fed through a gas diffuser, and the UV lamp was turned on. The solution was sampled at regular time intervals for chemical analysis, and the total sampling volume was less than 10% of the solution. The introduction of O_3 lasted for the entire process of the test. The O_3 fed rate was adjusted by the flow meter in the ozone generator which was used for the determination of the O_2 flow rate. The relationship between the O_2 flow rate and the O_3 production rate was investigated before the DBP degradation experiment by introducing the produced gaseous O_3 into a flask containing KI solution. The generated I_2 was then titrated with a $Na_2S_2O_3$ standard solution using an aqueous solution of starch as indicator [26].

2.3. Analytical methods

The DBP concentration was analyzed using an Agilent 7890A GC equipped with an HP-5 capillary column (30 m × 0.32 mm) and a flame ionization detector. Each sample (100 mL) was extracted with 100 mL hexane twice. The extraction was then dried using anhydrous sodium sulfate and concentrated to 1 mL under the nitrogen blowing. One microlitre concentrated extraction was injected into GC in the splitless mode, and the injector temperature was 260℃. Nitrogen (2 mL/min) was used as the carrier gas. The column temperature program was 55℃ (2 min), 50–130℃ (30℃/min), 130–200℃ (12℃/min), 200–280℃ (15℃/min), and 280℃ (3 min).

A solution containing 10.24 mg/L DBP with an adjusted pH of 7.0 was treated by O_3/UV for 1 h with an aqueous O_3 fed rate of 4.03 mg/(L min). The treated solution was then used for the intermediate analysis. Solid-phase extraction was employed for the GC-MS pretreatment. The extraction disk (C18 disk, 3 M Empore) was firstly washed with 5 mL mixture of dichloromethane and ethyl acetate (1:1), 5 mL methanol, and 5 mL ultrapure water. Then, 10 L sample was percolated through the disk at a flow rate of 50 mL/min. The compounds trapped in the disk were collected using several solvent eluents, namely 5 mL ethyl acetate, 5 mL dichloromethane, and 5 mL mixture of dichloromethane and ethyl acetate (1:1). Each fraction was concentrated to 1 mL under the nitrogen blowing and then injected into GC-MS (6890N-5973N, Agilent). Helium (1 mL/min) was used as the carrier gas. The column temperature was held at 40℃ for 3 min, increased to 280℃ at 5℃/min, where it was held for 3 min. For MS detection, electron-impact mode was employed for full scan.

LC-ES-MS (LCQ Deca XP MAX, Finnigan) equipped with a C8 column (250 × 4.6 mm, 5 μm particle size) was also used for the intermediate analysis. The mobile phase was 50% acetonitrile (1 mL/min). Samples were injected into LC-ES-MS without any pretreatment.

The total organic carbon (TOC) was determined by a TOC analyzer (TOC-$V_{CPH,}$ Shimadzu). The solution pH was determined by a digital pH meter (Sension 156, Hach).

3. Results and discussion

3.1. *DBP degradation by the O_3/UV process*

The degradation of DBP was investigated using UV, O_3, and the combination of both O_3 and UV, respectively (Fig. 2(a)). Under the UV irradiation only, 24% DBP disappeared after 60 min reaction. This was mainly attributed to the DBP photolysis, which was generally regarded as the initial and the most important step for the natural degradation of PAEs [27]. However, the DBP removal using a low power UV lamp (15 W) was, overall, not effective. The degradation of DBP by ozonation was much faster and stronger. With the aqueous O_3 fed rate of 4.03 mg/(L min), approximately 89% DBP was removed after 60 min reaction. Ozonation has been proved to be an effective method for the removal of PAEs from solution [28]. The excellent oxidation capabilities of both O_3 molecules and ·OH radicals formed during the O_3 decomposition were contributed to the high DBP removal. When the UV irradiation was introduced into the ozonation process, the DBP removal was further improved. The synergistic effect between the ozonation and the UV irradiation was outstanding especially in the initial 30 min reaction period, during which the overall DBP removal rate in the O_3/UV combined process was higher than the sum of those in the respective UV and O_3 processes. Almost complete removal of DBP (99.7%) was finally achieved after 60 min reaction. With the assistance of the UV irradiation, more ·OH radicals were generated compared to the mere ozonation process. Since ·OH radical was a nonselective and vigorous oxidant, DBP inclined to be degraded in a more thorough manner under the attack of those free radicals, for example, mineralization. The index of TOC removal rate was used to evaluate the mineralization degree. It can be seen in Fig. 2(b) that the TOC removal was significantly enhanced when the ozonation was combined with the UV irradiation; approximately 70% DBP was converted into H_2O and CO_2 after 60 min reaction. However, no mineralization took place under the mere UV irradiation, while the TOC removal rate was less than 50% in the mere ozonation process. Therefore, it can be inferred that in the O_3/UV process the DBP degradation by the ·OH mechanism was more prominent compared to the O_3 molecule mechanism. It should also be noted that the DBP removal rate was always lower than the corresponding TOC removal rate, indicating the presence of some intermediates in solution. Considering the possible toxicity of the degradation products [29], a high mineralization degree is always preferable for choosing a proper PAEs treatment technology. Therefore, the proposed O_3/UV system in this study was very promising, and its performance for PAEs removal was comparable to the well-studied TiO_2/UV system [30,31].

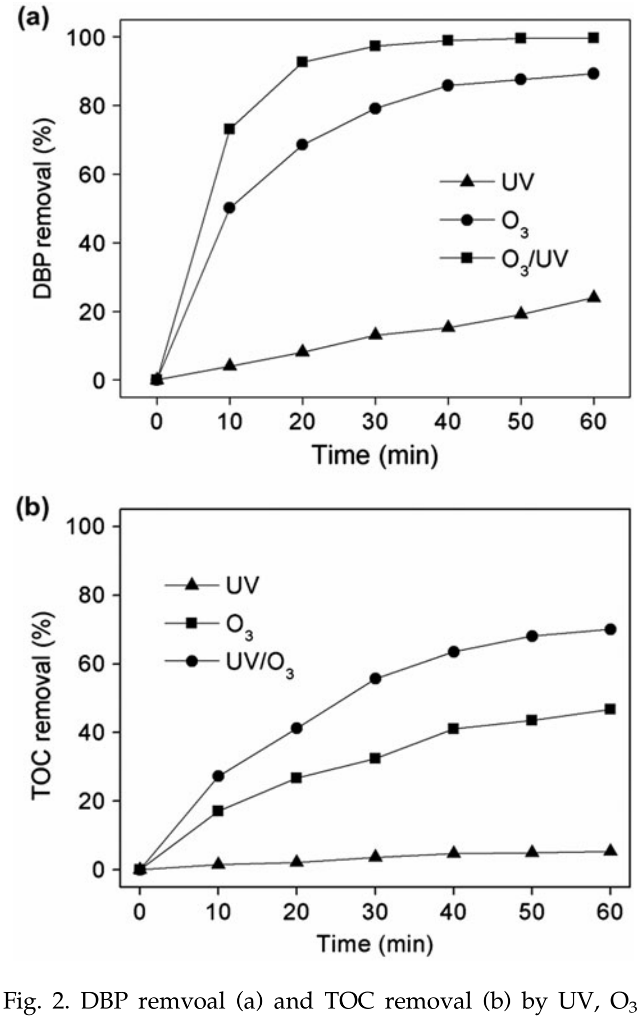


Fig. 2. DBP remvoal (a) and TOC removal (b) by UV, O_3, and O_3/UV processes. (Initial DBP concentration: 10.24 mg/L; UV power input: 15 W; aqueous O_3 fed rate: 4.03 mg/(L min)).

3.2. *Effect of initial DBP concentrations on its degradation by the O_3/UV process*

The DBP degradation kinetics by O_3/UV process was investigated under different initial DBP concentrations (Fig. 3). With the initial DBP concentration increasing from 5.30 to 12.78 mg/L, no significant decrease in DBP removals was observed by the end of the experiment. Therefore, at the aqueous O_3 fed rate of 4.03 mg/(L min), the O_3/UV system was able to completely remove DBP even when its concentration was close to its saturation concentration in water (~13 mg/L). The profile of DBP concentration (c) with

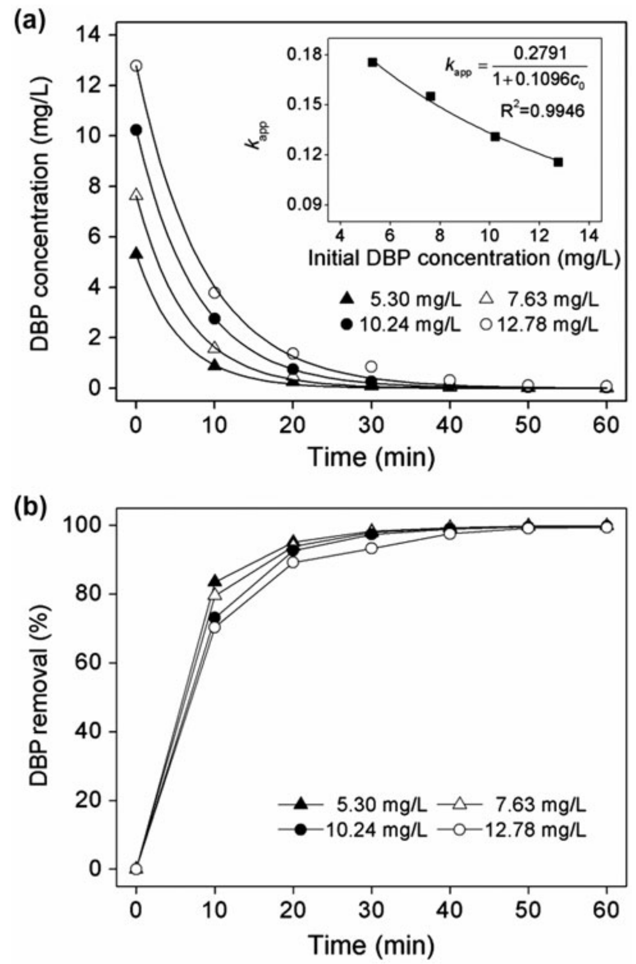


Fig. 3. Effect of initial DBP concentrations on its degradation by O_3/UV. Lines (a) represent the fitting results of the pseudo-first-order reaction kinetics. The insert (a) shows the relationship between the apparent pseudo-first-order rate constant and the initial DBP concentration in solution. (UV power input: 15 W; aqueous O_3 fed rate: 4.03 mg/(L min)).

time (t) during the degradation process was modeled by the pseudo-first-order reaction kinetics (Eq. (1)), and the correlation coefficients (r^2) of higher than 0.99 implied the fitting results were very good (Table 1). However, the calculated apparent first-order rate constants (k_{app}) decreased from 0.1753 to 0.1155 /min with the increase in the initial DBP concentrations (c_0) from 5.30 to 12.78 mg/L. Because the DBP molecules absorbed the UV light, more DBP in solution would decrease the effective UV light utilized by O_3. As a result, the amount of $^{\cdot}OH$ radicals generated was reduced and the DBP degradation rate was negatively affected. This result was also discussed in the photochemical degradation of DEP and herbicide 2,4-D by H_2O_2/UV [18,32]. The relationship between the apparent degradation rate constant and the initial DBP concentration was further depicted with reference to the Langmuir–Hinshelwood equation (Eq. (2)), which has often been used in the photocatalytic reaction kinetics [16,31]. The parameters k and K represent the reaction rate constant and the adsorption coefficient, respectively, and their calculated values are 2.55 /min and 0.11 L/mg (Fig. 3(a)).

Table 1
The fitting results of the pseudo-first-order reaction kinetics for DBP degradation by O_3/UV under different initial DBP concentrations ($[\mathrm{DBP}]_0$)

$[\mathrm{DBP}]_0$ (mg/L)	O_3 fed rate (mg/(L min))	Initial pH	Removal (%)	k_{app} (/min)	r^2
5.30	4.03	6.8	99.91	0.1753	0.999
7.63	4.03	7.1	99.86	0.1549	0.999
10.24	4.03	7.0	99.73	0.1307	1.000
12.78	4.03	7.2	99.39	0.1155	1.000

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k_{\mathrm{app}}c \tag{1}$$

$$k_{\mathrm{app}} = \frac{kK}{1 + Kc_0} \tag{2}$$

The DBP degradation by other processes, for example, electrochemistry, ultrasonic irradiation, anaerobic digestion, etc. followed the pseudo-first-order reaction kinetics as well [21,33,34]. In the electrolysis system with boron-doped diamond anodes, the calculated apparent pseudo-first-order rate constant for DBP degradation was 0.0615 /min [21], while the rate constant for the DBP biodegradation under methanogenic conditions was 9.5069×10^{-5} /min [34]. These values are much lower compared to that in the proposed O_3/UV system. Therefore, the DBP degradation by O_3/UV is a quite fast process.

3.3. Effect of aqueous O_3 fed rates on the DBP degradation by the O_3/UV process

Fig. 4 shows the effect of aqueous O_3 fed rate (2.02–5.78 mg/(L min)) on the DBP degradation in the O_3/UV system. As expected, the increase in the aqueous O_3 fed rate benefited the DBP removal, and it significantly accelerated the degradation dynamics. Compared to the case with an aqueous O_3 fed rate of 2.02 mg/(L min), the time required to achieve 90% DBP removal rate was cut from over 40 min to less than 20 min when O_3 was introduced into the solution at 4.03 mg/(L min) (Fig. 4(b)). A higher

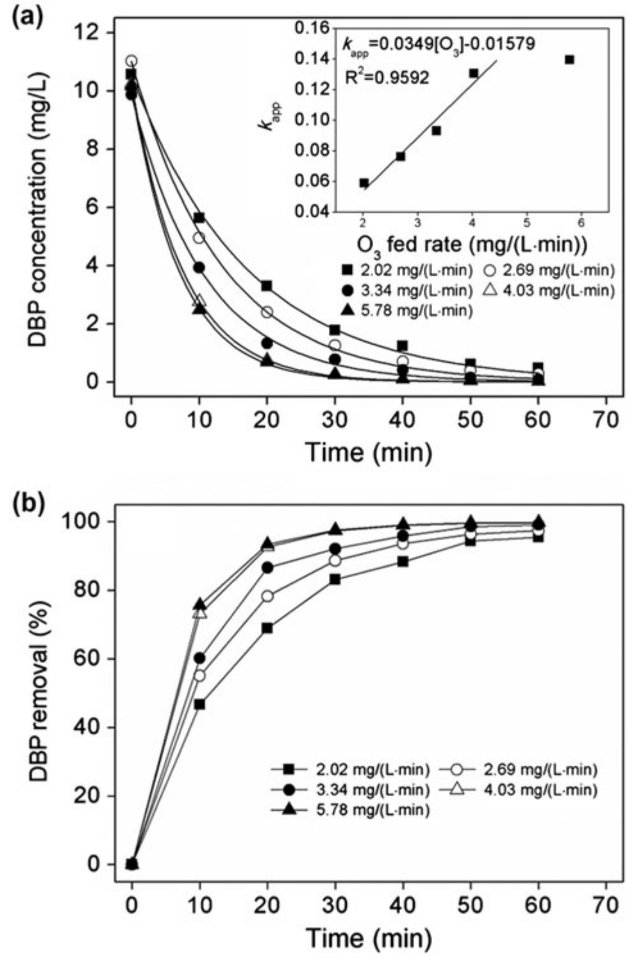


Fig. 4. Effect of aqueous O_3 fed rates on the DBP degradation by O_3/UV. Lines (a) represent the fitting results of the pseudo-first-order reaction kinetics. The insert (a) shows the relationship between the apparent pseudo-first-order rate constant and the aqueous O_3 fed rate. (UV power input: 15 W).

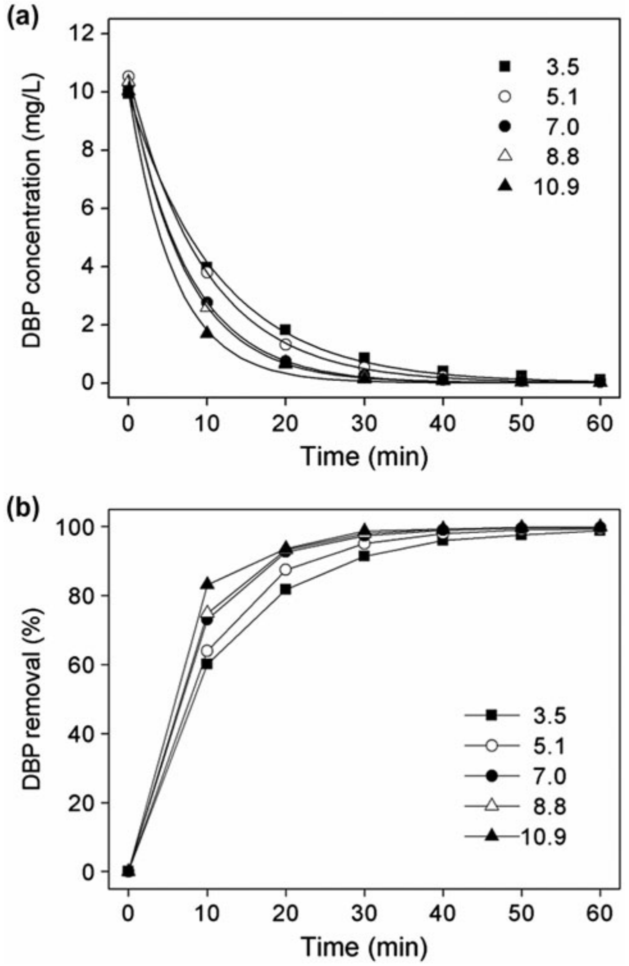


Fig. 5. Effect of initial solution pH on the DBP degradation by O_3/UV. Lines (a) represent the fitting results of the pseudo-first-order reaction kinetics. (UV power input: 15 W; aqueous O_3 fed rate: 4.03 mg/(L min)).

Table 2
The fitting results of the pseudo-first-order reaction kinetics for DBP degradation by O_3/UV under different aqueous O_3 fed rates

O_3 fed rate (mg/(L min))	$[DBP]_0$ (mg/L)	Initial pH	Removal (%)	k_{app} (/min)	r^2
2.02	10.56	7.1	95.49	0.0588	0.998
2.69	11.02	7.2	97.43	0.0760	0.998
3.34	9.87	6.9	99.10	0.0930	0.999
4.03	10.24	7.0	99.73	0.1307	1.000
5.78	10.16	7 0	99.84	0.1396	1.000

concentration of O_3 in solution would produce more ·OH radicals under the UV irradiation [35]. As a result, the degradation of DBP was improved. Since the power of the UV light was kept at 15 W in this study, the amount of ·OH radicals generated was restricted to the UV irradiation intensity under the condition of abundant O_3. Therefore, the positive effect of the aqueous O_3 fed rate augment was insignificant above 4.03 mg/(L min). This result indicated that the DBP degradation by O_3/UV depended on the amount of ·OH radicals available. The pseudo-first-order kinetics model was also employed to depict the DBP degradation with different aqueous O_3 fed rate. The fitting results are listed in Table 2. A good linear dependence of the calculated k_{app} on the aqueous O_3 fed rate was obtained when the aqueous O_3 fed rate was less than 4.03 mg/(L min), implying that the aqueous O_3 fed rate was a key factor for the control of the

Table 3
The fitting results of the pseudo-first-order reaction kinetics for DBP degradation by O_3/UV under different initial solution pH

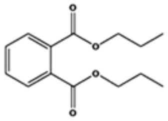
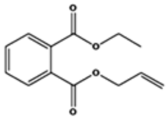
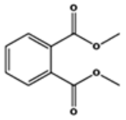
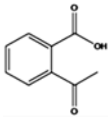
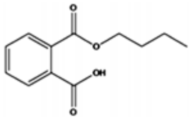
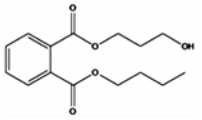
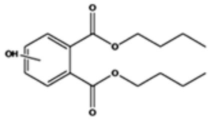
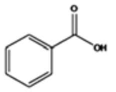
Initial pH	$[DBP]_0$ (mg/L)	O_3 fed rate (mg/(L min))	Removal (%)	k_{app} (/min)	r^2
3.5	9.93	4.03	98.85	0.0873	0.999
5.1	10.53	4.03	99.31	0.1022	1.000
7.0	10.24	4.03	99.73	0.1307	1.000
8.8	10.34	4.03	99.88	0.1371	1.000
10.9	10.02	4.03	99.93	0.1713	0.998

oxidation reaction rate. However, with a further increase in the aqueous O_3 fed rate to 5.78 mg/(L min), the k_{app} value slightly increased by 6.8% compared to that at the aqueous O_3 fed rate of 4.03 mg/(L min).

3.4. Effect of initial pH on the degradation of DBP

pH is an important parameter in the hydrolysis, photolysis, and oxidation of PAEs, and it has been well investigated in many studies [4,5,16]. It has also been reported that the solution pH could affect the domi-

Table 4
Molecular weight and mass fragment ions (m/z) of the intermediates during the DBP degradation by O_3/UV

No.	Chemical formula	Molecular weight	Detected ions (m/z)
I		250	149, 104, 76, 41
II		234	149, 104, 57
III		194	163, 104, 77,50
IV		164	149, 104, 59, 39
V		222	221 $[M–H]^-$
VI		294	317 $[M+Na]^+$
VII		294	317 $[M+Na]^+$
VIII		122	145 $[M+Na]^+$

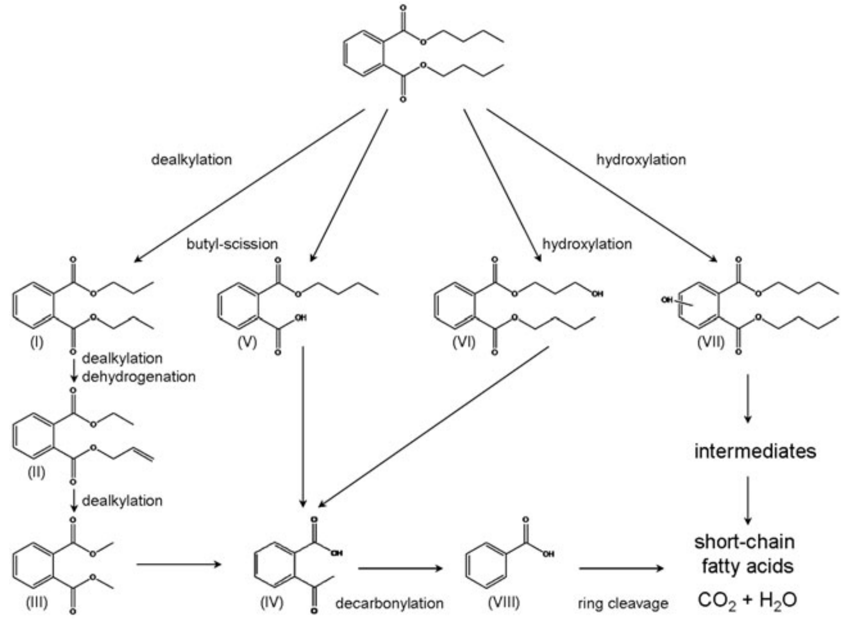


Fig. 6. Proposed DBP degradation pathway in the O_3/UV process.

nated reaction mechanisms of the PAEs degradation [5]. It is well known that the decomposition of aqueous O_3 accelerates with the increase in pH. Therefore, in the mere ozonation process, acid conditions would accelerate the removal of organic chemicals. However, since the pathway of the ·OH attack dominated the DBP degradation by O_3/UV, the quantity and activity of the produced ·OH radicals were crucial with regard to the reaction dynamics. At a high solution pH value, more hydroxide ions (OH^-) in solution benefited the generation of the ·OH radicals [4,16]. Hence, the degradation rate of DBP was faster at pH 10.9 compared to that at neutral pH, which in turn was faster than that at acid pH (Fig. 5). The fitting results based on the pseudo-first-order kinetics are shown in Table 3. The k_{app} values doubled when the initial solution pH increased from 3.5 to 10.9. However, it should also be pointed out that a high concentration of OH^- ions in solution might also trap CO_2 generated during the degradation of DBP. As a result, bicarbonate and carbonate would be formed. Since bicarbonate and carbonate are efficient ·OH scavengers, an excessive concentration of OH^- would, on the other hand, probably restrict the degradation rate of DBP.

3.5. Intermediate products and degradation pathway of DBP

The intermediate products formed in the solution during the degradation of DBP by O_3/UV were investigated using GC-MS and LC-ES-MS. Four products (I–IV) were identified through the comparison with the GC/MS NIST library data with the similarity higher than 85%, while the other four (V–VIII) were identified by the analysis of the mass spectra of LC-ES-MS (Table 4). The proposed pathway of DBP degradation by O_3/UV was illustrated in Fig. 6. Except intermediates IV and VIII, all the other intermediates were the products of dealkylation, hydroxylation, dehydrogenation, and scission of O-butyl bonds in the aliphatic chain. The aromatic ring of all the intermediates detected remained intact. Therefore, it can be concluded that the DBP degradation by O_3/UV mainly started with the attack of the aliphatic chain rather than the aromatic rings. This result was consistent with the DEP degradation by H_2O_2/UV, butyl benzyl phthalate and DBP degradation by TiO_2/UV, and DBP degradation by Fenton, which were all dominated by the OH oxidation [16,18,20,31]. In addition, although not detected in the present study, quinone, an important precursor for the aromatic ring cleavage, might also be produced in the mineralization of DBP [36]. During the DBP degradation by O_3/UV, the solution pH decreased by 1.2–4.7 unit (depending on the initial solution pH). Therefore, some short-chain fatty acids, such as acetic acid and formic acid, were supposed to be part of the finial products as well.

4. Conclusions

The ozonation was combined with the UV irradiation in this study for the DBP removal. Since more ·OH radicals were produced as a result of the

UV-induced O_3 decomposition, the hybrid system exhibited stronger capability for both DBP degradation and mineralization. Pseudo-first-order kinetics successfully depicted the DBP removal dynamics, and the calculated apparent first-order rate constants depended on the initial DBP concentration, aqueous O_3 fed rate, and the pH of the solution. Alkaline solution benefited the DBP removal. According to the intermediates detected, the DBP degradation by O_3/UV was inferred to mainly start with the $^{\cdot}OH$ attack to the aliphatic chain. High mineralization makes the O_3/UV system very attractive for the disposal of refractory organic pollutants considering the minimization of the unexpected secondary pollution. In addition, since both ozonation and UV irradiation are mature technologies for water treatment, this hybrid system can be easily accepted for the technology upgrade in the existing water treatment plants.

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