



Ozonation kinetics for the degradation of phthalate esters in water and the reduction of toxicity in the process of O_3/H_2O_2

Gang Wen^a, Jun Ma^{a,*}, Zheng-Qian Liu^{b,**}, Lei Zhao^c

^a State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, People's Republic of China

^b School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

^c School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, People's Republic of China

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ABSTRACT

The oxidation kinetics of four phthalate esters (PAEs) with ozone alone and hydroxyl radical ($\bullet OH$) were investigated. The toxicity reduction in the process of O_3/H_2O_2 was evaluated. The second order rate constants for the reaction of four PAEs with ozone and $\bullet OH$ were determined by direct oxidation method and competition kinetics method in bench-scale experiment, and found to be $0.06\text{--}0.1\text{ M}^{-1}\text{ s}^{-1}$ and $(3\text{--}5) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$, respectively. The oxidation kinetic rate constant of the selected PAEs (diethyl phthalate, DEP) was confirmed using Song Hua-jiang river water as the background. The results indicated that DEP degradation in this river water was close to the simulated value based on the determined rate constants. The toxicity test performed with bioluminescence test, showed that the toxicity expressed as the inhibition rate changed from 36% to below detection limit in the process of O_3/H_2O_2 , which means that catalytic ozonation is an efficient way for DEP degradation and toxicity reduction, but an ineffective method for DEP minimization on the basis of the total organic carbon determination.

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1. Introduction

Phthalate esters (PAEs) are frequently used as plasticizers for cellulosic and vinyl ester resins to improve their flexibility and softness, and also in ceramic, paper, cosmetic and paint industries [1]. The production of PAEs has reached 3.5 million tons per year [2]. PAEs have been detected in surface and ground-water in $\text{ng L}^{-1}\text{--mg L}^{-1}$ concentration range and associated with birth defects, organ damage, infertility, as well as testicular cancer, and are also known to be among the major endocrine disrupter chemicals (EDCs) [3,4]. Recently, it has been revealed that di-butyl phthalate (DBP) exhibits antagonistic thyroid receptor activity [5].

Drinking water treatment plant is the most important barrier to prevent the organic matters from human being contact. Previous investigation on 13 EDCs removal from traditional waterworks in China has demonstrated that four types of PAEs occurred almost in all samples with concentrations ranging from 20 to $163,760\text{ ng L}^{-1}$, which was inefficiently removed during traditional drinking water treatment processes [6]. Advanced treatment processes are required to attenuate the PAEs contamination. Various protocols are explored to enhance PAEs removal during water

treatment processes, including biotransformation [7], adsorption [8] and advanced oxidation processes [9–14]. The biotransformation of phthalates under both aerobic and anaerobic conditions has been investigated, but it is not suitable for applying in drinking water treatment due to less biomass existing in waterworks and requirement of long hydraulic retention time. Adsorption is an efficient way to remove PAEs due to its higher n-octanol/water partition coefficients (K_{ow}) (Table 1). However, it is only a method to shift the contaminations, but not to minimize them. Advanced oxidation processes would be the most powerful way for PAEs degradation and minimization. Several studies have been conducted for the elimination of PAEs by the processes of TiO_2/UV [9], H_2O_2/UV [10], electro-coagulation [11], ozonation [12] and catalytic ozonation processes [13,14].

Ozone is widely used in drinking water treatment for organic matter decomposition and microbiology disinfection all over the world. Several researchers conducted experiments on PAEs removal in the processes of ozonation and catalytic ozonation [12–14], with more attention to the removal efficiency and the way to improve it. However, the results of these studies illustrated that these processes could not be applied into practical water utilities due to the influence of natural water background. Elovitz and von Gunten [15] developed the hydroxyl radical/ozone ratio (R_{ct}) concept, which allows the prediction of the transformation of contaminations in natural water background combined with rate constants and oxidant behavior. In fact, ozonation and catalytic ozonation processes always involve in two active species: ozone

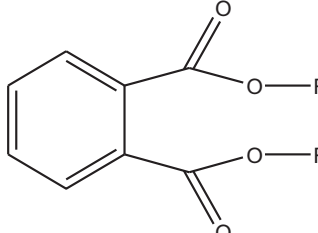
* Corresponding author. Tel.: +86 451 86282292/86283010;

fax: +86 451 82368074.

** Corresponding author.

E-mail addresses: majun@hit.edu.cn (J. Ma), liuzhengqian@gmail.com (Z.-Q. Liu).

Table 1
Chemical characteristics of four selected PAEs.



Compound	Structure (-R)	CAS number	Molecular weight	Solubility (mg L ⁻¹)	Log K _{ow}
Dimethyl phthalate (DMP)	-CH ₃	131-11-3	194.2	4200	1.66
Diethyl phthalate (DEP)	-CH ₂ CH ₃	84-66-2	222.2	1100	2.65
Dipropyl phthalate (DPrP)	-CH ₂ CH ₂ CH ₃	131-16-8	250.3	108	3.27
Dibutyl phthalate (DBP)	-CH ₂ CH ₂ CH ₂ CH ₃	84-74-2	278.4	11.2	4.50

and hydroxyl radical ($\bullet\text{OH}$) [16]. The knowledge about second order rate constants of oxidation processes involving in both ozone alone and $\bullet\text{OH}$ would provide a powerful tool to optimize the degradation of PAEs. Unfortunately, a few kinetic data are available for ozone alone and $\bullet\text{OH}$ with PAEs. David Yao [17] reported the second order rate constant of DMP and DEP for the first time with ozone alone by means of pseudo-first order reaction in excess of ozone. However, there are not any reported rate constants of DBP and DPrP with ozone alone. Haag and Yao [18] estimated the second rate constant of DMP and DEP with $\bullet\text{OH}$ using a model method based on structure-activity relationship, but no experimental result has been reported on the second order constant rate of PAEs with $\bullet\text{OH}$. Therefore, detailed kinetic constants of PAEs with ozone alone and $\bullet\text{OH}$ are required for further studies.

The aim of this study is to determine the second-order rate constants of ozone alone and $\bullet\text{OH}$ with four PAEs by bench scale experiments in pure aqueous solution and to validate its applicability through oxidation and simulation of DEP degradation in river water background, where only DEP was selected as a representative due to the similarity of kinetics constant and the structures of 4 types of PAEs. Furthermore, bioluminescence test was performed to evaluate the acute toxicity change in the process of $\text{O}_3/\text{H}_2\text{O}_2$ because of its higher degradation efficiency.

2. Experimental

2.1. Materials and reagents

DMP, DEP, DPrP, DBP (Guang Fu Chemical Inc., China, 99.5% purity), *p*-chloro benzoic acid (*p*CBA, Sigma-Aldrich Chemicals, USA, 98% purity), high performance liquid chromatography (HPLC) grade methanol (Fisher, American), H_2O_2 (30% w/w), ZnO powder (diameter 100 μm) and all other chemicals were of analytical grade and were used without further purification. Milli-Q water (Millipore Q Biocel system) was used for sample preparation. Ozone stock solutions were produced by sparging O_3/O_2 air into Milli-Q water. The chemical characteristics of four selected PAEs are listed in Table 1.

2.2. Determination of rate constants for the reaction of PAEs with ozone alone and $\bullet\text{OH}$

Determination of the second-order rate constant of 4 types of PAEs with ozone was conducted by direct oxidation method under the condition of excessive ozone concentration. A semi-continuous flow reaction model was used to determine the rate constant of PAEs with ozone, which was described by a previous study [19]. Briefly, experiments were performed in a 1 L

bench-scale glass reactor. Ozone delivered into the reactor via a medium porosity ceramic was kept constant concentration across the whole experiment process, which was supplied from an ozone generator (DHX-IIB model, Harbin Jiujiu Co.) with the inlet ozone concentration is 0.7 mg min⁻¹. When the ozone concentration in reactor was reaching a constant value (4–5 mg L⁻¹), a small aliquot (10 ml of DMP, DEP, DPrP and 25 ml of DBP) of PAEs stock solution (100 μM of DMP, DEP, DPrP and 40 μM of DBP) was injected into the reactor, followed by starting the reaction. An aliquot of 0.1 mol L⁻¹ sodium thiosulfate solution was used to quench the reaction after sampling at various intervals. Meanwhile, the ozone concentration in liquid was determined with indigo method [20]. The experiment was carried out in Milli-Q water using *tert*-butyl alcohol (TBA 10 mM) as the $\bullet\text{OH}$ scavenger and was adjusted to pH 2 with perchlorate (1 M). If not stated otherwise, the experiments were controlled at 25 °C by using cooling water. To determine the activation energy for the reaction of ozone with PAEs, the same experiments were also performed at 5, 10, and 15 °C. The experiment was repeated at least three times and the errors given were 95% confidence intervals.

Because of rapid reaction of $\bullet\text{OH}$ with organic matters, the rate constant of PAEs with $\bullet\text{OH}$ is difficult to determine directly, but can be measured by using competition kinetics method [16,18]. Considering the structure of PAEs, the rate constant of $\bullet\text{OH}$ with PAEs was constant throughout the pH range evaluated. These experiments were carried out with Milli-Q water at 25 °C and the pH was kept at 10 for ozone decomposition into $\bullet\text{OH}$. The reference compound was *p*CBA exhibiting a rate constant of $k_{\bullet\text{OH}} 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [17]. Under alkaline conditions, the half-life time of ozone is about several seconds, and the dominant reaction is between $\bullet\text{OH}$ and organic matters. Therefore, the reaction with molecular ozone can be ignored due to its short half-life time and lower second rate constant [19]. The equal concentrations of the compounds (1 μM *p*CBA and 1 μM PAEs) were spiked into the water samples. Thereafter different under-stoichiometric concentration levels of ozone (ranging from 0.1 to 1 μM) were added. After ozone injection, the solutions were vigorously stirred. The residual concentrations of target and referenced compound in the flask were analyzed by HPLC.

2.3. Degradation and simulation of DEP decomposition in different ozonation processes in river water

Song Hua-jiang river water (water quality parameters are shown in Table 2) was used as the background for PAEs degradation. Due to the similarity of structure and kinetic properties of 4 types of PAEs, DEP was selected as the representative chemical to investigate its degradation in river water. River water was quickly filtered (0.45 μm , cellulose acetate) within 8 h after sampled and stored at

Table 2
Water quality characteristics of the filtered Song Hua-jiang river.

pH	UV ₂₅₄ (cm ⁻¹)	UV ₂₁₅ (cm ⁻¹)	DOC (mgL ⁻¹)	SUVA (Lcm ⁻¹ mg ⁻¹)	Alkalinity (mM)
7.9	0.0875	0.5248	3.5	3.36	4.7

4 °C before use. During DEP degradation, river water was buffered to pH 8 by adding 10 mM borate buffer. The low concentration of DEP (1 μM) was spiked into river water, and 40 ml cold ozone stock solution (50 mgL⁻¹) was injected to start the chemical reaction. Samples were taken at presumed intervals to determine the DEP concentration with HPLC.

As described by Elovitz and von Gunten [15], R_{ct} value can be calculated from the extent of the decrease of a probe compound (pCBA) concentration, which reacts fast with •OH but slowly with ozone, and a simultaneous determination of the ozone concentration. Once the R_{ct} value is known, the elimination of a compound (M), which reacts with both oxidants, can be calculated by second-order kinetics and expressed as a function of R_{ct} , k_{O_3} , k_{OH} , and the ozone exposure ($\int [O_3] dt$) according to Eq. (1):

$$\ln \left(\frac{[M]}{[M]_0} \right) = - \left(\int [O_3] dt \right) (k_{OH} R_{ct} + k_{O_3}) \quad (1)$$

In order to simulate the degradation of DEP, another experiment was designed as follows. pCBA was added as a probe compound (0.5 μM) to determine R_{ct} . H₂O₂ and ZnO were used as catalyst in catalytic ozonation experiments, respectively, with a ratio of 0.34 mg of H₂O₂/mg of O₃, and ZnO added with a concentration of 0.1 gL⁻¹. The other part of this experiment was the same as the DEP degradation described as above. Before DEP and pCBA analysis, the samples were filtered with a filter (0.45 μm in pore size, cellulose acetate).

2.4. Toxicity test

The acute toxicity of DEP and its degradation intermediate were tested with luminescent bacterium bioassay following the Chinese standard method (GB/T 15441-1995, 1996) [21,22]. It was performed using gram negative luminescent bacteria of the species *Vibrio qinghaiensis* sp. Nov (Q67). Due to the higher decomposition efficiency of O₃/H₂O₂, which was selected to decrease the toxicity of DEP and its intermediates products, a semi-continuous experiment (volume 1 L) was taken for DEP degradation in Milli-Q water with initial concentration of DEP of 20 μM, ozone concentration of 0.7 mg min⁻¹ and H₂O₂ concentration of 0.3 mM. Different samples at each interval were taken for toxicity test and TOC determination. The samples chosen for toxicity test were concentrated in Milli-Q water and adjusted to pH 7 before the analysis. Starting from a concentration factor of 300 times, eight double consecutive elution were tested (dilution factor 1:2), and the bioluminescence was then measured with Glomax illumination equipment (Turner Biosystems) [23]. The toxicity variation is expressed as Eq. (2).

$$I(\%) = \frac{L_B - L_S}{L_B} \times 100 \quad (2)$$

where I represents the inhibition of the concentrated sample to luminescent bacteria, L_B is the luminescent intensity of blank, and L_S is the luminescent intensity of sample.

2.5. Analytical methods

The concentration of dissolved ozone in water was determined by the indigo method [20]. The concentration of ozone in gas phase was analyzed by iodometric method [24]. The concentration of PAEs were analyzed using HPLC equipped with an automatic Waters

717 plus autosampler injector and a Waters 1525 binary pump, using a waters symmetry C18 column (4.6 mm × 150 mm, 5 μm particle size) and methanol/water (50/50 for DMP, 60/40 for DEP, 70/30 for DPrP, 80/20 for DBP, v/v) as the mobile phase with a rate of 1 mL min⁻¹. The water sample was detected by a UV detector (Waters 2487 dual absorbance detector) at 230 nm and injected volume was 100 μL. The condition for pCBA analysis was as follows: an eluent with a rate of 1.0 mL min⁻¹ consisting of 60/40 (v/v) methanol/water (adjusted to pH 2 with H₃PO₄), UV wavelength of 240 nm was used.

The pH in aqueous solution was measured by pH acidometer (Delta 320, Shanghai Leici Apparatus Fac., China). The TOC was analyzed by a TOC Analyzer (Analytikjena Multi N/C 3100). A Cary 500 UV-Vis spectrophotometer was used to measure UV₂₅₄ value. The alkalinity of water was analyzed by titration method according to standard method [25].

3. Results and discussion

3.1. Determination of rate constant for reaction of PAEs with ozone alone

Several methods have been reported to determine second-order rate constant between ozone with compounds, including pseudo-first order reaction (ozone in excess or chemicals in excess) [16,17], competition kinetics [17] and direct oxidation method [19]. The second-order rate constant was determined by direct kinetics in semi-continuous batch reactor, and the exact experiment step can be found as above mentioned. Both •OH inhibition and ozone decomposition were considered in this study. The reaction between PAEs with •OH was expelled by using 10 mM TBA as a way for scavenging it, ozone concentration was kept constant during the whole process, so the second-order reaction could be transformed in pseudo-first order reaction. Table 1 shows that PAEs do not dissociate within all the range of pH, indicating that the second rate constant of PAEs is pH-independent. So, the experiment was carried out in pH 2 by using perchlorate for minimizing the reaction of •OH with PAEs.

Under the condition of acidic pH and higher concentration of TBA in the ozonation system, molecular ozone reacts with PAEs predominantly, and the influence of •OH can be ignored. So, the rate of PAEs degradation can be written as follows:

$$-\frac{d[PAEs]}{dt} = k_{O_3}[O_3][PAEs] \quad (3)$$

$$-\frac{d[PAEs]}{[PAEs]} = k_{O_3}[O_3]dt \quad (4)$$

Because of the constant ozone concentration, Eq. (4) can be converted to Eq. (5):

$$\ln \frac{[PAEs]_t}{[PAEs]_0} = -k_{O_3}[O_3]t \quad (5)$$

According to the above Eq. (5), k_{O_3} can be concluded from the plots of PAE degradation versus time. The result of experiment is shown in Fig. 1. Table 3 lists all the results of the present experiment and the previous study. The rate constant of DMP, DEP, DPrP and DBP are 0.072, 0.085, 0.11 and 0.092 M⁻¹ s⁻¹, respectively. Comparing the rate constants of four PAE compounds, there is no obvious relationship in the oxidation rate constants with the increase of PAE

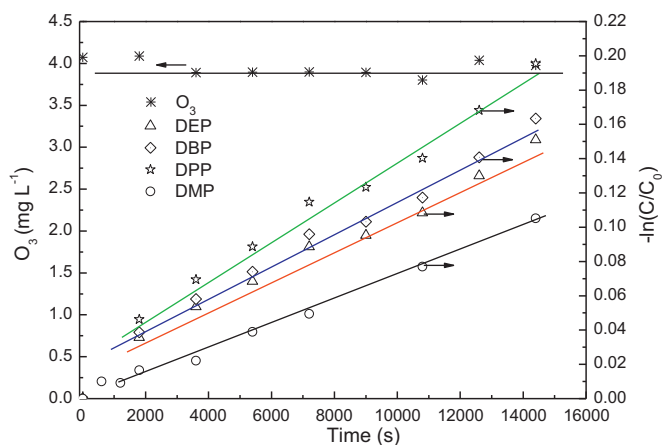


Fig. 1. Variation of ozone concentration with time and the second-order plots of four types of PAEs degradation by ozone alone. Experimental conditions: $[PAEs]_0 = 1 \mu M$, $[TBA] = 10 \text{ mM}$, $[O_3] = 3.85 \text{ mg L}^{-1}$, $\text{pH} = 2.0$, $T = 25^\circ \text{C}$.

carbon chain. The rate constants of DMP and DEP are close to those reported in previous study [17].

As can be seen from Table 3, PAEs are difficult to be oxidized by ozone alone. Previous study shows that ozone behaves as an electrophilic species, which reacts only with some electron-rich organic moieties, such as phenols, anilines, olefins, and deprotonated-amines [26]. Advanced oxidation process, especially catalytic ozonation, produces more $\bullet\text{OH}$ and would be the option for PAEs elimination. The reaction rate constant between PAEs and $\bullet\text{OH}$ would be discussed afterwards.

In order to figure out the activation energies, four different reaction temperatures were performed. Activation energy can be calculated according to the slope of the Arrhenius plot of $\ln k$ against T^{-1} to fit Eq. (6).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6)$$

where K is second order rate constant, E_a is reaction activation energy, T is reaction temperature, R is gas constant.

DMP, DEP, DPrP and DBP exhibited 66 ± 8 , 73 ± 4 , 54 ± 10 and $58 \pm 9 \text{ kJ mol}^{-1}$, respectively. They are endothermic reaction, enhanced reaction rate as the temperature increase. The results show no trends between the substitution groups with the activation energies.

3.2. Determination of rate constant for reaction of PAEs with $\bullet\text{OH}$

Rate constants for the reaction of 4 types of PAEs with $\bullet\text{OH}$ were determined by competition kinetics methods, which is the frequently used. Primary methods for generating $\bullet\text{OH}$ include UV/ H_2O_2 , γ -radiolysis, $\text{O}_3/\text{H}_2\text{O}_2$ [16], Fenton method, Walling's method [18] and O_3/OH^- [19]. In the present study, competition kinetics with $p\text{CBA}$ as reference compound was adopted and the O_3/OH^- method was selected for producing $\bullet\text{OH}$.

The second-order rate constants of the four types of PAEs compounds (M) with $\bullet\text{OH}$ were determined using Eq. (7) by plotting

Table 3
Second-order rate constants for the reaction between ozone and 4 types of PAEs.

Compound	$(T = 25^\circ \text{C}) (\text{M}^{-1} \text{s}^{-1})$		
	Measured	R^2	Reference
DMP	0.072 ± 0.012	0.99	0.2 ± 0.1 [17]
DEP	0.085 ± 0.021	0.98	0.14 ± 0.05 [17]
DPrP	0.110 ± 0.033	0.98	No report
DBP	0.092 ± 0.042	0.98	No report

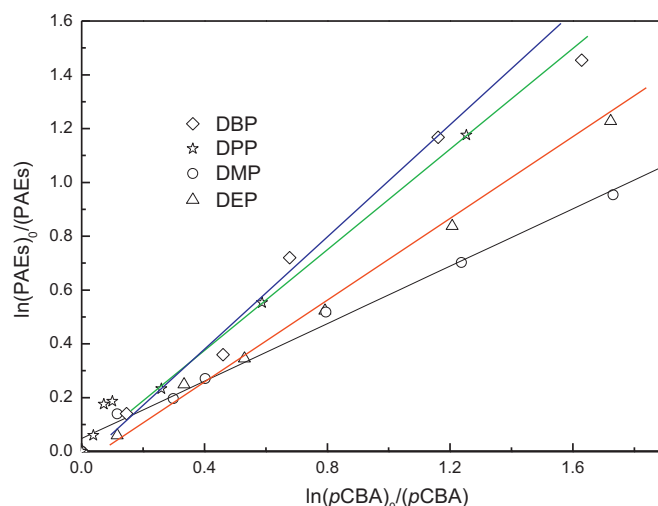


Fig. 2. The second-order plots of the degradation of four types of PAEs by $\bullet\text{OH}$. Experimental conditions: $[PAEs]_0 = 1 \mu M$, $[p\text{CBA}]_0 = 1 \mu M$, $[O_3] = 0.1\text{--}1 \mu M$, $\text{pH} = 10.0$, $T = 25^\circ \text{C}$.

the decrease of M versus the reference compound (C), which can be seen from Fig. 2, a typical plot of relative rate experiment for the degradation of two compounds.

$$k_{\text{OH}}^{\text{M}} = \frac{\ln([M]_0/[M]_\infty)}{\ln([C]_0/[C]_\infty)} k_{\text{OH}}^{\text{C}} \quad (7)$$

where k_{OH}^{M} and k_{OH}^{C} are the rate constant for PAEs and reference compound, respectively.

The measured second-order rate constants for the reaction of the PAEs with $\bullet\text{OH}$ are summarized in Table 4. The rate constant of DMP, DEP, DPrP and DBP is 2.67×10^9 , 3.98×10^9 , 4.47×10^9 and $4.64 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The rate constant of DMP is lower than that calculated by Haag, whereas DEP's rate constant is comparative to Haag's result [18]. Additionally, it is the first time to report the second order rate constant of DPrP and DBP. As seen from the results in Table 4, the rate constant increases as the carbon chain extends. It is well-known that $\bullet\text{OH}$ attacks compounds by abstracting a hydrogen atom (H-abstraction), electron transfer reaction or by addition to an unsaturated bonds (such as C=C bond). Seen from PAEs molecular structure, the attack to PAEs mainly depends on H-abstraction, and the electron donor capacity of the substitute group follows the sequence: $\text{C}(\text{CH}_3)_3 > \text{CH}_3\text{CH}_2\text{CH}_2 > \text{CH}_3\text{CH}_2 > \text{CH}_3 > \text{H}$, which can explain the phenomenon of the increasing rate constant of PAEs as the increase of carbon chain length. Those second rate constants of PAEs would be further validated to its applicability through PAEs elimination in the processes of ozonation and catalytic ozonation processes and are discussed below.

3.3. Degradation and simulation of DEP decomposition in different ozonation processes in river water

In natural water, the reactions of PAEs with ozone and $\bullet\text{OH}$ have to be considered together and it is essential to know their exposures

Table 4
Second-order rate constants for the reaction between $\bullet\text{OH}$ and 4 types of PAEs.

Compound	$K_{\text{OH}} (T = 25^\circ \text{C}) (\text{M}^{-1} \text{s}^{-1})$		
	Measured	R^2	Reference
DMP	$(2.67 \pm 0.26)\text{E}+9$	0.98	$4\text{E}+9$ [18]
DEP	$(3.98 \pm 0.21)\text{E}+9$	1.0	$4\text{E}+9$ [18]
DPrP	$(4.47 \pm 0.35)\text{E}+9$	0.99	No report
DBP	$(4.64 \pm 0.41)\text{E}+9$	0.99	No report

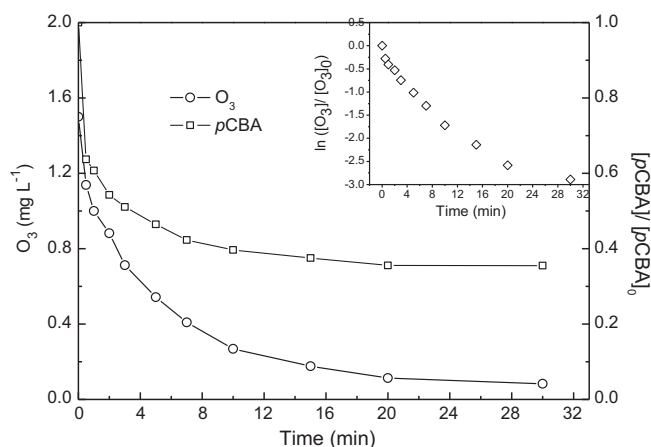


Fig. 3. Variation of ozone concentration with time and the plot of *p*CBA degradation in the process of ozonation. Experimental condition: $[O_3]_0 = 2 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$, $[pCBA] = 0.5 \mu\text{M}$, $\text{pH} = 8$, inset is the decomposition of ozone.

[27]. In natural river water background, a part of matrixes exists as $\bullet\text{OH}$ initiator, whereas another part of them serves as $\bullet\text{OH}$ scavengers. R_{ct} can be used to forecast the decomposition of compound in ozonation or catalytic ozonation processes in association with compound's second-order rate constant of ozone and $\bullet\text{OH}$.

3.3.1. Quantification of R_{ct} of ozonation and catalytic ozonation processes in river water

Ozone decomposition in natural water can be divided into an initial and a second phase. During the second phase ($>20 \text{ s}$), ozone decomposition follows an apparent first-order rate law, the rate constant in the second phase is 10–100 times smaller than that during the initial phase [28]. As seen from Eq. (8), R_{ct} describes that the ratio of $\bullet\text{OH}$ exposure to O_3 -exposure, which can be calculated from the decrease in concentration of *p*CBA and O_3 . The $\bullet\text{OH}$ exposure can be calculated by means of Eq. (9). The ozone exposure can be calculated from the integral of the ozone concentration versus time. Substitution of Eq. (9) into Eq. (8) gives the result of R_{ct} , shown as Eq. (10).

$$R_{ct} = \frac{\int [\text{OH}] dt}{\int [O_3] dt} \quad (8)$$

$$\int [\text{OH}] dt = -\frac{\ln([pCBA]/[pCBA]_0)}{k_{\text{OH},pCBA}} \quad (9)$$

$$R_{ct} = -\frac{\ln([pCBA]/[pCBA]_0)}{k_{\text{OH},pCBA} \cdot \int [O_3] dt} \quad (10)$$

The concentration of *p*CBA ($\bullet\text{OH}$ probe) and O_3 were detected, and typical results of R_{ct} are shown in Fig. 3. The results show that the decomposition of O_3 followed first order rate reaction. The calculated R_{ct} of three oxidation processes are shown in Table 5, indicating that the $O_3/\text{H}_2\text{O}_2$ process presents the most powerful capability to produce $\bullet\text{OH}$, followed by O_3/ZnO process in generating $\bullet\text{OH}$. As was reported previously, the mechanism of H_2O_2 and ZnO for improving organic matter removal is the enhancement of ozone decomposition and conversion of ozone into $\bullet\text{OH}$ [29,30]. H_2O_2 generates plenty of HO_2^- which enhances ozone decompo-

Table 5
Measured and calculated R_{ct} in different processes.

Different process	O_3 alone	$O_3/\text{H}_2\text{O}_2$	O_3/ZnO
R_{ct} (measured)	1.20E-08	1.37E-07	3.23E-08
R_{ct} (calculated)	6.06E-08	3.19E-07	6.06E-08

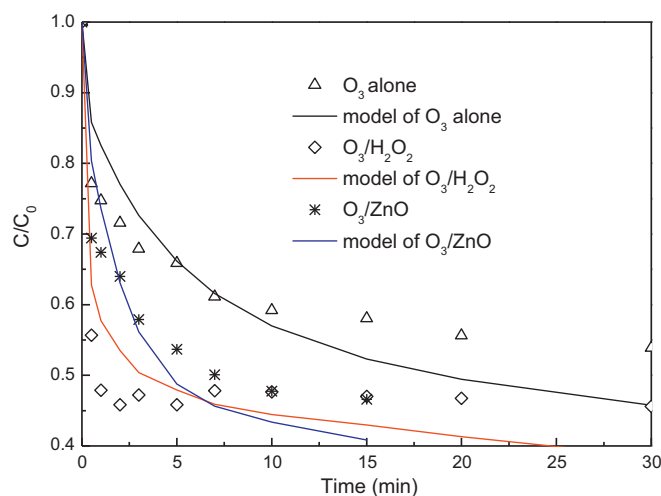


Fig. 4. Simulation and degradation of DEP removal during ozonation or catalytic ozonation in river water (dots mean experimental data and lines mean modeled results). Experimental condition: $[O_3]_0 = 2 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$, $[pCBA] = 0.5 \mu\text{M}$, $[\text{DEP}] = 1 \mu\text{M}$, $\text{pH} = 8$.

sition, meanwhile hydroxyl group on ZnO surface improves the decomposition of ozone and the formation of $\bullet\text{OH}$ [31].

Recently, a method for predicting R_{ct} in different natural water background was developed [32], which showed that R_{ct} was dependent on water quality characteristics and could be simulated ($R^2 = 0.92$), using water quality characteristics and experimental conditions (Eq. (11)).

$$\log R_{ct} = -10.12 + 2.04 D_{\text{H}_2\text{O}_2} - 0.325 \text{DOC} + 0.747 \text{pH} - 11.47 \text{UV}_{254} - 0.143 \text{URI} \quad (11)$$

URI = UV relative index (calculated as the ratio of UV_{215} over UV_{254});

$D_{\text{H}_2\text{O}_2}$ = peroxide dosage ($\text{mg H}_2\text{O}_2/\text{mg O}_3$);

UV_{254} = UV absorbance at 254 nm (cm^{-1});

DOC = dissolved organic carbon (mg CL^{-1}).

In our present study, the model was used to predict the R_{ct} in Song Hua-jiang river water, which can be seen in Table 5. Comparing the experimental results with the simulated results, the model data has the same order as experimental result. However, it cannot differentiate the processes of ozonation alone and O_3/ZnO catalytic ozonation because there is no consideration of the influence of heterogeneous catalyst on ozone decomposition. Therefore, the model is not appropriate for predicting the R_{ct} in heterogeneous catalytic ozonation processes.

3.3.2. Simulation of DEP decomposition in river water

Natural water matrixes have important impact on the ozonation process of organic matter, where natural organic matter may promotes or prohibits the radical chain reaction, acting as an initiator or scavenger, while, the alkalinity competes with organic matter for $\bullet\text{OH}$ as a scavenger [33]. Batch experiments with river water as background were performed to examine the removal efficiency of DEP in O_3 , $O_3/\text{H}_2\text{O}_2$, and O_3/ZnO processes. The water quality parameters are given in Table 2. As seen from the experimental results in Fig. 4, the oxidation of DEP was mainly determined in reactions with $\bullet\text{OH}$. The oxidation efficiencies increases with the increase of R_{ct} , namely $O_3/\text{H}_2\text{O}_2$ process with higher R_{ct} removes DEP much faster than that of O_3 alone or O_3/ZnO process.

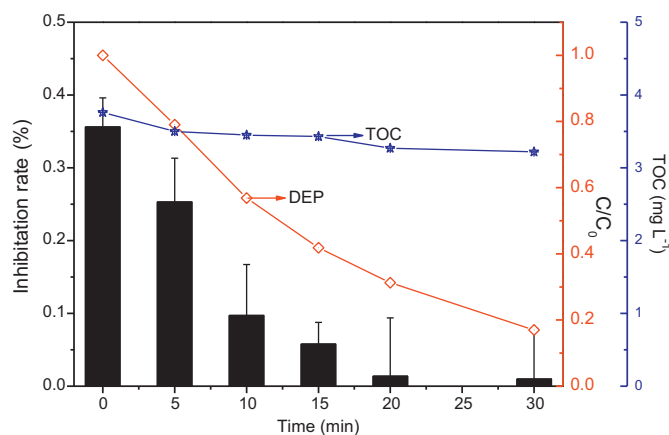


Fig. 5. Toxicity assessment of DEP oxidation and TOC change in the process of O_3/H_2O_2 .

Furthermore, it is possible to predict the DEP removal with a function of ozone exposure, R_{ct} , k_{OH} , and k_{O_3} according to Eq. (12).

$$\ln\left(\frac{[M]_t}{[M]_0}\right) = -\left(\int [O_3] dt\right)(k_{OH}R_{ct} + k_{O_3}) \quad (12)$$

Fig. 4 presents the data for the predicted and measured oxidation of DEP in the three oxidation processes. The results indicated that DEP removal efficiency in river water followed the sequence, $O_3/H_2O_2 > O_3/ZnO > O_3$, which is in accord with the R_{ct} , meaning that O_3/H_2O_2 shows the most powerful capability to produce $\bullet OH$ among the three processes. It was calculated with experimental R_{ct} and model R_{ct} for DEP removal with Eq. (12), which showed poor simulation results compared with the degradation data using the calculated R_{ct} (data not shown here). Using the experimental R_{ct} , the simulated results were well in consistence with the experimental data. From the consistence of experimental data with the simulated data, it can be concluded that above determined second-order rate constants of DEP with O_3 and $\bullet OH$ are applicable in natural water.

3.4. Toxicity assessment

Fig. 5 shows the variations of toxicity and TOC in the process of O_3/H_2O_2 . It is seen from the results that after 30 min oxidation, the acute toxicity expressing inhabitation rate decreases to below the detection limit, namely no acute toxicity was detected. The decrease in acute toxicity of DEP mainly occurs in the first 10 min, which coincides with the decrease of DEP concentration. Therefore, the primary toxicity to luminescent bacteria may come from the DEP parent molecular, while the intermediates contribute a little to the toxicity for Q67. After 30 min oxidation, the TOC decreases from 3.76 to 3.22 $mg L^{-1}$, indicating that only 14.4% of TOC is mineralized and the intermediates are accumulated in the oxidation process, which illustrated furthermore that the decrease of toxicity to Q67 was due to DEP parent molecular removal, but not the formation of intermediates. Through continuous oxidation of ozone and $\bullet OH$, the parent of DEP had been decomposed into nontoxic intermediate. However, the mineralization of DEP requires more powerful oxidation process or in combination with biotransformation.

4. Conclusions

The second-order rate constants for the reaction of 4 PAEs with ozone and $\bullet OH$ were determined by direct oxidation method and competition kinetics method by bench-scale experiments. Degradation of DEP in river and simulation decomposition based on

R_{ct} were conducted. Three different ozonation processes including ozone alone, O_3/H_2O_2 and O_3/ZnO were evaluated in Song Huajiang river water background, which showed that the O_3/H_2O_2 process had the highest capacity in degrading DEP. The DEP transformation was successfully simulated with the determined second-order rate constant in combination with R_{ct} . The acute toxicity in the process of O_3/H_2O_2 was assessed by luminescent bacteria, which showed that O_3/H_2O_2 was an efficient way for PAEs degradation and toxicity reduction, but it was a less efficient method for DEP mineralization.

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