

Removal of a type of endocrine disruptors—di-*n*-butyl phthalate from water by ozonation

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Abstract: Ozonation of synthetic water containing a type of endocrine disruptor—di-*n*-butyl phthalate (DBP) was examined. Key impact factors such as pH, temperature, ionic strength, ozone dosage and initial DBP concentration were investigated. In addition, the activities of radicals on uncatalysed and catalysed ozonation were studied. The degradation intermediate products were followed and the kinetic of the ozonation were assessed as well. Results revealed that ozonation of DBP followed two mechanisms. Firstly, the reaction rate of direct ozonation was slower at lower pH, temperature, and ionic strength. Secondly, when these factors were increased for indirect radical reaction, higher percentage of DBP was removed with the increase of the initial ozone dosage and the decrease of the initial DBP concentration. In addition, *tert*-butanol, humic substances and Fe(II) affected DBP ozonation through the radical pathway. It was determined that ozonation was restrained by adding *tert*-butanol for its radical inhibition effect. Furthermore, humic substances enhanced the reaction to some extent, but a slight negative effect would be encountered if the optimum dosage was exceeded. As a matter of fact, Mn(II) affected the ozonation by “active sites” mechanism. In the experiment, three different kinds of intermediate products were produced during ozonation, but the amount of products for each one of them decreased as pH, temperature, ionic strength and initial ozone dosage increased. A kinetic equation of the reaction between ozone and DBP was obtained.

Keywords: di-*n*-butyl phthalate (DBP); ozonation; key impact factors; reaction kinetics; degradation intermediate products

Introduction

Large quantities of DBP (di-*n*-butyl phthalate) are manufactured annually in China, and it is used primarily as additives in sealants, adhesives, and printing inks. It extensively exists in air, water, soil and organisms (Yie, 1993). As a type of endocrine disruptors, it influences the generative function of some living species on the earth. Makoto has found that it was embryo-lethal and teratogenic in rats (Makoto *et al.*, 2000). Therefore, it has been listed as priority pollutants by USEPA and Chinese EPA. Han found that DBP existed in water sources, water treatment plants and in water feeding line, etc., with the concentration of several $\mu\text{g/L}$ (Yie, 1993). As a consequence, researches on efficient methods to remove DBP from water have taken increased attention in recent years.

There were a lot of researches focused on DBP degradation in the wastewater, but few was paid attention to its removal from water, especially in the area regarding DBP degradation in the pre-oxidation stage. Nowadays chlorine and chlorine dioxide are widely used as pre-oxidants, but neither can degrade DBP completely. On the other hand, ozonation has been employed as an effective method for removing lots of hazardous chemicals from raw water during drinking water purification process (Rice *et al.*, 1981a). It was also used as a pre-oxidation agent to partly degrade pollutants and natural organic matter

(NOM) so as to enhance the coagulation and disinfection effect. As a result, hazardous substances became easier to be removed from water in the next purification process (Rice *et al.*, 1981b). Li (2002) reported that di-methyl phthalate (DMP) could be removed by ozone easily. Thus it is safe to say that DBP can be removed by ozonation process as they both share the similar structures.

In this study, the efficiency of DBP removal by ozonation was examined. The effectiveness of some key impact factors was investigated in detail. In addition, the influences of humic substances, *tert*-butanol, and metal ions on ozonation were also interpreted by radicals created during the ozonation process.

1 Materials and methods

1.1 Materials

DBP (99% purity) was obtained from AccuStandard Inc. (USA). Benzyl benzoate sample which was used as the internal standard in gas chromatography, and indigotrisulfonate were purchased from Acros Organics (New Jersey, USA). Acetonitrile of HPLC grade was purchased from Tedia Company, Inc. (USA). Other chemicals (KI, H_2SO_4 , Na_2HPO_4 , NaH_2PO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, H_3PO_4 , FeSO_4 , MnSO_4) were of the G.R.

Humic substances were obtained from the leaf mold of some brown forest. The mold was extracted by 1 mol/L of HCl, and then was dialyzed. After

filtration, it was freeze-dried, afterwards it was dissolved in the ultra-pure water at an approximate pH 10.0–12.0, and the pH level was later adjusted to 7.0–7.5 before use.

At the same time, synthetic raw water was prepared by dissolving 7.5 mg of DBP into 1.2 L ultra-pure buffered water (1 mmol/L $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$) at pH 7.0. All the glassware equipments used in the experiments were soaked in chromic acid and then in 1% HNO_3 overnight before experiments. Except for volumetric flasks, they were all muffled at 400°C for several hours after being rinsed by tap water and ultra-pure water.

1.2 Experimental procedures

Ozone was generated from oxygen by an ozonizer (Ozonizer Series OS-N, Mitsubishi, Japan). Following intermediate products, reaction kinetics and the influence of key impact factors on DBP removal were carried out by batch experiments. Semi-batch experiments were performed to study the relationship between hydroxyl radicals and DBP degradation. During the batch tests, a high concentration of gas phase ozone was applied to ultra-pure water (2°C) for an extended period until the concentration of the ozone stock solution reached about 40 mg/L. A certain volume of stock ozone and DBP solution were mixed immediately according to the final desired

concentration of DBP and ozone as soon as ozone was taken out. During this process the headspace of the reactor was sealed until the oxidation reaction has completed. In fact the process can be repeated accurately because the ozone dosage and consumption were easy to control and the procedure was relatively simple to perform at lower DBP concentration. At the same time, for DBP at higher concentrations, semi-batch ozonation was performed in a stainless reactor with a height of 300 mm and a diameter of 70 mm, as shown in Fig.1. The reactor was equipped with a Ti porous plate (10 μm porous size) at its bottom to obtain smaller gas bubbles. In addition, a water jacket around the reactor was used to maintain the desired and constant temperature with water circulating from a water bath. Experimental water containing DBP was pumped by a peristaltic pump from a holding beaker. Then an ozonized oxygen stream flowed through the solutions at a rate of 30 ml/min when the stationary state regime was attained. In order to absorb the excess ozone, effluent gas was introduced into a glass bottle containing 300 ml of 2% KI solution. During the reaction process, sample solutions of 1 ml were taken out at given intervals, followed by the addition of $\text{Na}_2\text{S}_2\text{O}_3$ which equals to the amount of residual ozone, and finally the DBP concentration was analyzed.

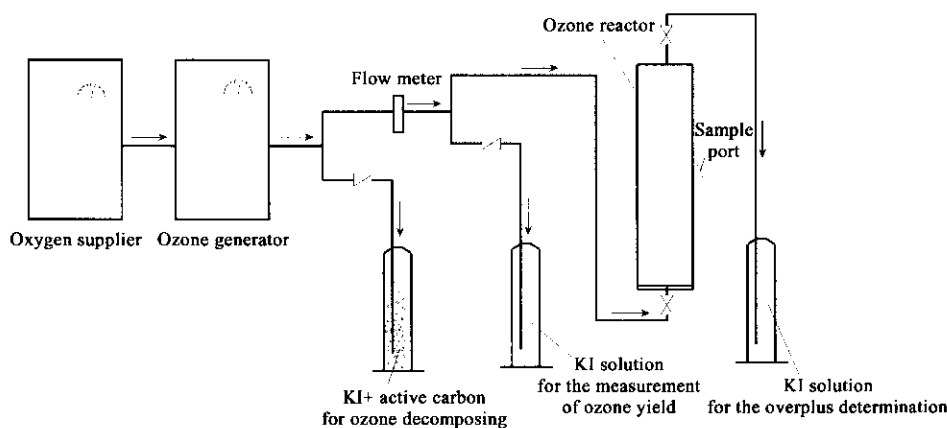


Fig.1 Flow chart of DBP ozonation

1.3 Analysis methods

During the experiment the concentrations of dissolved ozone were measured colorimetrically by the indigo method (Bader and Hoigne, 1981). The adsorption measurements were performed at 600 nm with a Model DR/2010 portable datalogging spectrophotometer (HACH, USA). Meanwhile, the gaseous ozone concentration was iodometrically measured before ozone was added into the reactor. A blank test was conducted to investigate the profiles of ozone concentration. The applied ozone was calculated by the equation:

$$O_3_{\text{applied}} = O_3_{\text{introduced}} - (O_3_{\text{off-gas}} + O_3_{\text{residual}})$$

For batch experiments, DBP concentration was determined by HP5890 II Gas Chromatography. A DB5MS (25 m length \times 0.2 mm i.d. \times 0.33 μm film thickness) fused silica capillary column (HP, USA) was employed for GC separation. Samples were concentrated by SPME method using PDMS-DVB fiber with added internal standard. The fiber was immersed in the sample solution for about 20 min at a constant temperature (60°C), and then was desorbed in the gas chromatography inlet for another 2 min. A split rate of 50:1 was applied with a column head pressure of 20 psi using high purity nitrogen as the carrier gas, producing a flow rate of 1.0 ml/min. The

initial column temperature was held for 0.5 min at 80°C, ramped at 20°C/min to 230°C, and was held for 13 min at 230°C. The residual concentrations of DBP in semi-batch experiments were determined by HPLC (Shimadzu, 10A, Japan) directly after the reaction for the high concentration of DBP. Liquid chromatography was carried out with a flow rate of 1.0 ml/min with acetonitrile/water mixture (90:10 v/v) on a ZORBAX Extend-C18 column (250 mm long, 4.6 mm i.d., Agilent, USA) with a column temperature of 40°C and a SPD-M10A UV/Visible detector. The injection volume was 20 μ l and the retention time of DBP was 10.056 min. Detection was performed at 224 nm, and quantification was done using a 5-point calibration curve.

2 Results and discussion

In this system, however, the concentration of the dissolved ozone varied considerably with different rates of self-decomposition, and the self-decomposition rate was directly affected by the water's characteristics. These characteristics were mainly controlled by some key factors such as pH, ionic strength, initial hazardous substances, ozone concentration, temperature, and gaseous flow rate etc. (Sotelo *et al.*, 1981; Domingncz *et al.*, 1989, Yocum *et al.*, 1978; Wu and Masten, 2001).

2.1 Key impact factors for ozonation of DBP

2.1.1 Initial DBP and ozone concentration (batch experiments)

In the experiment, 100 μ g/L DBP was ozonated in water buffered at pH 6.95 (Fig.2). High removal efficiency of DBP ozonation could be obtained when small amount of ozone was dosed. About 60% DBP was removed after being ozonated for 20 min at 0.53 mg/L ozone dosage. Higher degradation performance was achieved with the increase of the initial ozone dosage. When 2.0 mg/L ozone was added, 90% DBP was degraded within 5 min.

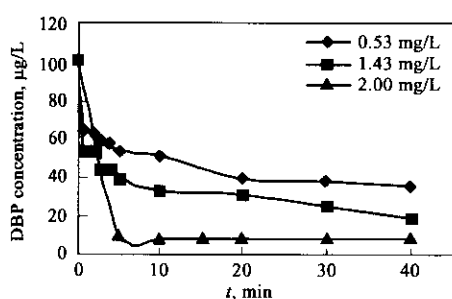


Fig.2 DBP ozonation at different initial ozone dosage
DBP concentration 100 μ g/L; *T*: 20°C; pH 6.95; 0.05 mol/L phosphate buffered

Fig.3 shows the ozonation results with different initial concentrations of DBP at ozone dosage of 2.0 mg/L. The results indicated that the higher DBP concentration resulted in lower DBP removal

efficiency. Approximately 80% of 10 μ g/L DBP was removed when the solution was not buffered, in contrast, about 40% removal rate was obtained for 800 μ g/L DBP with the same dosage of ozone.

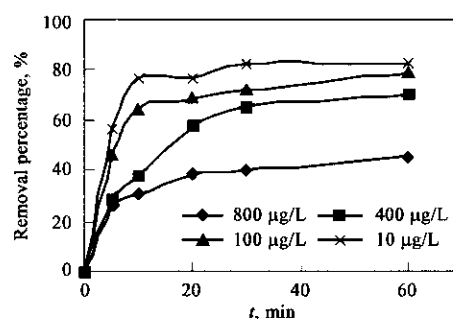


Fig.3 DBP ozonation at different initial DBP concentrations
Ozone dosage: 2.0 mg/L; *T*: 20°C; distilled water: no buffered

2.1.2 pH variation

Fig.4 shows that DBP was more effectively oxidized as pH increased from 4.30 to 9.16. Since the oxidation potential of hydroxyl radicals is much higher than that of molecular ozone, radical oxidation is faster than direct ozonation. At a higher pH, HO_2^- ion was generated from the reaction between O_3 and OH^- , which enhanced the production of $\cdot\text{OH}$, and $\cdot\text{OH}$ would be more active since it has a higher oxidation potential as 2.80 (Gunten, 2003). As a result, more DBP was removed.

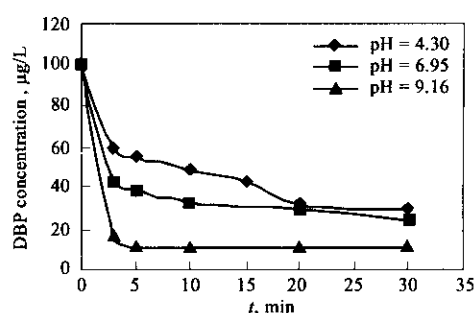


Fig.4 Ozonation at different pH
Ozone dosage: 2.0 mg/L; *T*: 20°C; 0.05 mol/L phosphate buffered

2.1.3 Temperature change

Fig.5 shows the DBP ozonation results at 20°C and 30°C respectively. An apparent higher degradation efficiency was obtained with a higher temperature. Increased temperature was expected to accelerate self-decomposition of the dissolved ozone in water to enhance $\cdot\text{OH}$ production. As a result, the removal rate of DBP would be increased. Furthermore, mass transfer coefficient of ozone was also increased (Wu and Masten, 2001), which resulted in a higher utilization of ozone in the oxidation reaction with DBP. Therefore, raising temperature should be a favorite factor in DBP ozonation.

2.1.4 Influence of ionic strength

The influence of ionic strength (*I*) on DBP

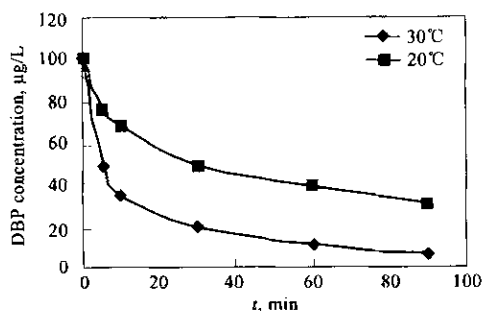


Fig. 5 DBP ozonation at different temperatures
Ozone dosage: 2.0 mg/L; distilled water: no buffered

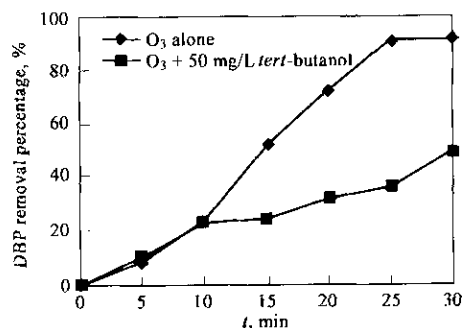


Fig. 7 Effect of *tert*-butanol on the ozonation of DBP
Ozone applied: 1.17 mg/(L·min); initial DBP: 6.0 mg/L; T: 20°C; pH: 7.0; 1 mmol/L phosphate buffered

ozonation was tested in the water buffered with phosphate and di-distilled water. As shown in Fig. 6, the ionic strength did not affect the degradation rate of DBP largely, but it significantly affected the production of intermediate product during the reactions as the chromatographic peak area of product decreased with an increase in ionic strength. It is suggested that ionic strength mainly affected the mass-transfer coefficient of ozone in water (Wu and Masten, 2001). Cogo *et al.* (1999) also verified that with an increase in ionic strength, the size of the bubbles emitted from the ozone diffuser decreased significantly, meanwhile the interfacial area between the gas and liquid increased consequently. Therefore, the oxidation performance was enhanced with an increase of ionic strength.

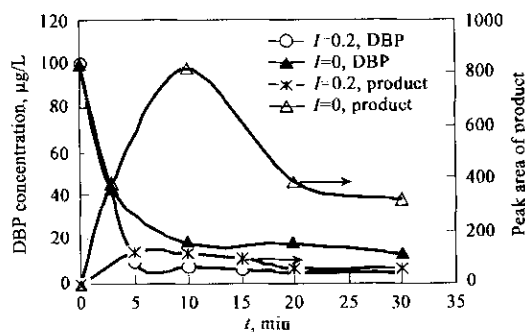


Fig. 6 Effect of ion strength on DBP degradation
Ozone dosage: 3.0 mg/L; T: 20°C; pH: 6.950; 0.05 mol/L phosphate buffered

2.2 Activity of ·OH in ozonation of DBP

2.2.1 Effect of *tert*-butanol

Tert-butanol was a well known strong ·OH scavenger. In this study, *tert*-butanol was added in the DBP ozonation at neutral pH level to detect the generation and effect of ·OH indirectly. Fig. 7 shows the ozonation results of DBP with and without *tert*-butanol added. As a result, the reaction was largely retarded by *tert*-butanol (50 mg/L). The existence of *tert*-butanol in water confirmed the kinetics of the hydroxide-initiated decomposition of O₃ in the ozone decomposition cycle. In this cycle, ·OH was produced continuously from the decomposition of ozone. But the cyclic effect was mostly

eliminated by the addition of *tert*-butanol as a chain inhibiting ·OH scavenger. Therefore, the reaction between O₃ and OH⁻ (O₃ + OH⁻ initiation step), and O₃ and HO₂⁻ (O₃ + HO₂⁻) became the reaction controlling steps. In addition, direct ozonation partly contributed to the degradation of DBP in the process with *tert*-butanol existed.

2.2.2 Effect of humic substances (HS)

Humic substances (HS) exist widely in the natural water sources, ranging from several mg/L to several tens of mg/L (Ma *et al.*, 1999). HS influences the ozonation process principally through direct reactions with molecular O₃ and indirect reactions with ·OH. HS can act as radical initiators, promoters, and scavengers (Stachelin and Hoigne, 1985). In addition, it consumes ozone easily by its direct reaction.

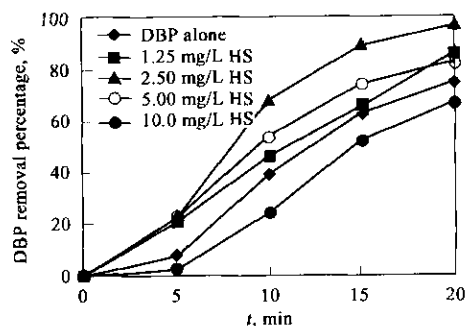


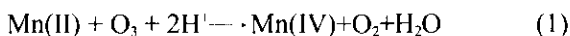
Fig. 8 Effect of different HS dosages on DBP ozonation
Ozone applied: 1.17 mg/(L·min); initial DBP: 6.0 mg/L; T: 20°C; pH: 7.0; 1 mmol/L phosphate buffered

A comparative study of the effectiveness of DBP ozonation was performed by two processes. One process was using ozone alone, and the other was the ozonation in the presence of different concentrations of HS. The results in Fig. 8 show that significantly higher ozonation efficiencies of DBP were obtained in the presence of HS (less than 10 mg/L as DOC). The optimal concentration of HS was found to be 2.5 mg/L. More DBP was oxidized probably through a mechanism involving the formation of radicals initiated by humic substances. In this case, the

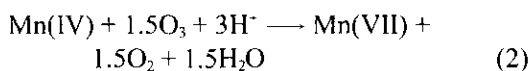
promotion effect played the dominant role in $\cdot\text{OH}$ formation. However, the ozonation rate decreased dramatically when the concentration of HS reached 10 mg/L as DOC. It was believed that not only do the radical scavenging effect of humic substances exceeds the initiation/promotion of radicals, but also more O_3 was consumed by HS through the direct reaction between HS and O_3 .

2.3 Catalysed ozonation by Mn(II) and ferrous ion

Some metal ions could accelerate the ozonation of organic substances (Gracia *et al.*, 1996). Thus, the ozonations of DBP in the presence of Mn(II) (MnSO_4) and ferrous ion (FeSO_4) were investigated. Fig.9 shows various degradation rates of DBP at different concentrations of Mn(II). As a matter of fact, the ozonation of DBP could be enhanced by low concentration of Mn(II) (< 1.0 mg/L). However, higher concentration of Mn(II) (1.0 mg/L) would prevent the ozonation. The results could be qualitatively explained by the proposed mechanism involved in the Mn(II) catalysed ozonation of organics (Rivas *et al.*, 2001). The initiating step would be the formation of Mn(IV) :



And the formation of hydrated manganese dioxide caused the generation of active sites on its surface. Nonetheless side-reactions not contributing to DBP removal would play a predominant role as the Mn(II) concentration increases due to the fact that oxidation of Mn (IV) to Mn (VII) would consume a large quantity of ozone, as shown by the equation:



Although MnO_4^- may be used as an additional oxidant for reduction of the organic and inorganic substances in water treatment (Doré, 1989), it results in completely ineffective DBP ozonation. Therefore, the excess of Mn(II) would in theory compete for the active sites which could lead to a lower DBP degradation rate (Rivas *et al.*, 2001).

For ferrous ion catalyzed ozonation (Fig.10), the

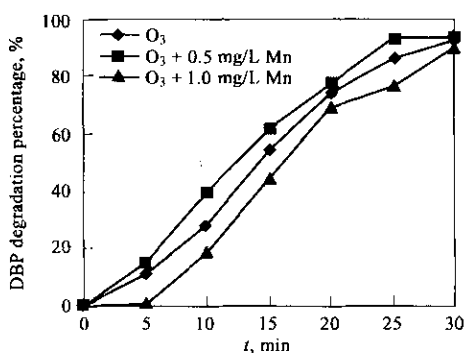


Fig.9 DBP ozonation with Mn(II) existed
Ozone applied: 1.17 mg/(L·min); initial DBP: 6.0 mg/L; T: 20°C;
pH: 7.0; 1 mmol/L phosphate buffered

addition of 0.2 mg/L ferrous ion could lead to a slight improvement on the DBP degradation. But the further increase of the ferrous ion concentration was redundant. This suggested that the ferrous ion at a proper concentration in the water could catalyse the ozonation of DBP. The mechanism of Fe(II) oxidation by ozone has been proposed to proceed either by generation of the hydroxyl radical (Equations (3) and (4)) or by the formation of the ferryl ion according to Equation (5). The catalytic system involves direct reaction of Fe^{2+} and ozone to give the intermediate $(\text{FeO})^{2+}$, species that evolves to $\cdot\text{OH}$ (Equation (6)). Regardless the mechanism that initiates the ozone decomposition, both the free hydroxyl radical and/or the ferryl ion are highly reactive species that can effectively oxidize organic compounds presented in the reaction media. Thus, as shown in Fig.10, a small amount of Fe(II) (0.2 mg/L) enhanced the ozonation of DBP. However, when the concentration of Fe(II) was 1.0 mg/L and 2.0 mg/L, the catalysed effect were nearly the same as that with 0.2 mg/L Fe(II) existed. This is likely that scavenging reactions (Equations (7) and (8)) became dominant, and hindered the positive influence of this ion on the ozonation. Hydroxyl radicals which contribute to the main removal of DBP reacted with excess Fe(II) and a mechanism of competition between DBP and Fe(II) was presented. Besides, $(\text{FeO})^{2+}$, an active species, also reacts with the superfluous Fe(II), leading to the smaller $\cdot\text{OH}$ production.

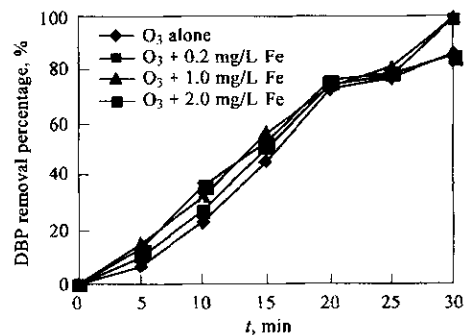


Fig.10 DBP ozonation with ferrous ion existed
Ozone applied: 1.17 mg/(L·min); initial DBP: 6.0 mg/L; T: 20°C;
pH: 7.0; 1 mmol/L phosphate buffered

The hydroxyl radical catalysed mechanism above could also be verified by the addition of *tert*-butanol. Fig.11 shows the ozonation results of DBP in a 50 mg/L *tert*-butanol contained water with or without ferrous ion. The results proved that DBP ozonation was largely blocked with *tert*-butanol added. However, higher degradation rate of DBP was achieved by adding 0.2 mg/L ferrous ion comparing with the uncatalysed process.



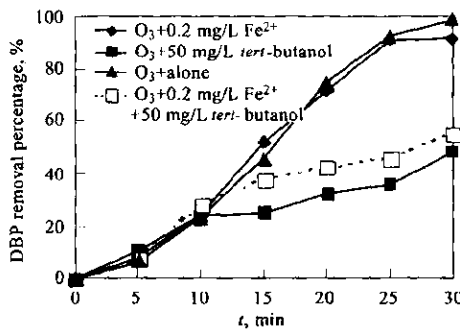
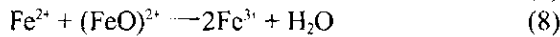
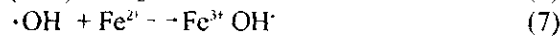
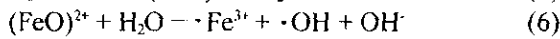
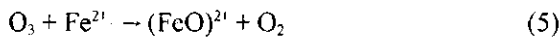


Fig.11 Ozonation of DBP with *tert*-butanol existed
Ozone applied: 1.17 mg/(L·min); initial DBP: 6.0 mg/L; T: 20°C;
pH: 7.0; 1 mmol/L phosphate buffered



2.4 Ozonation kinetics

The kinetic assessment was carried out as follows. Ozonations of DBP at different initial dosages of DBP and ozone were thoroughly investigated. The results are illustrated in Fig. 2 and Fig.3 respectively. The basic kinetics of DBP ozonation was assumed as Eq.(9).

$$r = -dp/dt = kp^mC^n \quad (9)$$

where *r* is the reaction rate of ozonation, *k* is the reaction rate constant, *p* is the DBP concentration, *C* is the ozone concentration in aqueous phase, and finally *m* and *n* are the reaction orders of DBP ozonation.

The initial concentration of DBP, O₃ dosage, and the reaction rate were presumed as *p*₀, *C*₀ and *dp*₀/*dt* respectively, and Eq.(9) can be presented by Eq.(10).

$$-dp_0/dt = kp_0^mC_0^n \quad (10)$$

Polynomial regression is done to the curves of Fig.2. The corresponding equations were obtained. The initial reaction rate of DBP and O₃ is calculated by the derivative equations of the curves at *t* = 0 (Eq.

(11)).

$$\lg(-dp_0/dt) = \lg k + m \lg p_0 + n \lg C_0 \quad (11)$$

If the dosages of O₃ are invariable, Eq.(9) can be expressed as Eq.(12)

$$\lg(-dp_0/dt) = k_1 + m \lg p_0 \quad (12)$$

where $k_1 = \lg k + n \lg C_0$

Then *m* and *k*₁ can be solved from the figure constructed with lg(-*dp*₀/*dt*) and lg*p*₀ as Y-coordinate and X-coordinate respectively: *m* = 0.8692, *k*₁ = -1.247.

With the same method as above, Eq.(11) can be presented as Eq.(13) when the concentration of DBP maintained at 100 μg/L:

$$\lg(-dp_0/dt) = k_2 + n \lg C_0 \quad (13)$$

where $k_2 = \lg k + m \lg p_0$

*k*₂ and *n* are deduced as: *n* = 0.442, *k*₂ = 0.554.

$$k_1 + k_2 = 2 \lg k + m \lg C_0 + n \lg C_0 \quad (14)$$

k = 22.32 μg/(L·min) from Eq. (14).

In conclusion, the kinetic equation of DBP ozonation can be described as follows:

$$r = -dp/dt = 22.32p^{0.8692} C^{0.442} \quad (15)$$

2.5 Degraded intermediate products in the ozonation

Several degradation intermediate products were produced in the ozonation of DBP (Fig. 12). The gas chromatography retention time of the products were 16.086 min (product 1), 16.699 min (product 2), and 17.576 min (product 3), respectively. They accumulated quickly to a maximum amount of quantity and then descended to the level that could not be detected. After 2.5 h ozonation, DBP and intermediate products were degraded below the detection limit. Therefore, DBP could be degraded almost completely by ozonation.

There are some differences between the degradation intermediate products produced during the DBP ozonation reactions at different temperatures,

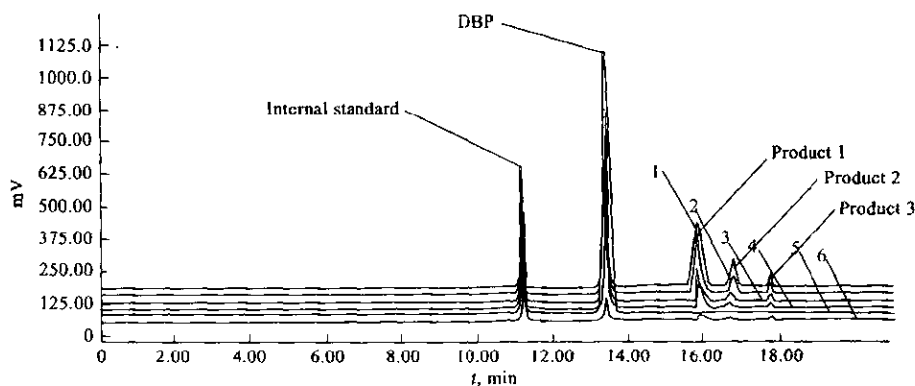


Fig.12 Intermediate products created in the DBP ozonation
Ozone dosage: 6.0 mg/L; DBP concentration: 0.8 mg/L; T: 20°C; di-distilled water: no buffered;
DBP ozonation time: 1: 1.5 h, 2: 2.0 h, 3: 1.0 h, 4: 0.5 h, 5: 0 h, 6: 2.5 h

ionic strengths, and pH (Table 1). Higher temperature, pH, and greater ionic strength would lead to lesser

by-products due to the higher ozonation efficiency.

Table 1 Degradation intermediate products (peak area) created in the DBP ozonation reactions at different temperatures, ion strengths and pH

	30°C (unbuffered)			20°C (unbuffered)			20°C (pH=9.50)			20°C (pH=4.30)			20°C (pH=6.95)		
	P1	P2	P3	P1	P2	P3	P1	P2	P3	P1	P2	P3	P1	P2	P3
5 min	490.1	211.9	41.8	346.3	157.7	50.0	-	-	-	380.5	185.4	71.3	120.7	70.5	-
10 min	593.5	170.8	33.6	453.9	188.6	57.0	-	-	-	520.4	243.7	80.7	117.5	121.3	-
30 min	254.0	-	-	537.7	218.5	67.7	-	-	-	645.3	270.3	94.6	98.2	143.5	-
60 min	22.2	-	-	478.4	157.2	42.0	-	-	-	530.0	243.5	79.2	59.3	105.4	-
90 min	-	-	-	415.0	143.5	23.2	-	-	-	493.4	201.3	51.5	57.2	45.6	-

Notes: P1. product 1; P2. product 2; P3. product 3

3 Conclusions

DBP reacts with ozone following two mechanisms: direct reaction with the molecular ozone and indirect reaction with the radical species formed when ozone decomposes in the water. At higher pH and ionic strength, the main reacting route followed the radical way and the removal rate of DBP could be above 90%, while DBP reacted with ozone through selective direct reaction at lower pH. Meantime HS and *tert*-butanol affected the ozonation through the radical path way.

When the applied ozone dose was increased, DBP removal efficiency increased as well, but its removal percentage decreased with the increase of the initial DBP concentration. Higher temperature could enhance the reaction due to the production of small amounts of $\cdot\text{OH}$ from further decomposition of ozone.

Hydroxyl radicals played a significant role in the DBP ozonation. *Tert*-butanol retarded the ozonation dramatically for its $\cdot\text{OH}$ scavenging effect. Low concentration of humic substances (< 10.0 mg/L) in the process of DBP ozonation enhanced the removal efficiency of DBP for its radical promoting effect, but excess HS would consume some amount of ozone, which would cause a decline in ozonation efficiency of DBP.

More DBP would be degraded through "active sites" catalysed ozonation with the existence of low concentrations of Mn(II) (0.2 mg/L, 0.5 mg/L), but a higher concentration of Mn(II) (1.0 mg/L) would retard the reaction. However, the difference of the ferrous ion concentration showed no apparent effect on DBP removal.

The types and amount of the intermediate products created in the ozonation of DBP showed great decrease at higher initial ozone dosage, pH and greater ionic strength, which meant a more complete ozonation. On the contrary, an inverse trend was displayed for higher initial DBP concentration. From the kinetic assessment, a kinetics equation be obtained.

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