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Efficacy of the Toxicity Control during the Degradation of TBBPA by Ozonation

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Abstract: This study has focused on the evaluation of the biotoxicity controlling effects during the TBBPA degradation by ozonation, including the acute, chronic and genetic toxicity under different [O_3]/[TBBPA] (1:1–11:1), initial solution pH (5.0–9.0) and temperatures (10–40 °C). In addition, the comprehensive biotoxicity of the treated water sample was evaluated by the method of potential ecotoxic effects probe (PEEP). The results showed that TBBPA could be completely degraded with an initial solution pH of 7.0, temperature of 25 °C and an [O_3]/[TBBPA] ratio of 9:1. The chronic toxicity of the untreated sample was as high as 41.7 TU, which represented the main toxicity of TBBPA itself. In contrast, the TBBPA showed a much lower acute and genetic toxicity in this study. During the process of TBBPA degradation, the ozonation could effectively control the toxicity of wastewater and showed strong adaptability. When the ratio of [O_3]/[TBBPA] was 11:1, the acute and chronic toxicity were reduced to 0.02 TU and 0.76 TU, respectively, with the controlling rates being as high as 96% and 98.2% and meeting the emission standards. The mutagenicity ratio of the water sample was less than 2.0, indicating no genotoxicity risk. The evaluation of the comprehensive biological toxicity showed that ozonation could control the PEEP value below 2.0 in ranges of low [O_3]/[TBBPA] ratio (3:1), wide pH (5–9) and temperatures (10–40 °C).

Keywords: ozonation; tetrabromobisphenol A; acute toxicity; chronic toxicity; comprehensive biological toxicity

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1. Introduction

Tetrabromobisphenol A (TBBPA) is one of the brominated flame retardants with the largest production and usage in the world. It is widely used as an additive in the production processes of various electronics, chemicals, plastics and other industries [1]. Thus, it often exists in the corresponding wastewater, and might enter the receiving waters along with the drainage, if the drainage is not being effectively treated [2]. The studies have shown that TBBPA manifests a range of acute and chronic toxicity, which poses a great threat to the aquatic organisms and the ecological balance of the receiving waters [3]. Through bioaccumulation, TBBPA could cause disturbance and damage to the kidneys, the nervous system, the endocrine system of animals and even threaten human health [4]. In addition, due to the refractory biodegradability of TBBPA, the traditional biodegradation technology cannot effectively remove it from wastewater. Therefore, it is necessary to develop an efficient technology for TBBPA degradation and the biological toxicity control.

In recent years, advanced oxidation technologies have been widely used for TBBPA degradation [5]. However, most of the studies have focused on the removal efficiency of TBBPA itself. There were still relatively few toxicity evaluations of the water samples in the degrading process. Only the single acute toxicity detection method was frequently applied and the analysis of chronic toxicity and genetic toxicity was lacking, rendering it difficult

to comprehensively evaluate the toxicity controlling effects of the technologies [6]. The PEEP method (potential ecotoxic effects probe), proposed by Costan [7], was considered as a comprehensive toxicity evaluation index that could integrate the results of various biological toxicity tests (including acute, chronic, genetic, etc.) and analyze the potential ecotoxicity effects of the treated wastewater. Thus, the PEEP method was widely applied in the United States, Canada, France and other countries to evaluate the toxicity of different water qualities, such as urban wastewater and industrial wastewater [8–10].

Among the technologies for TBBPA degradation, ozonation has the advantages of an obvious treatment effect, easy engineering implementation, easy popularization and application [11]. Thus, it has been widely used in wastewater treatment [12]. In this study, the performance of ozonation on TBBPA degradation was systematically investigated under different [O_3]/[TBBPA] (1:1–11:1) conditions, initial solution pH (5.0–9.0) and temperatures (10–40°C). The dominant active species was estimated and the reaction kinetics were evaluated. Meanwhile, this research focused on the evaluation of various toxicities of water samples in the process of TBBPA degradation by ozonation, including acute toxicity, chronic toxicity and genetic toxicity. In addition, the comprehensive biological toxicity was analyzed by the potential ecotoxicity effect index, PEEP, so as to explore the controlling effect of biological toxicity by ozonation during TBBPA degradation.

2. Materials and Methods

2.1. Chemicals, Reagents and Instruments

The high-grade pure chemicals used in this study include tetrabromobisphenol A (TBBPA), yeast extract, tryptone, histidine, biotin, agar powder, etc., which were all purchased from Aladdin Reagent Co., Ltd. (Los Angeles, CA, USA). The analytical reagents used in the tests were hydroxylamine hydrochloride, citric acid, glucose, etc., produced by Sinopharm Collective Chemical Reagent Co., Ltd. (Shanghai, China). The main biological reagents were the freeze-dried luminescent bacteria *Vibro fischeri* (SDIX, Newark, DE, USA) and salmonella typhimurium (TA100 strain, Moltox, Boone, NC, USA), which were, respectively, used for the acute and genetic toxicity test. The required large fleas used in the chronic toxicity evaluation were introduced from the South China Institute of Environmental Sciences and domesticated for a long-term period in our laboratory.

The main instruments used during the experiments included the Acquity HClass ultra high performance liquid chromatography (UPLC, Waters, Milford, MA, USA), the DeltaTox toxicity detector (SDIX, USA), the ozone generator (Guolin, Qingdao, China), the gas chromatography–mass spectrometry (Agilent 7890A/GC-5975C MS), the fluorescence microscope (Olympus, Tokyo, Japan), the ultra-pure water purification system (Milli-Q, Rockville, MA, USA), etc.

2.2. Experimental Methods

Before the experiments, a 0.28 μmol/L TBBPA solution was prepared by fully dissolving the TBBPA solid powder in ultra-pure water. The experiments were carried out in an ozone reaction column with an inner diameter of 25 cm. After being prepared by the ozone generator of the oxygen source, the ozone entered the reaction column containing TBBPA solution under the control of the gas flowmeter to participate in the reaction. After the reaction, the tail gas was absorbed by the potassium iodide solution, and the solution in the reaction column was circulated externally by the peristaltic pump. At the certain intervals, the 50 mL water sample was taken out and the reaction was terminated immediately by dosing 20 μL 0.1 mol/L hydroxylamine hydrochloride. After centrifugation, the supernatant of the water sample was taken for the subsequent related detection. All of the experiments were carried out in duplicate.

2.3. Analytical Methods

The residual concentration of TBBPA was detected and analyzed by a Waters Acquity H-class UPLC, which was equipped with a TUV detector and a Waters BEH C18 column

(1.7 × 100 mm, 3.5 μm). The UV wavelength and the column temperature were, respectively, set at 210 nm and 40 °C. The acetonitrile/water mixture (70/30, *v*/*v*) was chosen as the isocratic mobile phase, with the flow rate at 0.5 mL/min and injection volume of 1 mL, respectively.

In this study, the acute, chronic and genetic toxicity of the water samples were analyzed. Among of them, the acute toxicity test was detected by a SDIX DeltaTox toxicity detector. The bioluminescence intensity (X) was measured and the half-effect concentrations (EC_{50}) of the water samples to the luminescent bacteria were calculated. The chronic toxicity was referred to the OECD 21 d chronic toxicity test standard method of *Daphnia magna* [13], during which the maximum non-effect concentration (NOEC) was obtained. For the genotoxicity, the Ames test of the plate incorporation method was applied, to obtain the average revertant colony number of water sample and the control group [14]. Then, the mutagenic ratio (the MR value) was calculated by comparing the two above average numbers. The specific testing processes are illustrated in the Text S1 (Supplementary Materials).

The PEEP method was used for the evaluation of the comprehensive biological toxicity in this study. The specific calculation method was to convert the different types of toxicity test results into the toxic equivalents, which were proposed by the United States Environmental Protection Agency (USEPA) and expressed in toxicity units (the TU value, TU = 100%/EC_{50} or TU = 100%/NOEC). According to the American Wastewater Discharge Toxicity standards, the acute and chronic toxicity are required to be less than 0.3 and 1.0 TU, respectively. In addition, the tested water sample is mutagenic positive when the MR value ≥2, that is, it has mutagenicity.

Then, the above acute, chronic and genetic toxicity data were integrated to calculate the PEEP value of the water samples. The calculation Formula (1) is as follows:

$$\mathrm{PEEP} = \lg_{10}[1 + \mathrm{n}(\frac{\sum_{i=1}^{N} \mathrm{TU_i}}{\mathrm{N}})\mathrm{Q}] \quad (1)$$

where TU_i is the obtained toxic equivalent; N is the number of biological toxicity indices involved in the evaluation; n is the number of positive results of each bioassay; Q is the calculated discharge water volume (m^3/h) and 150 t/d was chosen in this study. The *PEEP* classification standard for wastewater risk assessment is [13]: when PEEP ≤ 1.99, it is non-toxic; when 2 ≤ PEEP ≤ 2.99, it is slightly toxic; when 3 ≤ PEEP ≤ 3.99, it is neutrally toxic; when 4 ≤ PEEP ≤ 4.99, it is highly toxic; when PEEP ≥ 5, it is severely toxic.

3. Results and Discussion

3.1. Performance of Ozonation and the Estimation of the Reactive Species

The performance of ozonation on TBBPA degradation under different [O_3]/[TBBPA] (1:1–11:1) was investigated and the results are shown in Figure 1a. It can be seen that ozonation could effectively degrade TBBPA in water. When the value of [O_3]/[TBBPA] gradually increased from 1:1 to 9:1, the degradation rate of TBBPA significantly increased from 29.74% to 100% after a reaction time of 60 min. When the value of [O_3]/[TBBPA] further increased to 11:1, the time required for the complete TBBPA removal was decreased to 20 min. That was because, with the increase in [O_3]/[TBBPA], the total amount of active species (including ozone molecule and generated •OH) in the solution increased, which enhanced the effective contacting frequencies between TBBPA with the oxidants and promoted the TBBPA degradation efficiency accordingly.

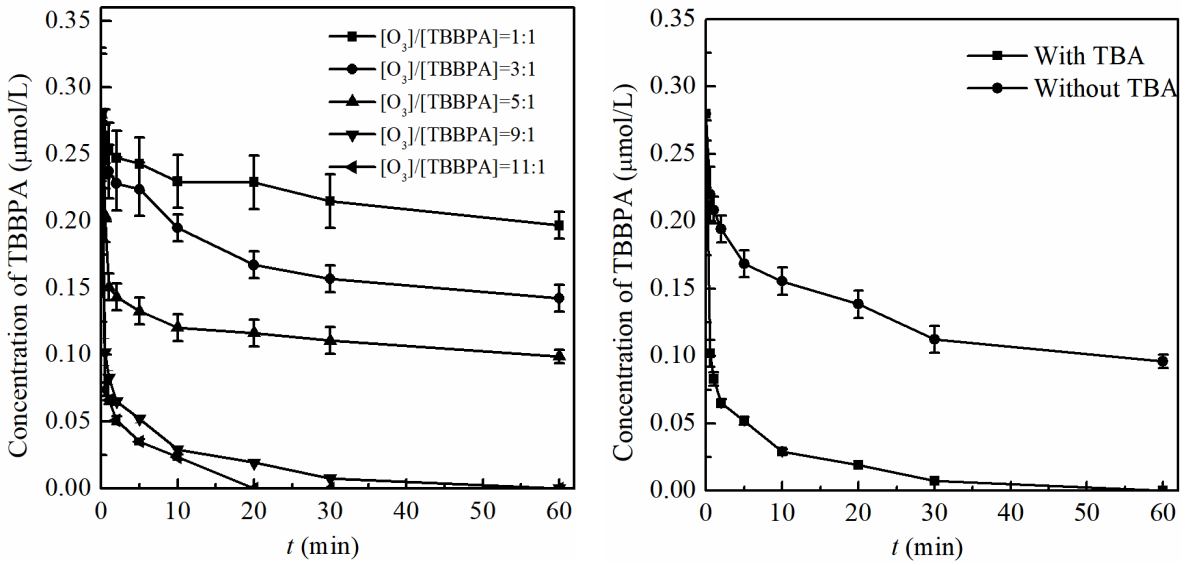


Figure 1. Performance of ozonation on TBBPA degradation under different (**a**) [O_3]/[TBBPA] (1:1–11:1) and the estimation of the dominant reactive species (**b**). (Experimental conditions: TBBPA concentration 0.28 μmol/L; [O_3]/[TBBPA] = 1:1, 3:1, 5:1, 9:1,11:1 for (**a**); 9:1 for (**b**); initial solution pH = 7.0; temperature = 25 °C).

According to our previous research [15], nine organic products were identified by GC/MS-MS. In addition, the possible mechanism of the TBBPA degradation by ozonation was speculated on and verified by the quantum chemical calculations, mainly including three reaction pathways: the addition and hydrogen extraction; the stepwise oxidative debromination; and the deprotonation, which were consistent with other reported studies [16,17]. With the increase in the ozone dosage and contacting time, the intermediates could be further effectively degraded or even mineralized. During the oxidation process, the ozone and generated •OH both played an important role in the pollutants' degradation [18].

As the reaction rate constant between TBA with •OH was as high as 7.6×10^8 $M^{-1}s^{-1}$, it could be considered as an effective quencher for •OH [19]. In order to identify the dominant active species for TBBPA degradation by the ozonation method, the radical quenching experiments were carried out by dosing the excessive quenching agent TBA (2.8 mmol/L), with the molar ratio of TBA to TBBPA at 10,000:1. The corresponding TBBPA degradation efficiency was analyzed and the results are shown in Figure 1b. The value of [O_3]/[TBBPA] was selected at 9:1, under which condition a 100% TBBPA removal was obtained after 60 min without the dosage of TBA. However, as the generated •OH in the reaction solution could be completely quenched by the excessive TBA, TBBPA could only be degraded through the direct oxidizing pathway by the ozone. In the presence of TBA, the residual concentration decreased from 0.28 to 0.10 μmol/L as the contacting time increasing from 0 to 60 min, a 65.65% TBBPA removal being obtained. Thus, the results indicated that the ozone might play a predominant role in TBBPA degradation in this study.

3.2. Effects of pH and Temperature on TBBPA Degradation and Reaction Kinetics

In this study, the effects of the initial solution pH (5.0–9.0) and temperatures (10–40 °C) on the TBBPA degradation efficiency and the reaction kinetics by ozonation were systematically analyzed and evaluated, as illustrated in Figure 2a–d. In order to analyze the influences of the initial solution pH and temperature on the TBBPA degradation by ozonation, the value of [O_3]/[TBBPA] 5:1 was chosen in the following degradation experiments, under which condition, a 64.73% removal of TBBPA was obtained.

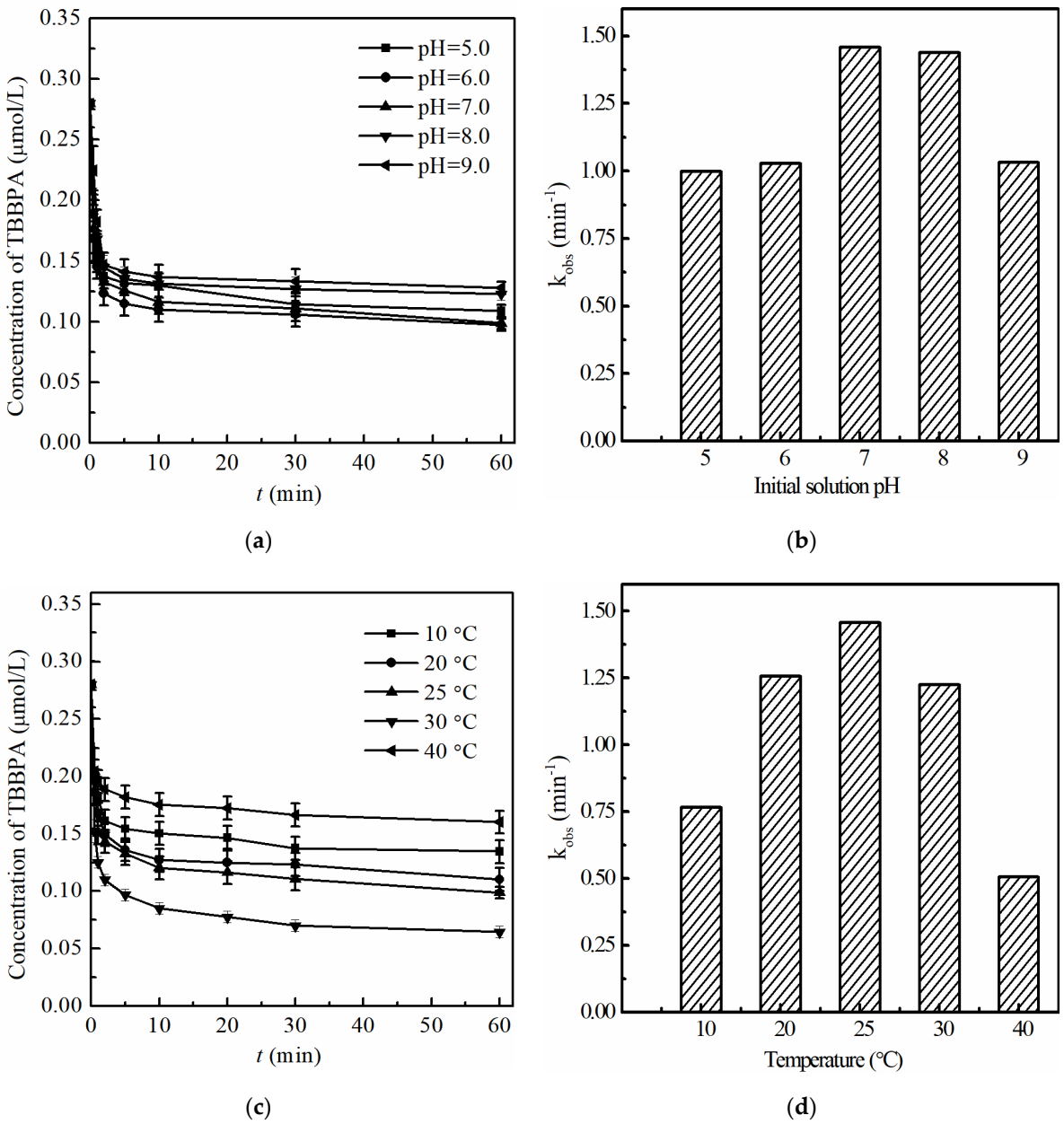


Figure 2. Effects of initial solution pH (5.0–9.0) (**a**,**b**) and temperatures (10–40 °C) (**c**,**d**) on TBBPA degradation. (Experimental conditions: TBBPA concentration 0.28 μmol/L; $[O_3]/[TBBPA]$ = 5:1; initial solution pH = 5.0, 6.0, 7.0, 8.0, 9.0 for (**a**,**b**); 7.0 for (**c**,**d**); temperature = 10, 20, 25, 30, 40 °C for (**c**,**d**); 25 °C for (**a**,**b**)).

As illustrated in Figure 2a, when the initial solution pH was 5.0, 6.0, 7.0, 8.0 and 9.0, the degradation rate of TBBPA was, respectively, 61.17%, 65.17%, 64.73%, 56.14% and 54.25%. In general, the degradation efficiency of TBBPA by ozonation under acidic conditions was little better than that under the alkaline one. The self-decomposition of the ozone was promoted with the increase in pH, which could result in the greater production of •OH and enhance the TBBPA degradation [20]. However, according to the molecular structure of TBBPA, it is a diprotic acid (TBBPA = $TBBPA^{-} + H^{+}$, $pK_{a,\ TBBPA}$ = 7.5; $TBBPA^{-} = TBBPA^{2-} + H^{+}$, $pK_{a,\ TBBPA^{-}}$ = 8.5). In the higher pH solution, TBBPA mainly exists in the form of salts ($TBBPA^{-}$ and $TBBPA^{2-}$) with strong electronegativity, which is not conducive to the degradation of TBBPA by ozonation [21]. In addition, as the ozone was the dominant active species for the TBBPA degradation. The amount and the redox potential of the ozone

involved in the TBBPA degradation both decreased with the increase in the solution pH, which also led to the decrease in the degradation efficiency of TBBPA.

It can also can be seen from Figure 2c that the degradation rate of TBBPA increased first and then decreased as the temperature of the reaction system increased from 10 to 40 °C. The better temperature range might be around 25–30 °C, indicating that ozonation needed a suitable reaction environment to achieve a better degradation effect, which was similar to other research results [20,21]. When the reaction system temperature was below 10 °C, the effective collision reactions between the oxidants and TBBPA were incomplete [22]. However, when the temperature was higher than 40 °C, the solubility of the ozone in the solution decreased, which was also unfavorable to the hydrolysis and oxidation reactions.

As shown in Figure 2a,c, the reactions of the TBBPA degradation underwent two stages under the different initial solution pH and temperatures, namely the initial rapid reaction stage and the stabilizing stage. A kinetic equation, which was between the first and second order reaction kinetics, was shown in Equation (2) to describe the two reaction stages. It could be further deformed, so as to obtain Equation (3):

$$\frac{[\mathrm{TBBPA}]_t}{[\mathrm{TBBPA}]_0} = 1 - \frac{t}{at + b} \quad (2)$$

$$\frac{t}{1 - \frac{[\mathrm{TBBPA}]_t}{[\mathrm{TBBPA}]_0}} = at + b \quad (3)$$

where t was the reaction time (min); $[\mathrm{TBBPA}]_t$ and $[\mathrm{TBBPA}]_0$ were, respectively, the concentration of TBBPA at t min and 0 min; 1/a was the theoretical maximum removal rate of TBBPA; 1/b was the apparent rate constant k_{obs} (min^{-1}). With $t/(1\text{-}[\mathrm{TBBPA}]_t/[\mathrm{TBBPA}]_0)$ as the *y* axis and t (0–60 min) as the *x* axis, the reaction kinetics of the TBBPA degradation under the different initial solution pH and temperatures were well fitted, as shown in Figure S1a,b (Supplementary Materials). It could be concluded that Equation (3) was well fitted for the tendencies of the TBBPA degradation ($R^2 \geq 0.998$ under different conditions), which was proved by other researchers [23].

Figure 2b–d illustrated the variations of the apparent rate constants k_{obs} under different initial solution pH and temperatures, whose trend was similar to that of the TBBPA degradation. With the increase of the initial solution pH from 5.0–7.0, the value of k_{obs} gradually increased from 1.00–1.46 min^{-1}. It was suggested the generation of •OH by the increasing pH played an important improving role on the degradation rate of TBBPA. As the initial solution pH further increased to 9.0, the degradation of the TBBPA was inhibited and the corresponding k_{obs} decreased to 1.03 min^{-1}. Similar to the initial solution pH, the results of the reaction kinetics also increased firstly and then decreased as temperature rose from 10–40 °C. The maximum rate constant k_{obs} was 1.46 min^{-1} with the temperature of 25 °C.

3.3. Acute Toxicity Evaluation

The acute toxicity of the water samples was evaluated during the TBBPA degradation by ozonation under the different $[O_3]/[\mathrm{TBBPA}]$ (1:1–11:1), initial solution pH (5.0–9.0) and temperatures (10–40 °C). The results are shown in Figure 3.

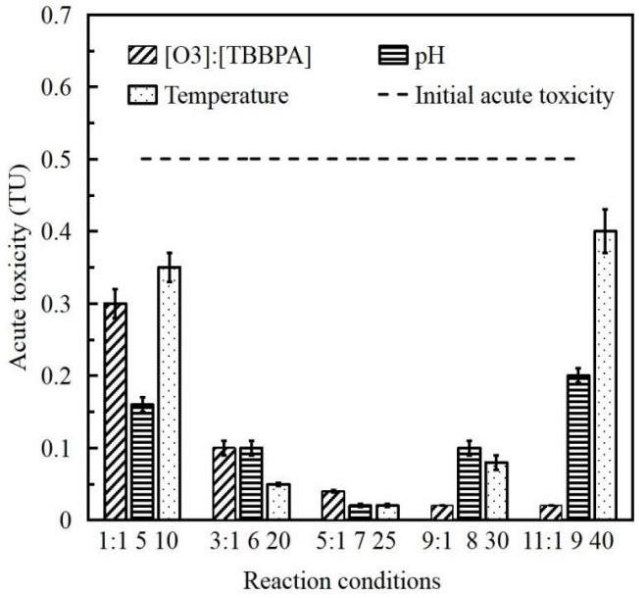


Figure 3. Variation and controlling effects of acute toxicity during TBBPA degradation by ozonation.

It can be seen from Figure 3 that before the reactions, the toxicity equivalent of the water sample was 0.5 TU, indicating the low acute toxicity of the TBBPA itself. In general, the acute toxicity could be effectively controlled with the increase in $[O_3]/[TBBPA]$. As the values of $[O_3]/[TBBPA]$ were 1:1, 3;1, 5:1, 9:1 and 11:1, the acute toxicities of the water samples, after reaction for 60 min, were 0.3, 0.1, 0.04, 0.02 and 0.02 TU, respectively, which were all below 0.3 TU and met the acute toxicity standard of the American Wastewater Discharge Toxicity standards. In order to investigate the controlling effect of the toxicity, the ratio of $[O_3]/[TBBPA]$ 9:1 was chosen for the subsequent toxicity tests.

Similar to the tendencies of the TBBPA degradation by ozonation, with the increase in the initial solution pH and temperature, the controlling effect of acute toxicity also increased at first and then decreased. The pH and temperature required for the best acute toxicity controlling effect were 7.0 and 25 °C, respectively. In addition, at the wide range of pH 5.0–9.0, all of the acute toxicity could be controlled under 0.3 TU, and met the emission standard. However, when the temperature was 10 and 40 °C, the acute toxicity was 0.35 and 0.40 TU, which might due to the incomplete removal of the TBBPA.

In general, the toxicities of the reaction solution were closely related to the produced intermediates [24]. During the TBBPA degradation by ozonation, some of the lower brominated intermediates with higher toxicity underwent the process of accumulation and further degradation, such as tribromobisphenol A, dibromophenols, tert-butyl benzene, etc. [25]. Thus, effectively controlling the impact of the solution toxicities might be achieved by increasing the ozone dosage and reaction time, which could fully degrade the TBBPA itself and its intermediates.

3.4. Chronic Toxicity Evaluation

Figure 4 illustrates the variation and controlling effects of the chronic toxicity during the TBBPA degradation by ozonation. It could be seen that TBBPA has a high chronic toxicity, with a toxic equivalent of up to 41.7 TU. However, the chronic toxicity of the water sample could also be significantly controlled with the increase in $[O_3]/[TBBPA]$. When the ratio of $[O_3]/[TBBPA]$ increased from 1:1 to 9:1, the chronic toxicity significantly decreased from 25.7 to 3.9 TU after the reaction, with the controlling rate correspondingly increasing from 38.37% to 90.65%. When the ratio of $[O_3]/[TBBPA]$ continuously increased to 11:1, the chronic toxicity equivalent decreased to 0.76 TU, which met the requirements of the wastewater discharge (below 1.0 TU) and a 98.18% controlling rate was obtained.

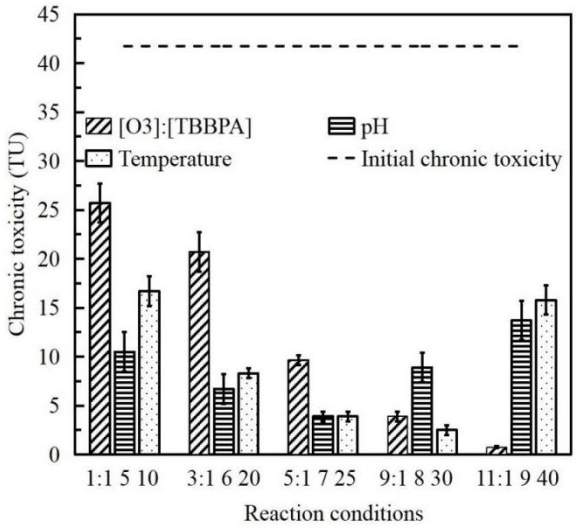


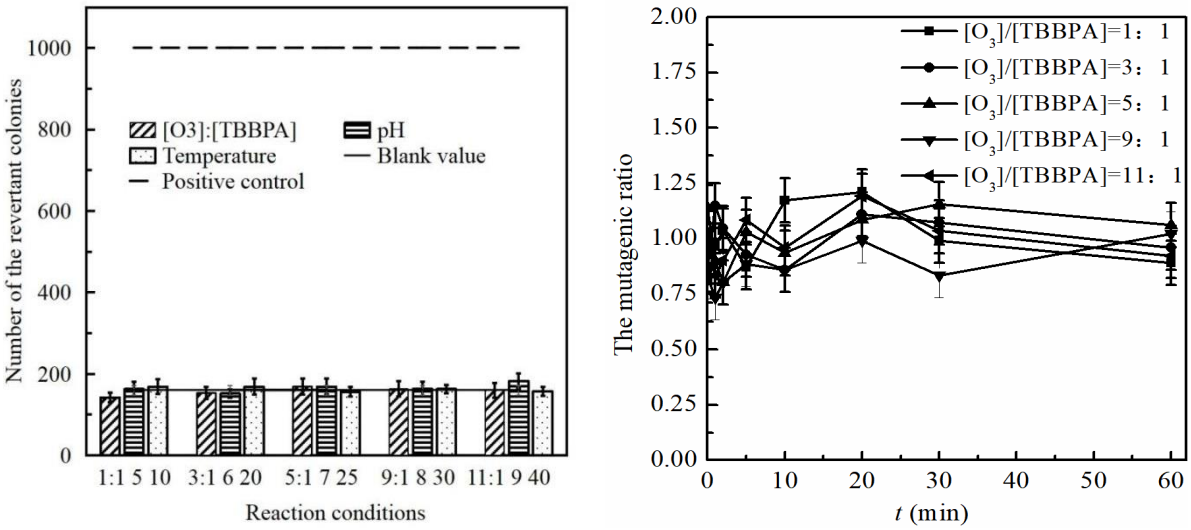
Figure 4. Variation and controlling effects of chronic toxicity during TBBPA degradation by ozonation.

In contrast, the controlling effect of the chronic toxicity by ozonation was slightly worse than that of acute toxicity. As the initial solution was at the range of pH 5.0–9.0, the chronic toxicity of water sample was controlled around 3.9–13.7 TU, which did not meet the discharge standard at all. In addition, only when the temperature was 30 °C could the chronic toxicity be reduced to 2.5 TU. This might be explained by the formation of more toxic intermediates. As the acute toxicity of TBBPA itself was low, it could be negligible compared with the chronic toxicity. The results of the previous research have shown that the LD_{50} (rat, oral dose) of the intermediates, such as the tribromobiphenol A, dibromophenols and tertbutyl benzene generated in the degradation of TBBPA by ozonation, are 2000, 282 and 2600 mg/kg, respectively, showing obvious characteristics of chronic toxicity [24]. These intermediates needed to be further degraded so as to completely control the chronic toxicity of the water samples, which can be achieved by increasing the $[O_3]$/[TBBPA] ratio to 11:1 and prolonging the ozone contact time.

3.5. Genotoxicity Evaluation

This study also evaluated the genotoxicity of water samples during the degradation of TBBPA by ozonation under different $[O_3]$/[TBBPA] (1:1–11:1) ratios, initial solution pH (5.0–9.0) and temperatures (10–40 °C). The number of the revertant colonies was recorded and the mutagenicity ratio (MR value) was calculated, which results were shown in Figure 5a,b.

As illustrated in Figure 5a, the average number of revertant colonies in the positive control group was 1000+. However, the revertant colonies' number of the TA100 strain in the test group was in the range of 142 ± 10–183 ± 15, which did not increase significantly as compared with that in the blank group (160 ± 12), and indicated the low genotoxic risk of the water samples. Taking a different $[O_3]$/[TBBPA] (1:1–11:1) as an example, the MR values of the water samples were further calculated in Figure 5b. The obtained MR values were in the range of 0.6–1.2, which were all less than 2.0 and indicated that the water samples did not have mutagenicity after being effectively treated by ozonation.



(**a**) (**b**)

Figure 5. Variation and controlling effect of the genotoxicity during TBBPA degradation by ozonation. (**a**) Numbers of revertant colonies in Ames tests; (**b**) Changes of the mutagenic ratio.

3.6. Comprehensive Biological Toxicity Assessment

Based on the evaluating results of acute, chronic and genetic toxicity, the PEEP values of water samples under different reaction conditions were further calculated, so as to analyze the comprehensive biological toxicity. The results are shown in Figure 6.

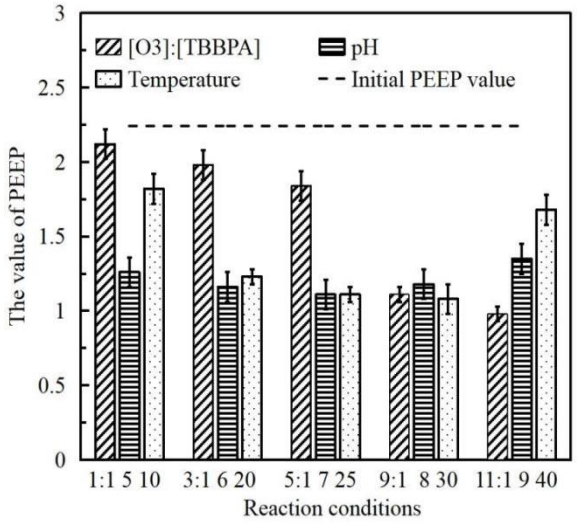


Figure 6. Variations and controlling effects of the comprehensive biological toxicity during TBBPA degradation by ozonation.

As calculated, the initial PEEP value of the raw water samples was 2.24, which indicating the micro-comprehensive toxicity of the TBBPA itself. When $[O_3]$/[TBBPA] increased from 1:1 to 3:1, the PEEP values of the water samples decreased from 2.12 to 1.98, revealing the effective controlling role of ozonation on the comprehensive toxicity. When the value of $[O_3]$/[TBBPA] further increased to 11:1, the PEEP value was as low as 0.98, with a controlling rate as high as 56.3% being obtained. In summary, the treated water samples could be non-toxically controlled with the increase in $[O_3]$/[TBBPA].

The PEEP values of the reaction system under the different initial solution pH and temperatures were calculated by choosing $[O_3]$/[TBBPA] as 9:1 (where the TBBPA was completely removed, the PEEP value was 1.11 and the treated water samples were nontoxic).

The results showed that the ozonation had a strong adaptability to the reaction conditions during the process of the TBBPA degradation. All of the PEEP values of the water samples could be effectively controlled below 2.0 at a wide range of initial solution pH (5–9) and temperatures (10–40 °C), reflecting no risk of the comprehensive biological toxicity.

4. Conclusions

The TBBPA degradation and toxicity control by ozonation was systematically investigated in this study, and the major conclusions are summarized as follows:

1. Ozonation could effectively degrade TBBPA in water. The TBBPA of 0.28 μmol/L could be completely removed with the $[O_3]$/[TBBPA] value of 9:1, the initial solution pH of 7.0 and the temperature of 25 °C;
2. TBBPA has low acute toxicity (TU is 0.5), high chronic toxicity (TU is 41.7) and a low genotoxicity risk. The ozonation could effectively control the biological toxicities of the water samples in the process of TBBPA degradation. In addition, the acute and chronic toxicity could be controlled faster and more significantly by ozonation with the increase in the ozone dosage and contacting time;
3. When the value of $[O_3]$/[TBBPA] was 11:1, the acute and chronic toxicity of the water samples after the reaction were 0.02 and 0.76 TU, respectively, with the toxicity controlling rates being correspondingly 96% and 98.2%, which all met the toxicity standards for wastewater discharge. Moreover, the MR values of the treated water samples ranged from 0.6 to 1.2 (<2), all of which showed no risk of genotoxicity;
4. The evaluation results of the comprehensive biological toxicity showed that the TBBPA itself was slightly toxic. The PEEP value was controlled at 1.98 under a low ozone concentration ($[O_3]$/[TBBPA] ratio was only 3:1), indicating its effective controlling effect of the toxicity. In addition, the ozonation could control the PEEP values of the water samples all below 2.0 and non-toxic in a wide range of pH (5–9) and temperature (10–40 °C), revealing its strong adaptability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14162543/s1, Figure S1: Reaction kinetics under different initial solution pH (5.0–9.0) (a) and temperatures (10–40 °C); (b). (Experimental conditions: TBBPA concentration 0.28 μmol/L; $[O_3]$/[TBBPA] = 5:1; initial solution pH = 5.0, 6.0, 7.0, 8.0, 9.0 for (a), 7.0 for (b); temperature = 10, 20, 25, 30, 40 °C for (b), 25 °C for (a)); Text S1. Toxicity testing methods.

Author Contributions: Q.H. performed the data analyses, wrote and revised the manuscript; W.D. contributed to the conception of the study; H.W. performed the experiments; B.Y. helped perform the analysis with constructive discussions; P.L. contributed to the conception of the study and contributed significantly to the analysis and manuscript preparation; L.X. helped perform the revisions of the manuscript; Z.D. helped perform the experiments and analysis. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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