Mechanism and Kinetic Analysis of the Degradation of Atrazine by O₃/H₂O₂

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Abstract: In phosphate buffer, the degradation of ATZ by ozone/(O₃/H₂O₂) under various circumstance was explored and the degradation mechanism and dynamics were probed. The findings revealed that when maintaining the reaction temperature at 25 °C, the H₂O₂ concentration and the O₃ concentration were 20 mol/L and 20 mol/L, respectively. Moreover, the degradation rate of 5 mol/L ATZ under the influence of O₃/H₂O₂ was 92.59% in phosphate buffer at pH7. The mechanism analysis showed that HO• and O₃ underwent co-oxidized degradation and that the HO• and O₃ oxidation degradation ratios were close to 1:1 under acidic conditions. Furthermore, HO• oxidative degradation dominated the ATZ degradation process. The kinetics analysis showed that the ATZ kinetics of O₃/H₂O₂ degradation were more compatible with quasi-second-order reaction kinetics under different temperatures, pH values, and H₂O₂ concentrations.

Keywords: ozone; hydrogen peroxide; atrazine; degradation mechanism; kinetics

1. Introduction

Atrazine (ATZ, common molecular formula: C₈H₁₄ClN₅) is now the world’s second most extensive herbicide, with cheap cost, low toxicity, and good weeding properties [1,2]. Since it is considered to be one of the most polluting pesticides, seven European countries, including Germany, France and Sweden, banned the use of atrazine in 2007 [3]. Atrazine consumption is reported to be between 80,000 tons on average per year worldwide [4]. Nevertheless, China’s yearly atrazine consumption has been estimated to be greater than 108 tons [5]. Although not very toxic, ATZ is structurally stable and is often found in water resources due to its long half-life (30–100 days) [6]. A survey has shown that the residual concentration of atrazine in most bodies of water in China is 1–20 µg/L, and the mass concentration of atrazine detected in some lakes and streams in many EU countries is between 0.1–30.3 µg/L [7]. Buster et al. investigated 18 lakes in Sweden, and the test results show that atrazine exists in the waters, and the highest mass concentration reaches 4 µg/L [8]. ATZ can migrate and be transformed within different environmental media, such as water, atmosphere, and soil. Overland runoff, lixiviating, and dry and wet deposition are the most typical methods by which ATZ reaches the aquatic environment [9,10].

The harmful effects of ATZ on various organisms in nature are mainly manifested in the interference of ATZ in the normal operation of the endocrine system and its causing organisms to produce toxic reactions. From the viewpoint of Sun et al. [11], ATZ with a concentration of 10 mg/L or above inhibited the germination rate of rice seeds. Fu et al. [12] found that an ATZ concentration of 0.125 mg/cm² inhibited the embryonic development of the red-eared turtle. The research of Bellona et al. [13] suggests that ATZ has considerable
effects on the growth of the mature F1 mouse brain during a vital and sensitive stage, resulting in a change in behavioral development trajectories. Stradtman et al. [14] reported that atrazine use in the United States and the rest of the world constitutes a substantial threat to life, health, and the environment due to its neurotoxicity properties and to its being an endocrine-disrupting compound and a reproductive toxin. Sagarkar et al. [15] studied how a battery of nuclear and mitochondrial-encoded genes involved in oxidative phosphorylation (OXPHOS) were affected by short-term atrazine treatment in human liver (HepG2) and rat muscle (L6) cell lines. The results showed that the EC50 amount of atrazine for mitotoxicity in HepG2 and L6 cells was around 0.162 and 0.089 mM, respectively. Mitochondrial dysfunction could be introduced by atrazine induction. According to the study by Marcus et al. [16], as a result of exposure to a dose of atrazine, the proportion of pups that emerged, the proportion of adults that emerged, and adult survival all decreased. Atrazine sped up the development of the flies, causing them to pupate and emerge earlier than the controls. Therefore, the residual ATZ in the environment has attracted the attention of many scholars [17,18].

In recent years, studies have found that SO$_4^-$ (2.5~3.1 V) has a higher redox potential than HO• (2.3~2.7 V), since it can efficiently remove organic pollutants and it is less affected by the water quality environment. Therefore, persulfate (PS) has attracted the attention of many researchers. The most important of its forms are peroxymonosulfate (PMS) and peroxodisulfate (PDS). Phosphate is an excellent buffer in the degradation of ATZ by O$_3$/PMS. In addition, pH has a significant effect on the degradation of ATZ by O$_3$/PMS. The degradation efficiency under alkaline conditions is much better than that under acidic conditions. Phosphate can stimulate PMS to produce SO$_4^-$, which shows that the excitation effect under acidic conditions is better than that under alkaline conditions. Furthermore, the phosphate system alone has no degradation effect on ATZ. Studies have shown that O$_3$ has a better degradation effect on ATZ in the phosphate system, and PMS alone has a degradation effect on ATZ in the phosphate buffer system. Under the same conditions, using NaOH to adjust the pH, PMS has no degradation effect on ATZ [19].

At the moment, various ozone (O$_3$)-based AOPs have been shown to be able to effectively degrade ATZ in water, including ozonation [20], ferrosilite/O$_3$ [21], UV/O$_3$/ultrasound [22], peroxide [23], photo-fenton and photo-fenton-like processes [24], and photocatalysis [25]. Among these technologies, the UV/O$_3$-based ATZ water treatment method is more eco-friendly and more suitable for many kinds of wastewater [20]. Wen et al. indicated that the UV/O$_3$/US process can effectively degrade atrazine in manufacturing wastewater [26]. However, there are few reports on the degradation of ATZ by O$_3$/H$_2$O$_2$, even though some studies have shown that the O$_3$/H$_2$O$_2$ system has been used in the treatment of water pollution and that it has shown excellent degradation ability for pollutants in actual treatment [27,28]. Therefore, this paper investigates the effect of O$_3$/H$_2$O$_2$ on ATZ in a phosphate buffer system under different conditions. Through the obtained experimental results, the mechanism of ATZ degradation in the system and the kinetic model of ATZ degradation are discussed. This study thereby contributes to the further enrichment of the chemical processing technology of ATZ.

2. Materials and Methods
2.1. Reagents and Instruments

Reagents: All reagents used in the experiments were of analytical grade unless otherwise specified: methyl alcohol for chromatography, caustic soda, sodium phosphate monobasic, sodium nitrite, TBA (tertiary butanol), hydrogen peroxide (H$_2$O$_2$ ≥ 30%), ATZ purchased from Aladdin Co., Ltd. (Shanghai, China), and oxygen with a purity greater than 99%.

Instruments: HPLC (Waters 2695–2996); electronic balance; laboratory pH-meter of Shanghai Lei Magnetic Co., Ltd. (Shanghai, China) (PHSJ-3F); KH5 200 DB CNC ultrasonic cleaner; Ultrapure Water Polishing System from ULUPURE Co., Ltd. (Chengdu, China); intelligent constant temperature bath (DC-1030); constant temperature magnetic stirrer
(78HW-1); and a laboratory O$_3$ generator from Harbin Jiujii Electrochemical Engineering Technology Co., Ltd. (Harbin, China) (DHX-SS-1G).

2.2. Experimental Scheme

2.2.1. Solution Preparation

In this experiment, ultrapure water (resistivity 18.24 MΩ·cm) was used to prepare ATZ mother liquor with a concentration of 100 µmol/L, 0.2 mol/L of NaH$_2$PO$_4$ solution, 0.2 mol/L of NaOH solution, 0.01 mol/L of NaNO$_2$ solution, 0.01 mol/L of H$_2$O$_2$ solution, and 8 g/L of tert-butanol solution. Table 1 shows the preparation methods for the pH6, pH7, and pH8 phosphate buffers (both to 1 L). The phosphate buffer (PB) solution was used to adjust the pH of the reaction, so that the pH value was constant at 7 (except for the single factor of pH). We compared the pH of the reaction system to 6.26 and 6.58 after the reaction was completed when the initial pH of the reaction system was adjusted by NaOH to 7 and 8, respectively. The main reason for the pH change was that the initiation and participation of O$_3$ by OH- decomposes the chain reaction, and the chain reaction consumes the amount of OH- in the reaction system, causing the pH of the reaction system to drop and become acidic. The chain reaction is then terminated, and PB has the function of maintaining the pH of the solution.

Table 1. The preparation method for the NaH$_2$PO$_4$-NaOH buffer.

| pH | 0.2 mol/L NaH$_2$PO$_4$-NaOH (mL) | 0.2 mol/L NaOH (mL) |
|----|---------------------------------|---------------------|
| 6  | 250                             | 28.50               |
| 7  | 250                             | 148.15              |
| 8  | 250                             | 244.00              |

2.2.2. Experimental Scheme of ATZ Degradation by O$_3$/H$_2$O$_2$

The degradation efficiency of O$_3$/H$_2$O$_2$ for ATZ in a 12.5 mmol/L phosphate buffer solution was investigated under the following conditions: different H$_2$O$_2$ concentrations of 5, 10, 15, and 20 µmol/L; pH values of 6, 7, and 8; and different temperatures of 10, 15, 20, and 25 °C. In a water bath at 20 °C, the concentration of O$_3$ was 20 µmol/L, the concentration of phosphate was 12.5 mmol/L, the concentration of H$_2$O$_2$ was 20 µmol/L, and the concentration of ATZ was 5 µmol/L. The mechanism of the degradation of ATZ by O$_3$/H$_2$O$_2$ was investigated by adding different concentrations of tert-butanol and adjusting the pH. The reaction was stopped using a 0.01 mol/L solution of NaNO$_2$.

In the actual experiment, three parallel samples were set for each group of experiments, and the experimental results were taken as the average of three parallel experiments.

2.3. Analytical Method

2.3.1. Liquid Chromatography Analysis

To detect ATZ, the Symmetry® C18 StableBond was used, and the particular test procedure was as follows: a 60:40 methyl alcohol to ultrapure water mobile phase ratio, a flow velocity of 0.8 mL/min, operating temperatures of 40 °C, and a determinate wavelength of 225 nm. O$_3$ concentration was determined through the UV$_{258}$ method [29].

2.3.2. Kinetic Analysis of ATZ Degradation by O$_3$/H$_2$O$_2$

The pseudo-first-order kinetic equation was first introduced by Lagergren, and it is usually used in the form proposed by Ho and McKay [30].

\[
\ln(q_e - q_t) = \ln q_e - K_1 t 
\]

(1)

Combine formula:

\[
q_e = \frac{(C_0 - C_e)V}{m} 
\]

(2)
Deduced:
\[
\frac{C_t - C_e}{C_0 - C_e} = e^{-K_1t}
\]  

Assuming that ATZ can be completely degraded in the O₃/H₂O₂ system, that is, that the concentration of ATZ in the solution is 0 (Ce = 0) at equilibrium, we can obtain:
\[
\frac{C_t}{C_0} = e^{-K_1t}
\]  

Therefore, the kinetic model of the O₃ oxidative degradation of ATZ is established according to the following kinetic equation, and the first-order reaction kinetic equation is:
\[
\ln \frac{C_t}{C_0} = -K_1t
\]

where \( C/C_0 \) represents the surplus rate of ATZ in the reactor, and the elimination rate of ATZ in the reactor \( \beta = 1 - C/C_0 \); thus, \( C/C_0 = 1 - \beta \).

A linear second-order rate equation was then introduced [31]:
\[
\frac{1}{C_t} = K_2t + \frac{1}{C_0}
\]

Substitute \( C/C_0 = 1 - \beta \) into Equation (2) to obtain the following result:
\[
\frac{1}{1 - \beta} = K_2C_0t
\]

\( q_e \): Adsorption capacity value at equilibrium, mg/g;  
\( q_t \): Adsorption capacity value at time \( t \), mg/g;  
\( K_1 \): Pseudo-first-order rate constant, 1/min;  
\( K_2 \): Pseudo-second-order rate constant, L/(µmol·min);  
\( \beta \): Represents the elimination rate of ATZ;  
\( m \): Mass of the adsorbent, g;  
\( C_0 \): Initial concentration of ATZ;  
\( C_e \): Reaction ATZ concentration at equilibrium;  
\( C_t \): ATZ concentration at any time, mg/L.

3. Results and Discussion
3.1. Effect of Temperature on ATZ Degradation by O₃/H₂O₂

When the concentrations of ATZ, O₃, and H₂O₂ were 5 µmol/L, 20 µmol/L, and 20 µmol/L, respectively, the impact of the temperature changes on ATZ decomposition by O₃/H₂O₂ in phosphate buffer at pH7 is illustrated in Figure 1. According to Figure 1, the effect of ATZ degradation by O₃/H₂O₂ was enhanced when the temperature of the reaction increased. This was mainly due to the increase in the temperature: the percentage of activated O₃ increased and the decomposition of O₃ was accelerated to generate HO•. At the same time, increasing the temperature speeds up the movement of molecules, thereby increasing the collision frequency between ATZ and O₃ and HO•, thereby accelerating the degradation rate. The ATZ removal rate increased from 83.96 to 95.52% when the temperature of the reaction system was gradually adjusted from 10°C to 25°C, and although there was no obvious difference in the removal effect, the reaction rate was considerably different. The degradation rate of ATZ at 25°C changed slowly after five minutes, and basically tended to be stable. At five minutes, the degradation rate of ATZ by O₃/H₂O₂ quickly reached 92.59%. The elimination rate of ATZ decreased slightly at 20°C compared to the other temperatures and increased at 25°C. The reason for this is that in the ozonation process, on the one hand, increasing the temperature can increase the rate constants of activated molecules and chemical reaction rates, thereby
improving the degradation efficiency. On the other hand, the increase in temperature reduces the solubility of ozone in aqueous solution, resulting in a lower degradation efficiency. When discussing the utilization efficiency of ozone at different temperatures, Lei Zhao et al. [32] mentioned that in a separate ozone system, with the increase in temperature, the utilization of ozone first increased, then gradually became stable, and finally dropped. At the same time, the presence of heterogeneous catalysts can reduce the negative effects of decreasing ozone solubility in water with increasing temperature, resulting in an increase in ozone utilization, and contributing to the production of •OH during ozonolysis [33]. Therefore, in the combined result of the two opposite effects, the removal rate of ATZ by O3/H2O2 decreased at 20 °C. At 25 °C, due to the increase in the temperature of the reaction solution, the chemical reaction and mass transfer rate were accelerated, and more •OH was generated, thereby increasing the removal rate of ATZ. It is easy to observe that when the temperature increased from 15 °C to 20 °C, the removal rate of ATZ was significantly improved, indicating that the temperature change in the normal temperature range has a greater impact on the degradation of ATZ by O3.

![Graph showing the ATZ removal rate under different temperatures.](image)

**Figure 1.** The ATZ removal rate under different temperatures.

In addition, with the progress of the reaction, different temperatures caused different dissolved concentrations of O3 in the system, resulting in different contents of HO•; the removal of ATZ in aqueous solution was also gradually different. Within the same time period, the increase in the reaction temperature can speed up the reaction rate of ATZ with O3, HO•, and other oxidants, but at the same time it will accelerate the ineffective decomposition of O3 and reduce the solubility of O3 in water; it is thus not conducive to the degradation of ATZ in solution. These two contradictory reactions lead to the process of degrading ATZ by O3/H2O2, and the removal rate of ATZ showed a trend of increasing first and then leveling off with the increase in reaction temperature. Within a certain range of conditions, the increase in temperature promotes the improvement of the reaction rate, which is beneficial to the degradation of ATZ in the O3/H2O2 system [34]. Therefore, under the experimental conditions, the optimal temperature for degrading ATZ by O3/H2O2 is 25 °C.

### 3.2. The Effect of H2O2 Concentration on ATZ Degradation by O3/H2O2

In Figure 2, the effect of the amount of H2O2 in the reaction system concentration on the degradation of ATZ by O3/H2O2 is shown. As shown in the figure, there was no obvious change in ATZ degradation by O3/H2O2 when the quantity of H2O2 in the reaction process rose. This is mainly because a small amount of deprotonated H2O2 could give a strong boost to O3 to generate more HO• [35], whose reaction rate with ATZ (2.54 × 10^9 /Ms [36])
is far greater than that of O$_3$ with ATZ. Therefore, even a small amount of H$_2$O$_2$ input could result in distinct ATZ degradation when the O$_3$ concentration maintains a certain value in the O$_3$/H$_2$O$_2$ system, indicating that the O$_3$/H$_2$O$_2$ system is suitable for the treatment of high concentrations of ATZ solution. The ATZ removal rate reached its highest level at 92.92% when the H$_2$O$_2$ concentration was 10μmol/L in the system; that is, ATZ degradation by O$_3$/H$_2$O$_2$ achieved its highest efficiency when the ratio of nH$_2$O$_2$ to nO$_3$ was 1:2.

![Figure 2](image-url)  

**Figure 2.** The ATZ removal rate under different H$_2$O$_2$ densities.

When only O$_3$ is used for oxidation, the degradation process for organic pollutants usually includes two aspects: one is the direct oxidation of pollutants by molecular O$_3$, and the other is the indirect oxidation of organic pollutants by HO• produced by O$_3$ conversion [37]. When the O$_3$/H$_2$O$_2$ system is used to degrade ATZ, there is not only the direct oxidation of ATZ by O$_3$ and H$_2$O$_2$, but more importantly, due to the existence of H$_2$O$_2$, H$_2$O$_2$ is rapidly dissociated to form HO•, which can react with O$_3$ to promote its rapid and efficient production. A large amount of HO• is generated, which in turn strengthens the indirect oxidation of ATZ [38–40]. Therefore, compared with O$_3$ oxidation alone, the use of an O$_3$/H$_2$O$_2$ advanced oxidation process can greatly improve the ability to generate HO•. The reaction is shown in Formulas (4)–(8) [41,42].

$$H_2O_2 \rightarrow HO^- + H^+ \quad (8)$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (9)$$

$$O_3 + HO_2^- \rightarrow HO^- + O_2^- + O_2 \quad (10)$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2 \quad (11)$$

$$O_3^- + H_2O \rightarrow HO^- + OH^- + O_2 \quad (12)$$

When the concentration of H$_2$O$_2$ is low, the excitation effect of HO• is poor, which is not conducive to the improvement of ATZ removal efficiency. However, excess H$_2$O$_2$ molecules can react quickly with HO•. The reaction formula is: H$_2$O$_2$+HO•→HO$_2$• + H$_2$O. The presence of excess H$_2$O$_2$ will thus also reduce the degradation efficiency of HO• for ATZ. In addition, the high concentration of H$_2$O$_2$ will also cause unnecessary waste and the risk of secondary pollution. Therefore, choosing the appropriate concentration of H$_2$O$_2$ is of great practical significance for improving the efficiency of ATZ degradation in the O$_3$/H$_2$O$_2$ system. When using the O$_3$/H$_2$O$_2$ oxidation process to treat wastewater,
the optimal concentration ratio of O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} should be determined through practical experiments [43,44].

3.3. The Effect of pH Value on ATZ Degradation by O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}

In phosphate buffer solution at 20 °C, the degradation results of ATZ at different pH values were provided in Figure 3. The quantity of ATZ, O\textsubscript{3}, and H\textsubscript{2}O\textsubscript{2} were 5 \mu mol/L, 20 \mu mol/L, and 20 \mu mol/L, respectively. From the figure, the results of the decomposition of ATZ by O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} showed a rapid enhancement as the pH value increased in the reaction process. When the pH was raised from 6 to 8, the clearance rate of ATZ improved from 52.95 to 89.03%. After gradually adjusting the pH value from 6 to 7, the ratio of the decomposition amount of ATZ to the initial amount increased significantly from 52.95 to 83.96%. Furthermore, the ratio of the decomposition amount of ATZ increased from 83.96 to 89.03% when the pH value was adjusted from 7 to 8; the removal rate did not rise significantly, but the reaction rate increased notably. The removal rate reached 89% at 2 min under pH8, then tended to be stable. When the pH of the reaction system increased from 6 to 8, the removal rate of ATZ was significantly enhanced. This was because when the pH was acidic, O\textsubscript{3} mainly relied on selective direct oxidation to degrade the target, and the oxidation ability was low; on the other hand, when the pH is alkaline, O\textsubscript{3} mainly relies on the chain reaction to generate non-selective strong oxidizing HO• to oxidatively degrade the target, and HO• has a significantly stronger oxidative ability for ATZ than O\textsubscript{3}. It can be seen that the pH of the reaction system has a very significant effect on the degradation of ATZ by O\textsubscript{3}. Yang et al. [45] investigated the ozonation-induced degradation of atrazine in the presence of hydroxylamine, and discovered that pH had a substantial impact on atrazine degradation.

![Figure 3. The ATZ removal rate under different pH values.](image)

The dissociation of H\textsubscript{2}O\textsubscript{2} is a key step in the chain reaction of the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} reaction system. The conjugate base HO\textsubscript{2} is the active substance in the reaction, and its concentration is closely related to the pH value. Under acidic conditions, the reaction rate of H\textsubscript{2}O\textsubscript{2} and O\textsubscript{3} slowed down, and when the pH value was greater than 5, the decomposition rate of O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} increased rapidly. With the increase in pH value, the amount of HO• produced by the combined action of H\textsubscript{2}O\textsubscript{2} and O\textsubscript{3} gradually increased, which triggered a free-radical chain reaction, more fully oxidized ATZ, and an improved degradation effect. Under higher pH conditions, the initiator HO\textsubscript{2}, which can effectively promote the decomposition of O\textsubscript{3}, can be dissociated even in a lower concentration of H\textsubscript{2}O\textsubscript{2} solution [46,47].

Feng et al. [48] used the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} process to treat the mother liquor of gas field wastewater, and found that pH had the most critical effect on the treatment effect. The
best operating conditions can be obtained when the pH value is 10.9, the flow rate of O₃ is 0.8 L/min, and the amount of H₂O₂ is 6.2 mL. Ochir et al. [49] used the O₃/H₂O₂ system to treat tebuconazole, carbenzimid, and pyrimethanil in turn with an initial concentration of 2 μmol/L. When the reaction temperature was 25 °C, the reaction time was 0.5 h, and the pH value increased from 5 to 9; the removal rates of tebuconazole, carbenzimid, and pyrimethanil also increased from 17.0 ± 1.0%, 66.4 ± 2.2%, and 90.9 ± 1.6% to 30.3 ± 2.0%, 80.5 ± 1.4%, and 99.5 ± 0.4%, respectively. A higher pH value is not always better. Farzaneh et al. [50] studied the effect of pH value on the removal of ibuprofen by the O₃/H₂O₂ advanced oxidation process. After 5 min of ozone oxidation at pH7.6, the residual ozone concentration was analyzed and found to have increased from 1.5 mg/L drops to about 0.15 mg/L, which means that at pH 7.6 and above, ozone is almost completely decomposed within 5 min, and other compounds will quickly consume the free radicals. Therefore, even at higher pH, HO• is not sufficient for achieving greater ibuprofen removal. From the existing research, for different water bodies or different pollutants, the pH value required by O₃/H₂O₂ is different, but most of them are in the range of 6~12.

3.4. Mechanism Analysis of ATZ Degradation by O₃/H₂O₂

3.4.1. Mechanism Analysis of ATZ Degradation by O₃/H₂O₂ in Phosphate Buffer at pH6

In phosphate buffer at pH6, different amounts of tertiary butyl alcohol were added to the O₃ alone and O₃/H₂O₂ systems to capture HO• in the reaction system, so as to investigate the O₃/H₂O₂ degradation mechanism of ATZ [51,52]. The results are shown in Figure 4. It was found that H₂O₂ alone had virtually no degradation effect on ATZ. The degradation amount of ATZ by O₃ alone was basically the same when the tertiary butyl concentration was 8 and 16 mg/L, respectively, proving that all HO• in the O₃ alone system can be captured when the concentration of tertiary butyl is 8 mg/L.

![Figure 4](image)

**Figure 4.** The effect of free radical scavenger on the degradation of ATZ by O₃/H₂O₂ in pH6 phosphate buffer.

The percentage of ATZ elimination dropped from 23.38% to 11% when excessive tertiary butanol was added to the O₃ reaction system, indicating that only 10% of ATZ in the system was directly oxidatively removed by O₃. The amount of ATZ directly oxidized by O₃ accounted for 47.05% of the total removal rate, while ATZ degraded by HO• made up the other 52.95%, showing that O₃ and HO• each accounted for half of the ATZ degradation in phosphate buffer at pH6.

The degradation effect of O₃/H₂O₂ on ATZ was basically the same when the tertiary butanol concentration was 16 and 32 mg/L in the O₃/H₂O₂ reaction system, revealing that all the HO• in the system was captured when the concentration of tertiary butanol
was 16 mg/L. The percentage of ATZ elimination dropped from 52.95% to around 13% when excessive amounts of tertiary butanol were added to the O₃/H₂O₂ system, indicating that only 13% of ATZ was directly oxidized by O₃. The O₃ oxidation accounted for 24.55% of the overall ATZ removal rate, whereas HO• degradation accounted for the remaining 75.45%, indicating that HO• was superior for degrading ATZ in phosphate buffer at pH6.

The ATZ degradation efficiency by O₃ alone and H₂O₂ alone was 23.38% and 2%, respectively, in phosphate buffer at pH6, while the degradation efficiency of O₃/H₂O₂ was 27.57% higher than the sum of the two, proving that O₃ and H₂O₂ can excite each other to produce more HO• than each would produce separately.

### 3.4.2. Mechanism Analysis of ATZ Degradation by O₃/H₂O₂ in Phosphate Buffer at pH7

In the phosphate buffer at pH7, different amounts of tertiary butyl alcohol were added to the O₃ alone and O₃/H₂O₂ systems to capture HO• in the reaction system, so as to investigate the O₃/H₂O₂ degradation mechanism of ATZ. The results are shown in Figure 5. According to early research, when the concentration of tertiary butyl in the O₃ alone environment was 16 mg/L, all of the HO• in the system could be collected.

**Figure 5.** The effect of free radical scavenger on the degradation of ATZ by O₃/H₂O₂ in pH7 phosphate buffer.

From Figure 5, the degradation rate of ATZ by O₃ alone decreased from 40.76% to 9.4% when the concentration of tertiary butanol was 16 mg/L in the system, suggesting that only 9.4% of ATZ was directly oxidized by O₃. The O₃ oxidation accounted for 23.06% of the total ATZ removal rate, while the amount of ATZ degraded by HO• accounted for the other 76.94%, reflecting the dominant role of HO• in the ATZ degradation of O₃ alone in phosphate buffer at pH7.

The degradation effect of O₃/H₂O₂ on ATZ was basically the same when the tertiary butanol concentration was 32 and 48 mg/L in the O₃/H₂O₂ reaction system, revealing that all the HO• in the system was captured when the concentration of tertiary butanol was 32 mg/L. The rate of ATZ degradation fell from 83.96% to roughly 12% when excessive amounts of tertiary butanol were added to the O₃/H₂O₂ system, indicating that only 12% of ATZ was directly oxidized by O₃. The O₃ oxidation contributed a 14.29% degradation rate of ATZ, while HO• removal accounted for the remaining 85.71%. In phosphate buffer at pH7, O₃ and HO• both played a role in ATZ degradation and HO• played the leading role.

### 3.4.3. Mechanism Analysis of ATZ Degradation by O₃/H₂O₂ in Phosphate Buffer at pH8

In phosphate buffer at pH8, different amounts of tertiary butyl alcohol were added to the O₃ alone and O₃/H₂O₂ systems to capture HO• in the reaction system, so as to
investigate the \( \text{O}_3/\text{H}_2\text{O}_2 \) degradation mechanism of ATZ. Figure 6 depicts the experimental consequences. According to prior tests, all the \( \text{HO}^• \) in the system can be captured when the tertiary butyl concentration inside this \( \text{O}_3 \) alone system is 32 mg/L.

**Figure 6.** The influence of free radical scavenger on the degradation of ATZ by \( \text{O}_3/\text{H}_2\text{O}_2 \) in pH8 phosphate buffer.

From Figure 6, the degradation rate of ATZ by \( \text{O}_3 \) alone decreased from 71.83% to 8% when the tertiary butyl concentration inside this \( \text{O}_3 \) alone system was 32 mg/L, suggesting that only 8% of ATZ was directly oxidized by \( \text{O}_3 \). The \( \text{O}_3 \) oxidation accounted for 11.14% of the total ATZ removal rate, while the amount of ATZ degraded by \( \text{HO}^• \) accounted for the other 88.86%, indicating the dominant role of \( \text{HO}^• \) in the ATZ degradation of \( \text{O}_3 \) alone in phosphate buffer at pH8.

The degradation effect of \( \text{O}_3/\text{H}_2\text{O}_2 \) on ATZ was basically the same when the tertiary butanol concentration was 48 and 64 mg/L in the \( \text{O}_3/\text{H}_2\text{O}_2 \) reaction system, revealing that the \( \text{HO}^• \) in the system was basically captured when the concentration of tertiary butanol was 48 mg/L. The removal efficiency of ATZ dropped from 89.03% to roughly 10% when excessive amounts of tertiary butanol were added to the \( \text{O}_3/\text{H}_2\text{O}_2 \) system, indicating that only 10% of ATZ was directly oxidized by \( \text{O}_3 \). The \( \text{O}_3 \) oxidation was responsible for a 11.23% ATZ elimination rate, while \( \text{HO}^• \) degradation was responsible for the remaining 88.77%. In phosphate buffer at pH8, \( \text{O}_3 \) and \( \text{HO}^• \) both played a role in ATZ degradation and \( \text{HO}^• \) played the leading role [53,54].

### 3.4.4. Intermediate Products and Degradation Mechanism of ATZ Degradation

The results of the product analysis with HPLC-ESI-MS show that, as shown in Figure 7, the degradation pathways of ATZ mainly include the following four pathways: (I) Hydroxylation: During the degradation process of ATZ, the methyl group was replaced by a hydroxyl group, and the mass-to-charge ratio became \( m/z = 218 \); (II) De-isopropylation: Under the action of oxidant, the ATZ de-isopropyl group is generated to form de-isopropyl ATZ, and the mass-to-charge ratio becomes \( m/z = 174 \) and \( m/z = 146 \); (III) De-ethylation: During this process, ATZ removes the ethyl group to form de-ethylated ATZ, and the mass-to-charge ratio changes from \( m/z = 216 \) to \( m/z = 198 \) and \( m/z = 156 \); (IV) De-chlorination: ATZ removes Cl- and combines with -OH to form de-chlorinated ATZ, and the mass-to-charge ratio changes from \( m/z = 216 \) to \( m/z = 198 \) and \( m/z = 156 \). Therefore, the degradation pathways of ATZ by \( \text{O}_3/\text{H}_2\text{O}_2 \) mainly include hydroxylation, de-isopropylation, de-ethylation, and de-chlorination.
K.H Chan et al. [55] indicated that ten intermediate products were found in the degradation of ATZ in Fenton’s system of 0.1 mmol/L [Fe^{2+}] and [H₂O₂]. During this process, the main oxidant is HO•, and the presence of HO• triggers the degradation of ATZ through alkyl oxidation, dealkylation, and de-chlorination, and produces the corresponding intermediates. Yuchan Liu et al. [56] proposed that the main pathways for ATZ reduction in UV/PS systems include de-chlorination, demethylation, and de-ethylation to form various intermediates. The intermediates undergo dichlorination, hydroxylation and de-isopropylation to form secondary intermediates. Zeng-Hui Diao et al. [57] used LCQTOF-MS technology to analyze ATZ intermediates in the ATZ degradation process using B-nZVI/FeS₂/H₂O₂. Their results showed that in the degradation process, on the one hand, the degradation of ATZ is caused by the decomposition of the alkyl side chain of ATZ by HO•, which undergoes dealkylation to form an intermediate product. On the other hand, the corresponding intermediates are formed by dealkylation. The intermediate products are then dealkylated and hydroxylated to form secondary intermediates. At the same time, the authors also indicated that with the increase or decrease in the reaction time, the molecular weight of the intermediate product gradually decreased, indicating that the ATZ molecule can be effectively decomposed by HO• [57]. Due to the different degradation methods and operating conditions, the degradation pathways of ATZ are also different, but they all reflect that HO• plays a very important role in the process of degrading ATZ. The degradation pathway is mainly through hydroxylation, de-isopropylation, dealkylation and de-chlorination.

The whole reaction process can be simplified as:

\[
\text{ATZ} + \text{HO•} \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]  
(13)

3.5. Kinetic Analysis of ATZ Degradation by O₃/H₂O₂

3.5.1. Kinetic Analysis of ATZ Degradation by O₃/H₂O₂ under Different Temperatures

When the concentrations of ATZ, O₃, and H₂O₂ were 5 mol/L, 20 mol/L, and 20 mol/L, respectively, in phosphate buffer solution at pH7, the quasi-first-order reaction kinetics of ATZ degradation by O₃/H₂O₂ at different temperatures were matched with Ln(C/C₀)(y) as the Y-axis and t(x) as the X-axis. At various temperatures, the quasi-second-order reaction kinetics of ATZ degradation by O₃/H₂O₂ were matched using 1/(1 – β)(y) as the Y-axis and t(x) as the X-axis. The parameters for the dynamic fitting...
equation are presented in Tables 2 and 3, and the dynamic matching curves are displayed in Figures 8 and 9.

Table 2. The kinetics equations and parameters of quasi-first-order reactions of O₃/H₂O₂ degradation of ATZ at various temperatures.

| T(°C) | Fitted Equation | Reaction Order | K₁ (1/min) | R² |
|-------|-----------------|----------------|------------|----|
| 10    | Y = -0.11198x - 0.37774 | First-order reaction | 0.11198 | 0.91718 |
| 15    | Y = -0.11688x - 0.63552 | First-order reaction | 0.11688 | 0.84758 |
| 20    | Y = -0.06995x - 0.65722 | First-order reaction | 0.06995 | 0.65698 |
| 25    | Y = -0.10641x - 1.42622 | First-order reaction | 0.10641 | 0.48264 |

Table 3. The kinetics equations and parameters of quasi-second-order reactions of O₃/H₂O₂ degradation of ATZ at different temperatures.

| T(°C) | Fitted Equation | Reaction Order | K₁ (1/min) | R² |
|-------|-----------------|----------------|------------|----|
| 10    | Y = 0.48111x + 1.00352 | Second-order reaction | 0.48111 | 0.99749 |
| 15    | Y = 0.6592x + 1.38581 | Second-order reaction | 0.65920 | 0.99585 |
| 20    | Y = 0.23151x + 1.08379 | Second-order reaction | 0.23151 | 0.87706 |
| 25    | Y = 0.9533x + 0.83282 | Second-order reaction | 0.95330 | 0.82373 |

Figure 8. The kinetics of quasi-first-order reactions of O₃/H₂O₂ degradation of ATZ at various temperatures.

Figure 9. The kinetics of quasi-second-order reactions for ATZ degradation at various temperatures.
From Figures 8 and 9 and Tables 2 and 3, the values of $R^2$ (linear correlation) fitted by quasi-second-order reaction kinetics were all larger than those fitted by quasi-first-order reaction kinetics, indicating that the reaction kinetics of ATZ degradation by $O_3/H_2O_2$ at different temperatures are more consistent with quasi-second-order reaction kinetics [58]. The quasi-second-order reaction rate constant increased from 0.48111 to 0.95333 when the reaction temperature rose from 10 °C to 25 °C, with the lowest reaction rate at 20 °C and reaction rate constant at 0.23151. The highest reaction rate increased by 4.12 times compared with the lowest reaction rate. Since the $R^2$ fitted for the secondary reaction at 25 °C was only 0.82373, the linear correlation was poor, and the actual reaction rate cannot be accurately reflected.

3.5.2. Kinetic Analysis of ATZ Degradation by $O_3/H_2O_2$ under Different $H_2O_2$ Concentrations

In phosphate buffer solution at pH7, when the concentrations of ATZ, $O_3$, and temperature were 5 mol/L, 20 mol/L, and 20 °C, respectively, the quasi-first-order reaction kinetics of ATZ degradation by $O_3/H_2O_2$ at varied $H_2O_2$ concentrations were matched using $\ln(C/C_0)$ ($y$) as the Y-axis and $t(x)$ as the X-axis. The quasi-second-order reaction kinetics of ATZ degradation by $O_3/H_2O_2$ were matched under different $H_2O_2$ concentrations adopting $1/(1-\beta)$ ($y$) as the Y-axis and $t(x)$ as the X-axis. The factors for the dynamic fitting equation are presented in Tables 4 and 5, and the dynamics matching curves are displayed in Figures 10 and 11.

Table 4. The kinetics equations and parameters of quasi-first-order reactions of $O_3/H_2O_2$ degradation of ATZ at different $H_2O_2$ densities.

| $C(H_2O_2)$ (µmol/L) | Fitted Equation | Reaction Order | $K_1$ (1/min) | $R^2$ |
|----------------------|-----------------|-----------------|---------------|-------|
| 5                    | $Y = -0.08137x - 0.38598$ | First-order reaction | 0.08137       | 0.84815 |
| 10                   | $Y = -0.11383x - 0.630929$ | First-order reaction | 0.11383       | 0.85080 |
| 15                   | $Y = -0.07185x - 0.70582$ | First-order reaction | 0.07185       | 0.68089 |
| 20                   | $Y = -0.06995x - 0.65722$ | First-order reaction | 0.06995       | 0.65698 |

Table 5. The kinetics equations and parameters of quasi-second-order reactions of $O_3/H_2O_2$ degradation of ATZ at different $H_2O_2$ densities.

| $C(H_2O_2)$ (µmol/L) | Fitted Equation | Reaction Order | $K_1$ (1/min) | $R^2$ |
|----------------------|-----------------|-----------------|---------------|-------|
| 5                    | $Y = 0.24548x + 1.36493$ | Second-order reaction | 0.24548       | 0.97377 |
| 10                   | $Y = 0.62450x + 1.388$ | Second-order reaction | 0.62450       | 0.99343 |
| 15                   | $Y = 0.25765x + 2.05714$ | Second-order reaction | 0.25765       | 0.90920 |
| 20                   | $Y = 0.23151x + 1.99153$ | Second-order reaction | 0.23151       | 0.87706 |

From Figures 10 and 11 and Tables 4 and 5, the values of $R^2$ (linear correlation) fitted by quasi-second-order reaction kinetics were all larger than those fitted by quasi-first-order reaction kinetics, indicating that the reaction kinetics of ATZ degradation by $O_3/H_2O_2$ at various $H_2O_2$ concentrations were more compatible with the quasi-second-order reaction kinetics. The highest and lowest secondary reaction constant was 0.6245 and 0.23151 when the $H_2O_2$ concentration was 10 and 20 µmol/L, respectively, with the reaction rate increased by 2.70 times.
3.5.3. Kinetic Analysis of ATZ Degradation by O$_3$/H$_2$O$_2$ at Different pH Values

In phosphate buffer solution at 20 °C, the quasi-first-order reaction kinetics of ATZ degradation by O$_3$/H$_2$O$_2$ under different pH values were matched utilizing $\ln(C/C_0)$ as the Y-axis and $t(x)$ as the X-axis when the concentration of ATZ was 5, O$_3$ was 20 μmol/L, and H$_2$O$_2$ was 20 μmol/L. The quasi-second-order reaction kinetics of ATZ elimination by O$_3$/H$_2$O$_2$ were matched under different pH values adopting $1/(1-\beta)$ as the Y-axis and $t(x)$ as the X-axis. The dynamic matching splines are demonstrated in Figures 12 and 13, and the parameters for the dynamic fitting equation are shown in Tables 6 and 7.
The kinetics of quasi–first–order reactions of O₃/H₂O₂ degradation of ATZ at different pH values.

Table 6. The kinetics equations and parameters of quasi-first-order reactions of O₃/H₂O₂ of degradation ATZ at different pH values.

| pH | Fitted Equation | Reaction Order | $K₁$ (1/min) | $R²$ |
|----|----------------|----------------|--------------|------|
| 6  | $Y = -0.03397x + 0.15995$ | First-order reaction | 0.03397 | 0.86677 |
| 7  | $Y = -0.06995x + 0.65722$ | First-order reaction | 0.06995 | 0.65698 |
| 8  | $Y = -0.04215x + 1.59326$ | First-order reaction | 0.04215 | 0.06647 |

Table 7. The kinetics equations and parameters of quasi-second-order reactions of O₃/H₂O₂ degradation ATZ at different pH values.

| pH | Fitted Equation | Reaction Order | $K₁$ (1/min) | $R²$ |
|----|----------------|----------------|--------------|------|
| 6  | $Y = 0.05299x + 1.16329$ | Second-order reaction | 0.05299 | 0.92574 |
| 7  | $Y = 0.23151x + 1.99153$ | Second-order reaction | 0.23151 | 0.87706 |
| 8  | $Y = 0.19067x + 6.14035$ | Second-order reaction | 0.19067 | 0.19382 |
The fitting linear correlation of pseudo-first-order reaction kinetics or pseudo-second-order reaction kinetics at pH 8 was not very ideal, and the real reaction rate in the reaction system cannot be accurately determined. Moreover, when the pH value was 8, the degradation reaction of ATZ was very rapid, and the concentration of ATZ in the system tended to be stable after 2 min, which can be seen from Figures 12 and 13. The pseudo-second-order reaction rate constant was 6.62253 and the $R^2$ value was 0.76401 by fitting the period before 2 min. The $R^2$ (linear correlation) values of the pseudo-second-order reaction kinetics fit were all larger than the $R^2$ values of the pseudo-first-order reaction kinetics, and we believe that the reactions were more in line with the pseudo-second-order reaction kinetics model.

4. Conclusions

The addition of a small amounts of H$_2$O$_2$ in the O$_3$/H$_2$O$_2$ system can significantly accelerate O$_3$ chain decomposition, resulting in the generation of a large amount of HO•. The higher the temperature and pH value, the better the degradation effect of O$_3$/H$_2$O$_2$ on ATZ. When the concentration of H$_2$O$_2$ went from low to high, the efficiency of O$_3$/H$_2$O$_2$ in degrading the ATZ first increased and then decreased. The optimal reaction ratio of H$_2$O$_2$ to O$_3$ was 1:2. The pH value had a considerable impact on the degradation of ATZ by O$_3$/H$_2$O$_2$, and the degradation efficiency under alkaline conditions was better than that under acidic conditions. Under acidic conditions, the proportion of direct oxidative degradation by O$_3$ and HO• inside the phase of ATZ decomposition was close to 1:1. Under alkaline and neutral conditions, HO• oxidative degradation dominated the ATZ degradation process. The kinetics of ATZ decomposition by O$_3$/H$_2$O$_2$ were more compatible with quasi-second-order reaction kinetics under varied temperatures, pH values, and H$_2$O$_2$ concentrations, according to the kinetic study.

Atrazine is not easy to degrade, and it can exist stably in aqueous environments for a long time, which not only affects the survival of animals and plants, but also threatens human health. Most studies do not clarify the types and hazards of ATZ degradation intermediates. Therefore, paying attention to the degradation efficiency of atrazine while taking into account the toxicity of intermediate degradation products is of great significance for optimizing ATZ degradation technology, which is also one of the future development directions. In addition, current research mainly focuses on the water environment with only ATZ, while ignoring the possible effects of the coexistence of various substances in natural water bodies; the effects of various natural conditions should therefore be fully considered and the cross-combination of various technologies applied to water. The degradation of atrazine can further optimize and improve the degradation efficiency, reduce the operating cost, and thus be more suitable for practical applications.

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