Decolorization and Mineralization of Rhodamine B in Aqueous Solution with a Triple System of Cerium(IV)/H2O2/Hydroxylamine

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ABSTRACT: Hydroxylamine (HA) can react with hydrogen peroxide (H2O2) to generate hydroxyl radical (HO•), but the reaction rate between them is very slow (2.2 × 10−4 M−1 s−1). We propose a new system to accelerate the formation of aminoxy radical (NH2O•) by the addition of cerium [Ce(IV)] to induce the continuous production of HO• through reaction with H2O2. We also investigate the decolorization and mineralization of rhodamine B (RhB) and mechanism in the Ce(IV)/H2O2/HA system. The initial pH plays a significant role in decolorization of RhB. In this work, observation of the rapid decolorization process after 60 min revealed that approximately 80% of RhB was degraded at the initial pH of 4.0. The HO• radicals were considered as the primary reactive oxidant in the system, during its investigation through coumarin capturing, benzoic acid capturing, and radical quenching experiments. The results of the present study suggest that the addition of Ce(IV) can greatly enhance the production of HO•, and the rapid decolorization and mineralization of RhB can occur through the Ce(IV)/H2O2/HA system at acidic pH conditions.

1. INTRODUCTION

An efficient method for advanced oxidation processes based on the hydroxyl radical (HO•) has gained widespread attention. For decades, it has been widely used to degrade various organic contaminants, such as pesticides, medicines, and dyes, which are toxic and refractory biological degradation products in environmental water. The HO• radical (E0 = 1.8–2.7 V) is more powerful in the degradation process than the parent oxidant hydrogen peroxide (H2O2) (E0 = 1.78 V), and HO• can be produced by various methods, such as the electrochemical, ultraviolet irradiation, heating, alkaline treatment, and Fenton reaction methods. Among these active approaches, the homogeneus Fenton oxidation, which is based on the addition of a transition metal, has been the most viable methods of achieving H2O2 activation.

In practical applications, a narrow pH range and the iron sludge formation are the major obstacles in the homogeneous Fenton oxidation system. Recently, researchers have found that the addition of hydroxylamine (HA) significantly broadens the pH range in a Fenton or a Fe(II)/peroxymonosulfate system. Furthermore, the HA can accelerate the Fe(II)/Fe(III) redox cycles, greatly enhancing the generation of reactive radicals. Similarly, the addition of HA can also increase the efficiency of the Cu(II)/H2O2 or Cu(II)/persulfate system by accelerating the reduction of Cu(II). Moreover, some metal ions, such as transition-metal ions, can decompose HA to form the protonated aminoxy radical (NH2O•). Regardless of the metal ion, H2O2 can also react with protonated HA to produce NH2O•, and then NH2O• further reacts with H2O2 to form HO•. This finding indicates that NH2O• plays a key role in the production of HO• radicals. Besides, even though the reaction rate of H2O2 and HA is very slow, it gives us a new way of producing HO•, different from the traditional Fenton reaction, by introducing a catalyst to promote the production of NH2O• in key species.

Cerium(IV) compounds are relatively mild oxidant and less toxic compared with other oxidizing compounds. The oxidizing potentials of Ce(IV) in sulfuric acid solutions (E0 = 1.6–1.74 V) have been established. Due to the change in the redox potential (E Ce4+/Ce3+) with the acidity of the solution, the oxidation of Ce(III) to Ce(IV) is natural in weak acidic or alkaline solution. In addition, researchers have confirmed that hydroperoxyl radicals (HO2•) are formed by the reaction of Ce(IV) and H2O2 instead of the HO• radical. Considering that the Ce(IV) can react individually with HA or H2O2, it can be proposed that Ce(IV) can be instrumental in enhancing the efficiency of the H2O2/HA system by accelerating the production of the important intermediate NH2O•. Accordingly, this study proposes a novel oxidation
system using Ce(IV), H₂O₂, and HA, which is potentially applicable to decolorization and mineralization of rhodamine B (RhB). RhB is an important xanthene dye with good stability that is used as a colorant, but which is dangerous if swallowed by human beings and animals. RhB has been effectively removed by various advanced oxidation processes, such as electro-Fenton, heterogeneous electro-Fenton, heterogeneous Fenton, persulfate oxidation, and peroxycoagulation. The main purpose of this study is to explore the performance of Ce(IV)/H₂O₂/HA system under different conditions. For this purpose, the effect of three reactants and the initial pH are each investigated in this study. Furthermore, a possible mechanism is proposed based on the detected HO· and the consumption of HA and H₂O₂. Finally, the mineralization ability of the system and degradation pathway for RhB removal was also evaluated.

2. RESULTS AND DISCUSSION

2.1. Decolorization of RhB in Different Systems. To evaluate the performance of the Ce(IV)/H₂O₂/HA triple system, all the decolorization processes of RhB under various conditions are compared in Figure 1a. The results reveal that neither H₂O₂ nor HA alone changed the concentration of RhB, and the combination of Ce(IV) with HA did not degrade RhB either. The decolorization of RhB was negligible in the Ce(IV)/H₂O₂ system due to its inability to activate H₂O₂. In contrast, the H₂O₂/HA and Ce(IV)/H₂O₂/HA systems were shown to be capable of inducing RhB decolorization; the decolorization rate of RhB by the Ce(IV)/H₂O₂/HA system was greater than that of the simple sum of the Ce(IV) and the H₂O₂/HA system alone. More than 80% of the RhB was decolorized within 60 min in this system, compared to only 31.1% in the H₂O₂/HA system. Meanwhile, very slow degradation of RhB was observed by the Ce(IV) system under acidic pH conditions. This can be explained by the strong oxidation ability of Ce(IV) under acid condition that leads to the formation of the Ce(OH)₂·H₂O·Ce(IV) complex, which has a large surface area and acts as an oxidizing agent in the hydrolysis of ceric sulfate.

It was observed that the removal rate of RhB reduced with time in the H₂O₂/HA or Ce(IV)/H₂O₂/HA system (Figure 1a). For example, 50% of the RhB was removed within 20 min of oxidation, whereas 32% of the RhB was removed over the next 40 min. This can be explained by the high RhB concentration leading to an increase in the rate of effective collision between molecules and HO·. As the reaction time increases, the concentration of RhB decreases and that of coproducts increases. This increases the collision rate between HO· and coproducts, rather than that of HO· with RhB molecules, which reduces the RhB removal rate at the later stages. Similar type of degradation pattern was obtained by Nidheesh et al. The degradation of RhB by the H₂O₂/HA and Ce(IV)/H₂O₂/HA systems both followed pseudo-first-order kinetics (Figure 1b). The observed rate constant for the RhB degradation by the Ce(IV)/H₂O₂/HA system (k = 2.91 × 10⁻⁵ min⁻¹) was approximately 5-fold higher than that by the H₂O₂/HA system (k = 5.90 × 10⁻⁶ min⁻¹).

It is well established that the H₂O₂/HA system produces reactive oxidants by activating H₂O₂ in two steps. In the first step, it forms an intermediate protonated aminoxyl radical (H₂NO₂⁺) during the oxidation of HA with H₂O₂ by an H-atom abstraction reaction, synchronously generating hydroxyl free radical (HO·) via reaction 1. In the second step, the reactive oxidant (HO·) is produced by the reaction of H₂O₂ with the intermediate protonated aminoxyl radical via a one-electron-transfer mechanism (reaction 2), which is capable of degrading RhB. However, reaction 1 is slow and limits the overall kinetics for the production of hydroxyl free radicals.

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{NOH}^+ \rightarrow \text{H}_3\text{NO}^* + \text{HO}^* + \text{H}_2\text{O} \tag{1}
\]

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{NO}^* \rightarrow \text{HNO} + \text{HO}^* + \text{H}_2\text{O} + \text{H}^+ \tag{2}
\]

In the reaction medium, Ce(IV) is in equilibrium with its anionic complexes depending on the acid used. It has been reported that cerium(IV) species in sulfate acid exist mainly in the form of monomeric species Ce(IV), Ce(OH)₃⁺, and Ce(OH)₂⁺. However, a previous study and thermodynamic calculations showed that the hydrated form, the Ce(IV) ion, is the predominant species at low pH values (pH < 1.3), whereas Ce(OH)₂⁺ is the predominant species at a relatively higher pH (pH > 4). Therefore, under our experimental conditions of pH > 3, Ce(IV) and Ce(OH)₂⁺ may be considered as the active species of cerium(IV). It has been demonstrated that cerium(IV)=hydroxyamine complexes between the ceric
species \([\text{Ce(IV)}] \) and \([\text{Ce(OH)}^2\text{+}]\) and the protonated hydroxylamine \((\text{NH}_2\text{OH}^+)\) form prior to the fast step, and these complexes further decompose to form the \(\text{NH}_2\text{O}^*\) radical and \(\text{Ce(III)}\). At the same time, the reaction does not stop as a result of the formation of nitroxyl radical by a reaction of the excess cerium(IV) with \(\text{NH}_2\text{O}^*\) radical. The rate of \(\text{NH}_2\text{O}^*\) radical production by the reaction of \(\text{Ce(IV)}\) with \(\text{HA}\) is higher than that by the reaction of \(\text{H}_2\text{O}_2\) and \(\text{HA}\). Thus, we proposed that the addition of \(\text{Ce(IV)}\) changes the kinetics of the above oxidation reactions by forming \(\text{Ce(IV)}-\text{HA}\) complexes as follows

\[
\text{Ce(IV)} + \text{NH}_2\text{OH}^+ \rightarrow \text{Ce(NH}_2\text{O})^\text{2+} + \text{H}^+ + \text{H}_2\text{O} \\
(3)
\]

\[
\text{Ce(OH)}_2^{\text{2+}} + \text{NH}_2\text{OH}^+ \\
\rightarrow \text{Ce(NH}_2\text{O})^\text{2+} + \text{OH}^- + \text{H}_2\text{O} \\
(4)
\]

\[
\text{Ce(NH}_2\text{O})^\text{2+} \rightarrow \text{Ce(III)} + \text{NH}_2\text{O}^* + \text{H}^+ \\
(5)
\]

\[
\text{Ce(IV)} + \text{NH}_2\text{O}^* \rightarrow \text{Ce(III)} + \text{HNO} + \text{H}^+ \\
(6)
\]

As a result of the elimination of the choke point caused by the slow rate of reaction 1, the production of \(\text{NH}_2\text{O}^*\) is accelerated, resulting in an increase in \(\text{RhB}\) degradation.

The actual stoichiometric ratio of \(\text{HA}\) depletion to \(\text{H}_2\text{O}_2\) consumption in different systems is shown in Figure 2. It was also observed that the consumption of hydrogen peroxide is relatively low, with about 10% \(\text{HA}\) and 50% \(\text{H}_2\text{O}_2\) remaining in the system after 12 h, indicating that hydroxyl radicals were still produced in the system. The slope in Figure 2 indicates that the stoichiometric ratio of \(\text{HA}\) depletion to \(\text{H}_2\text{O}_2\) consumption was about 0.512 in the \(\text{H}_2\text{O}_2/\text{HA}\) system, supporting the two major steps (reactions 1 and 2) involved in the reaction between \(\text{HA}\) and \(\text{H}_2\text{O}_2\). In contrast, the slope of the stoichiometric ratio in the \(\text{Ce(IV)}/\text{H}_2\text{O}_2/\text{HA}\) system was 1.576, indicating that the amount of \(\text{HA}\) consumed was much higher than the amount of \(\text{H}_2\text{O}_2\) consumed. Evidently, the higher \(\text{HA}\) consumption will result in rapid \(\text{RhB}\) degradation.

**2.2. Effect of Initial pH.** To understand the effect of the initial pH on the \(\text{RhB}\) decolorization process by the \(\text{Ce(IV)}/\text{H}_2\text{O}_2/\text{HA}\) system, experiments were conducted at pH 2.0–8.0. The effect of the pH on the removal of \(\text{RhB}\) is illustrated in Figure 3. The results of these experiments revealed that the

![Figure 2](image-url)  
Figure 2. Ratio of \(\text{HA}\) depletion to \(\text{H}_2\text{O}_2\) consumption during the oxidation of \(\text{RhB}\) by \(\text{H}_2\text{O}_2/\text{HA}\) and \(\text{Ce(IV)}/\text{H}_2\text{O}_2/\text{HA}\), respectively. Reaction conditions: \([\text{RhB}]_0 = 10 \text{ mg/L}, [\text{Ce}^{4+}]_0 = 0.1 \text{ mmol/L}, [\text{H}_2\text{O}_2]_0 = 2 \text{ mmol/L}, [\text{HA}]_0 = 2 \text{ mmol/L}].

![Figure 3](image-url)  
Figure 3. Effect of the pH on the decolorization of \(\text{RhB}\) by the \(\text{Ce(IV)}/\text{H}_2\text{O}_2/\text{HA}\) system. Reaction conditions: \([\text{RhB}]_0 = 10 \text{ mg/L}, [\text{Ce}^{4+}]_0 = 0.1 \text{ mmol/L}, [\text{H}_2\text{O}_2]_0 = 2 \text{ mmol/L}, [\text{HA}]_0 = 2 \text{ mmol/L}].

\[
\text{HO}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} \tag{7}
\]

\[
\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2^+ \tag{8}
\]

RHB degradation decreased with increasing pH; the maximum color removal efficiency was observed when the pH value of the dye solutions was 4. Hence, pH 4 is considered to be the optimal pH for \(\text{RhB}\) degradation and selected as the solution pH for further experiments. The degradation of \(\text{RhB}\) was significantly inhibited at pH 2.0, which can be explained by the presence of high proton concentrations that inhibited the reaction of hydroxyl radical with dye molecules, as hydrogen ions can scavenge hydroxyl radicals via reaction 7.29,30 In addition, formation of electrophilic protonated \(\text{H}_2\text{O}_2 (\text{H}_3\text{NOH}^+)\) is another scavenging reaction via reaction 8.31

\[
\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2^+ + \text{H}^+ \tag{9}
\]

In the case of pH \(\leq 6\), a sharp increase in efficiency after 30 min was observed. The change in pH of the solution during the experiment was monitored and significant decrease from 5 to 4.5 after reaction 30 min in the solution pH was noted, which resulted in an increase in the rate of \(\text{RhB}\) degradation. It is believed that the \(\text{H}^+\) is generated through reactions 2–4, which are the main sources of hydrogen production.

At high pH values (pH > 6), the degradation of \(\text{RhB}\) is almost completely inhibited. The observed decrease in \(\text{RhB}\) degradation with the increase in pH may be attributed to the scavenging of \(\text{HO}^*\) by the increase of \(\text{HA}\) with increasing pH value. Because the p\(K_a\) value of \(\text{HA}\) is 5.96,32 when the pH value is below 5, most of the \(\text{HA}\) is in its protonated form (\(\text{H}_3\text{NOH}^+)\), whereas at a pH value in the range of 6.0–14.0, it is mainly in its unprotonated form (\(\text{H}_2\text{NOH}\)). It has been reported that the reaction rate between \(\text{HO}^*\) with \(\text{H}_2\text{NOH}\) is
faster than that between HO• with H3NOH+ via reactions 833 and 9,34 respectively. In addition, some researchers have proposed that the protonated form of NH2O•+, the one-electron transfer intermediate of HA with a pK_a1 of about 4.2, reacts much faster with H2O2 than the unprotonated NH2O• to produce HO•.35 Under acidic conditions, most of the NH2O• are protonated, and thus the HO• production increases with decreasing pH. Moreover, another factor controlled by the pH is the activity of Ce(IV). The solubility product K_sp of Ce(OH)4 is 3.98 × 10^−51, thus a large percentage of Ce(IV) converts to Ce(OH)4 which may not be sufficient in the Ce(IV)/H2O2/HA process at pH higher than 6.0.25,36

\[
\text{HO}^* + \text{NH}_2\text{OH} \rightarrow \text{NOH}^* + \text{H}_2\text{O} \quad k = 9.5 \times 10^9 \text{M}^{-1} \text{s}^{-1}
\]

\[
\text{HO}^* + \text{NH}_3\text{OH}^+ \rightarrow \text{NH}_2\text{OH}^* + \text{H}_2\text{O} \quad < 5.0 \times 10^6 \text{M}^{-1} \text{s}^{-1}
\]

### 2.3. Effects of Ce(IV), H2O2, and HA Concentrations.

To investigate the application of the Ce(IV)/H2O2/HA system, RhB decolorization at pH 4.0 in the presence of varying concentrations of Ce(IV), H2O2, and HA was evaluated, as shown in Figure 4. When the concentrations of these reagents were changed, the degradation of RhB exhibited a similar trend, which suggests a close correlation between the decolorization efficiency and the concentration of Ce(IV), H2O2, and HA. However, although the degradation of RhB was considerably enhanced with increasing amounts of the initial Ce(IV), H2O2, and HA concentrations until the optimal dosage was reached, the excess of these three reagents resulted in different degrees of decrease in the degradation efficiency.

![Figure 4](image_url)

**Figure 4.** Effects of various conditions on the performance of RhB decolorization in the Ce(IV)/H2O2/HA triple system. (a) Effect of Ce(IV) dose; (b) effect of H2O2 dose; and (c) effect of HA dose. Reaction conditions: [RhB]₀ = 10 mg/L, pH_initial = 4, [H2O2]₀ = 2 mmol/L for (a) and (c), [HA]₀ = 2 mmol/L for (a) and (b), and [Ce^{4+}]₀ = 0.1 mmol/L for (b) and (c).

Notably, the observed phenomena when the concentration of Ce(IV), H2O2, and HA exceeds the optimal dosage may be attributed to the excess reagents competing with RhB to consume HO• free radicals. Consequently, the presence of superfluous reactants slows the formation of HO• radicals. In this system, it can be assumed that Ce(IV) can react with HA to produce NH2O• free radicals through reactions 3 and 4, but can also consume NH2O• free radicals by reaction 6. In addition, excessive Ce(IV) can react with H2O2 with a high rate constant following reactions 1137 and 12,38 whereas the HO• radical competes with the reduction product Ce(III) by reaction 14.39

\[
\text{Ce(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{Ce(III)} + \text{HO}_2^* + \text{H}^+
\]
Increased degradation of RhB was observed with the increase in the initial HA concentration. This is because more HA was used to combine with Ce(IV) to produce more NH2O radicals, and HO radicals were further generated by reactions 1, 3, and 4. However, a vast number of HO radicals could be quenched by HA with high rate constants, especially when the HA concentration was sufficiently high via reactions 9 and 10, resulting in a decrease in RhB removal. Similarly, excess H2O2 reacts with HO radicals through reaction 16. Therefore, a defined amount of Ce(IV), H2O2, and HA should be selected in the application to maximize the degradation of target compounds and reduce costs.

\[ \text{HO}_2^* + \text{Ce(IV)} \rightarrow \text{Ce(III)} + \text{O}_2 + \text{H}^+ \]  
\[ \text{HO}_2^* + \text{Ce(III)} \rightarrow \text{Ce(IV)} + \text{HO}_2^- \]  
\[ \text{Ce(III)} + \text{HO}^* \rightarrow \text{Ce(IV)} + \text{OH}^- \]

2.4. Identification of Primary Reactive Oxidants.
Considering the reactions discussed above, it is proposed that hydroxyl radicals are the main active species in the Ce(IV)/H2O2/HA system. Because HO radicals have a short lifetime (usually 10^{-6} s in a cell), it is difficult to measure directly. Coumarin is a low-fluorescence molecule but can form the strong fluorescent compound 7-hydroxycoumarin (7OHC, also known as umbelliferone) by reacting with hydroxyl radicals in aqueous solutions. Therefore, an indirect detection method was used in this experiment in which coumarin was regarded as a probe in the medium. All the time, the fluorescence intensity of 7OHC under various conditions is presented in Figure 5. These results show that H2O2/HA and Ce(IV)/H2O2/HA systems were able to induce HO production, and the yield of HO between the two systems is quite different. In the Ce(IV)/H2O2 system, the fluorescence intensity of 7OHC was negligible, which confirmed that the reaction between Ce(IV) and H2O2 does not produce hydroxyl radicals. The phenomena observed above are consistent with the degradation trend of RhB shown in Figure 1a. In addition, further quantitative experiment of hydroxyl radical production was investigated. Figure 6 shows HO concentrations as a function of reaction time in the H2O2/HA and Ce(IV)/H2O2/HA systems, respectively. Reaction conditions: \([\text{benzoic acid}]_0 = 1 \text{ mmol/L}, [\text{Ce}^{4+}]_0 = 0.1 \text{ mmol/L}, [\text{H}_2\text{O}_2]_0 = 2 \text{ mmol/L}, [\text{HA}]_0 = 2 \text{ mmol/L}, \text{and pH}_{\text{ini}} = 4.\]

\[ \text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
\[ \text{H}_2\text{O}_2 + \text{HO}^* \rightarrow \text{HO}_2^-/\text{O}_2^- + \text{H}_2\text{O} \]

Figure 5. Fluorescence intensity of 7-hydroxycoumarin (7OHC) at different reaction time by the Ce(IV)/H2O2/HA system. Reaction conditions: \([\text{coumarin}]_0 = 0.1 \text{ mmol/L}, [\text{Ce}^{4+}]_0 = 0.1 \text{ mmol/L}, [\text{H}_2\text{O}_2]_0 = 2 \text{ mmol/L}, [\text{HA}]_0 = 2 \text{ mmol/L}, \text{and pH}_{\text{ini}} = 4.\]

Figure 6. HO concentrations as a function of reaction time in the H2O2/HA and Ce(IV)/H2O2/HA systems. Reaction conditions: \([\text{benzoic acid}]_0 = 1 \text{ mmol/L}, [\text{Ce}^{4+}]_0 = 0.1 \text{ mmol/L}, [\text{H}_2\text{O}_2]_0 = 2 \text{ mmol/L}, [\text{HA}]_0 = 2 \text{ mmol/L}, \text{and pH}_{\text{ini}} = 4.\]
and chromophore cleavage happened simultaneously. How-
blue-shifted. Accordingly, we postulated that treatment time, and the absorption peak at 554 nm was slightly nm gradually decreases to disappear with the increase of the spectrum, as shown in Figure 8. The absorption peak at 554 times was determined by scanning across the full UV −
ultraviolet treated with the Ce(IV)/H2O2/HA triple system at di-
rapid decolorization and mineralization of dyes. Thus, the Ce(IV)/H2O2/HA triple system can accomplish
degradation time of 0, 5, 10, 20, 30, and 60 min by the Ce(IV)/
E
Figure 7. Effect of quenching agents on degradation of RhB by Ce(IV)/H2O2/HA triple system. Reaction conditions: [Ce4+]0 = 0.1 mmol/L, [H2O2]0 = 2 mmol/L, [HA]0 = 2 mmol/L, and pHini = 4.

and then reached 44.4, 70.4, and 85.6% after reacting for 3, 6, and 12 h, respectively. As the reaction time increases, the amount of TOC removal increases, basically due to the further decomposition of the formed intermediates. In contrast, only a low TOC removal efficiency (3.7%, data not shown) was observed in the H2O2/HA system even after 12 h of reaction. Thus, the Ce(IV)/H2O2/HA triple system can accomplish rapid decolorization and mineralization of dyes.

To investigate the mechanism of RhB degradation, the ultraviolet–visible (UV−vis) absorbance of the RhB solutions treated with the Ce(IV)/H2O2/HA triple system at different times was determined by scanning across the full UV−vis spectrum, as shown in Figure 8. The absorption peak at 554 nm gradually decreases to disappear with the increase of the treatment time, and the absorption peak at 554 nm was slightly blue-shifted. Accordingly, we postulated that N-deethylation and chromophore cleavage happened simultaneously. However, the diminishment of the absorption band was much more obvious than the blue-shift, indicating that the chromophore cleavage was the major step of RhB degradation, and this inference can be further authenticated by gas chromatography–mass spectrometry (GC–MS) analysis.

GC–MS analysis was performed to further investigate the major degradation intermediates to propose the possible RhB oxidation pathway in the Ce(IV)/H2O2/HA triple system. The detected intermediates included phenol, ethanamine, 2-hydroxypropanoic acid, phthalic acid, 3-(isopropoxynamino)-propane-1,2-diol, malonic acid, propane-1,2,3-triol, and terephthalic acid, which are shown in Table 1. The formed intermediate compounds are similar to those previously reported in the literature on the degradation of RhB dye by the conventional Fenton process. According to all the identified products, we concluded that the oxidation process of RhB can be described to two main steps. They are (1) chromophore cleavage and N-deethylation and (2) mineralization of dye. Normally, the RhB was first degraded to aromatic compounds and then oxidized to ring-opening products and organic acids. It has been determined that the chromophore cleavage and N-deethylation process occurs through the diminishment of the absorption band of RhB at 554 nm. After chromophore cleavage, the generation of malonic acid and 2-hydroxypropanoic acid indicate that the RhB dye molecule is effectively oxidized into smaller carboxylic acid compounds. These carboxylic acid compounds could avoid an increase in the pH value and the accumulation of Ce(IV), thereby reducing the production of insoluble cerium hydroxide. Ultimately, all the small molecular intermediates could be mineralized into CO2 and H2O, as evidenced by the TOC content measurements. According to the above experimental results, we propose a possible degradation pathway of RhB in the Ce(IV)/H2O2/HA triple system (Figure 9).

These results confirmed that the complex macromolecule of RhB could be opened to form small molecules after its degradation, demonstrating that the degradation-competent form of the Ce(IV)/H2O2/HA system is desirable.

3. CONCLUSIONS
In this study, rapid decolorization and mineralization of RhB were observed in the Ce(IV)/H2O2/HA system. Additionally, a possible reaction mechanism for Ce(IV)/H2O2/HA system, which is different from the traditional Fenton-like reaction, is proposed. First, Ce(IV) and its hydrolyzed hydroxide [Ce(OH)2+] were combined with protonated hydroxylamine (NH2OH+) to form an intermediate ligand Ce(IV)−HA. The intermediate was further decomposed to produce the aminoxyl radical (NH2O•) and the reduced Ce(III). Then, the NH2O• generated in the first step reacted with H2O2 to produce highly oxidative HO• radicals, and Ce(III) was oxidized by H2O2 and HO• into Ce(IV). Eventually, the HO• radicals attacked the central carbon of RhB and degraded it to carboxylic acids. The decolorization efficiency of RhB increased with decreasing pH. In the optimum ratio of Ce(IV)/H2O2/HA (0.1:2:2), about 80% of the RhB was decolorized within 60 min. The HO• radicals were found to be the main reactive oxidant through coumarin-capturing and radical-quenching experiments. Furthermore, the TOC content analysis, UV−vis spectroscopy, and GC–MS analysis results demonstrated that the degradation-competent form of the Ce(IV)/H2O2/HA system is satisfactory. Moreover, additional studies should not be confined to Ce(IV) only but also involve other metal ions that can react with HA to enhance the production of NH2O•.
which may act similar to Ce(IV) in the Ce(IV)/H₂O₂/HA process.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Rhodamine B (RhB, ≥90%), selected as substrate, was supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). All the other chemicals used in this study, including hydroxylamine hydrochloride (HA, ≥99%), hydrogen peroxide (H₂O₂, 35 wt %), ceric sulfate [Ce(SO₄)₂·4H₂O], coumarin, p-benzoquinone (p-BQ), H-histidine, benzoic acid (BA), salicylic acid, and tert-butyl alcohol (TBA) were of analytical grade and purchased from Aladdin Reagent Co., Ltd. NaOH and H₂SO₄, used to adjust the pH of solutions, were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared using 18.15 MΩ cm ultrapure water from a Millipore system (Water purifier, Sichuan, China). The H₂O₂ and HA solutions were freshly prepared before each experiment to minimize variations in concentration caused by self-decomposition.

4.2. Oxidation Reaction. All experiments were performed in a 100 mL round-bottom flask at air-conditioned room temperature (23 ± 2 °C) and under normal laboratory light. Each reactor was operated in batch mode with constant magnetic stirring provided at the bottom of the reactor. The reaction solution was prepared by adding HA solutions and the organic contaminant (and Ce⁴⁺). RhB stock solution (500 mg/L) was prepared in deionized distilled water, and specific aliquots of the solution were added into the reactors to achieve a predetermined initial concentration. The pH of the solution was adjusted using 1 N H₂SO₄ or 1 N NaOH solution to the desired value. The reaction was initiated by adding an aliquot

| m/z | Retention time (min) | Identified intermediates | Structural formula |
|-----|---------------------|-------------------------|--------------------|
| 94  | 8.30                | pheno                   | ![Pheno Structure](image) |
| 45  | 8.44                | ethanamine              | ![Ethanamine Structure](image) |
| 138 | 8.60                | 2-hydroxyproanoic acid  | ![2-Hydroxyproanoic Acid Structure](image) |
| 166 | 8.82                | phthalic acid           | ![Phthalic Acid Structure](image) |
| 149 | 12.57               | 3-(isopropoxyamino)propane-1, 2-diol | ![3-(Isopropoxyamino)propane-1, 2-diol Structure](image) |
| 104 | 13.19               | malonic acid            | ![Malonic Acid Structure](image) |
| 92  | 13.80               | propane-1,2,3-triol     | ![Propane-1,2,3-triol Structure](image) |
| 166 | 20.71               | terephthalic acid       | ![Terephthalic Acid Structure](image) |
| 278 | 22.50               | dibutyl phthalate       | ![Dibutyl Phthalate Structure](image) |
of a freshly prepared stock solution of H₂O₂. At the same time, the pH was measured once again; the variation in pH after the addition of H₂O₂ was less than 0.1 pH units. Samples (3 mL) were withdrawn at predetermined intervals and mixed immediately with appropriate amount of sodium sulfite (0.16 mL) to quench the reaction. The experiments were performed in replicate and the mean value were taken into account; the standard deviations were limited to <10%.

4.3. Analysis. The concentration of the RhB dye (λ_max = 554 nm) in the treated solution was analyzed with a UV−vis spectrophotometer (UV-2550, Shimadzu Corp., Kyoto, Japan). The H₂O₂ concentration was determined spectrophotometrically using the Ti(SO₄)₂ method, and the concentration of HA was measured by Molybdenum Blue Photometry. The pH was measured with a Mettler-FE20 pH meter (Mettler-Toledo, Zürich, Greifensee, Switzerland). The fluorescence intensity of 7-hydroxycoumarin and salicylic acid was analyzed on a Fluorescence Spectrometer (RF-5301PC, Shimadzu Corp.). The total organic carbon (TOC) content of the samples was determined using a TOC analyzer (Liqui TOC II; Elementar Analysensysteme GmbH., Hanau, Germany). For each TOC analysis, 20 mL of RhB solution was treated immediately after the treatment with scavenging reagent (0.1 M Na₂SO₃) to obtain the accurate TOC values, and this procedure led to a complete reduction of the residual H₂O₂. The productivity of HO* in the system was investigated by using the oxidation of benzoic acid (BA) as the model reaction according to the method described by Grossman.

The intermediate products of RhB degradation were examined on a gas chromatography−mass spectrometry (GC−MS) system (QP2010 Ultra, Shimadzu Corp.). The GC column was operated in a temperature-programmed mode at an initial temperature of 40 °C held for 4 min, then ramped to 80 °C at a rate of 10 °C/min and held for 2 min, and finally increased to 280 °C at a rate of 10 °C/min and held at that temperature for 10 min. An injection volume of 0.1 μL was used with helium as carrier gas. The system was operated in the electron impact mode at 70 eV and the spectra were recorded in a scan range of 10−400 m/z. The product analysis was referred to the NIST11 mass spectral library database.

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**Figure 9.** RhB degradation pathway in the Ce(IV)/H₂O₂/HA triple system.

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**Notes**

The authors declare no competing financial interest.

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