

Ozonation of dimethyl phthalate in water activated by N-methyl hydroxylamine

Zhang Gucheng, Zhang Jing, Zhang Yongli, Zhou Peng, Wei Chenmo, Li Wenshu and Liang Tao

ABSTRACT

The degradation of dimethyl phthalate (DMP), which is a pollutant of concern in the water environment, was carried out by catalytic ozonation with N-methyl hydroxylamine (N-HA) at different pH. The process and mechanism were investigated for the removal of DMP and ozone (O_3) under various experimental conditions including pH, N-HA dosage, and with or without tert-butyl alcohol (TBA). The results indicated that the removal of DMP was more efficient in the O_3 /N-HA system than sole O_3 , and the efficiency improved with increasing N-HA dosage. The levels of N-HA protonation were 99.89%, 8.36%, and 0.06% at pH 3.0, 7.0, and 9.2. Protonated N-HA ($N\text{-CH}_3\text{NH}_2\text{OH}^+$) enhanced the degradation of DMP from 6.93% to 100% at pH 3.0, and it decreased when pH was raised to 7.0 and 9.2 because of the lower level of N-HA protonation. The results of adding TBA confirmed that hydroxyl radicals ($\bullet\text{OH}$) were the main active species involved in the removal of DMP during the ozonation process.

Key words | advanced oxidation process, dimethyl phthalate, N-methyl hydroxylamine, ozone

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INTRODUCTION

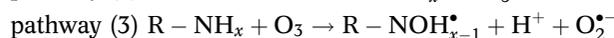
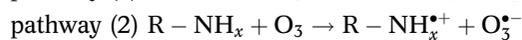
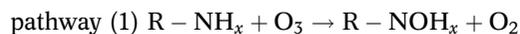
Nowadays, with the pollutants in water becoming more complex and persistent, traditional water treatment faces great challenges. Dimethyl phthalate (DMP) is a kind of phthalic acid ester (PAE) which increases human health risk due to its toxicity and persistence (Abdel daiem *et al.* 2012). A little DMP occurs in hydrolysis and photolysis reactions (Wolfe *et al.* 1980; Bajt *et al.* 2001), with most of it still existing in natural environmental systems. Traditional water treatment technology also cannot remove the compound effectively (Halmann 1992; Crisp *et al.* 1998), so advanced oxidation processes (AOPs) that can promote the degradation efficiency of organic pollutants have attracted increasing attention because of the generation of hydroxyl radical ($\bullet\text{OH}$), which is a strong oxidant ($E_0 = 1.8\text{--}2.7\text{ V}$) (Chen *et al.* 2012) that can degrade micro molecular refractory compounds into innocuous molecules (Ding *et al.*

2008; Yuan *et al.* 2008; Souza *et al.* 2013). In order to degrade DMP, researchers have achieved some good results with AOPs, such as catalytic ozonation (Chen *et al.* 2008, 2011), photocatalysis oxidation (Yuan *et al.* 2008), ultrasonic oxidation (Xu *et al.* 2013), and so on.

Ozone (O_3) is commonly used in water treatment on account of its high oxidation activity with the pollutant (Broseus *et al.* 2009). Catalytic ozonation process can overcome the limitation of ozonation processes, especially the selective oxidation reactions of O_3 (Andreozzi *et al.* 1996; Legube & Leitner 1999), and enhance the generation of $\bullet\text{OH}$ through accelerating its chain decomposition (Elovitz & von Gunten 1999).

The catalytic ozonation process aiming to degrade organic pollutants utilizes the characteristic of some organics with the functional groups of $-\text{NH}_x$, such as amines,

which can react with O_3 , rapidly accelerating the decomposition of O_3 to generate $\cdot OH$ in order to improve the degradation efficiency of organic pollutants (Buffle & von Gunten 2006). Previous studies have shown the mechanism to be summarized by pathways (1)–(3), as follows (Hoigne *et al.* 1985; Buffle & von Gunten 2006) ($R-NH_x$ represents amines):



The primary products are a kind of aminoxide and oxygen (pathway (1)). The generation of amine radical cation and $O_3^{\bullet-}$ (pathway (2)) is believed to be the result of electron transfer from the nitrogen atom of the amine to ozone with subsequent transformation of the ion pair (Denisova & Denisov 1998), while pathway (3) acts as a promoter for the O_3 decomposition with hydrogen atom abstraction. In addition, dimethylamine and trimethylamine reacted with O_3 rapidly at neutral initial pH (Buffle & von Gunten 2006), because O_3 reacts several orders of magnitude faster with deprotonated amines than protonated amines (von Gunten 2003), and the protonation of amines depends on pH (Munoz & von Sonntag 2000). Thus, the reaction between amines and O_3 in acidic solution can hardly be triggered, and the protonated amines cannot cause O_3 decay.

Hydroxylamine (HA) is a common reducing agent and also an intermediate during the oxidation of amines by O_3 (Johnson *et al.* 2002; Yang *et al.* 2009). However, HA is different from other amines, because of the $^+NH_3O^-$ structure (Kirby *et al.* 2006), and it may react as an oxygen nucleophile with O_3 at acid solution. Therefore, the aim of this paper is to investigate the oxidation ability of N-methyl hydroxylamine (N-HA) which has a similar structure to HA and pathway of $\cdot OH$ generation in O_3 /N-HA system at different pH.

METHODS

N-HA was supplied by Sigma-Aldrich. Sodium dihydrogen phosphate, tert-butyl alcohol (TBA), disodium hydrogen phosphate, sodium tetraborate, sodium hydroxide, vitriol, sodium thiosulfate and indigo were purchased from

Sinopharm Chemical Reagent Co., Ltd. DMP was obtained from TCI Shanghai Company. All the chemicals were analytical grade and solutions were prepared from reagent-grade chemicals and ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) purified using a lab pure water system (ULUPURE).

Ozone was synthesized by using an ozone generator (HTU-500SE, AZCO Industries Limited, Canada) with dry oxygen as the supply gas. The O_3 decomposition experiments were carried out under initial O_3 concentration = 2 mg/L in a 1,000 mL flask, while O_3 mixed solution in the other experiments was produced by continuous bubbling of ozone-containing oxygen gas.

All experiments were carried out at $20 \pm 1^\circ\text{C}$ with constant stirring using a magnetic stirrer. pH was adjusted before the addition of O_3 , then the desired dosages of DMP and N-HA were simultaneously added into the reactor to start the reactions. Samples were collected at set intervals and quenched by sodium thiosulfate before analysis. TBA was employed as the hydroxyl radical scavenger to identify the main reactive oxidant in the whole process.

The concentrations of DMP were analyzed by a high-performance liquid chromatography (HPLC, LC-10A, Shimadzu) equipped with SPD-10A UV-vis detector and a reverse-phase C18 column ($5 \mu\text{m}$ particles, $4.6 \times 150 \text{ mm}$). The mobile phase was methanol and water with the ratio of 50:50 (v/v) at a flow rate of 1 mL/min. The sample injection volume was 20 μL and DMP was detected at the wavelength of 232 nm. The pH was measured by pH meter (FE28-Standard, Mettler Toledo). Dissolved O_3 was measured by the Indigo method (Bader & Hoigne 1982) using UV-vis spectrophotometer (UV-1800, Mapada Instruments, China) under 610 nm. Measurements display the following statistics: 95% confidence intervals of O_3 concentration measurements in O_3 decomposition experiments, and DMP displays 95% confidence intervals.

RESULTS AND DISCUSSION

Figure 1 shows the effect of degradation of DMP at pH (a) 3.0, (b) 7.0, and (c) 9.2 with the different N-HA dosages. As shown in Figure 1(a), it was weak for the O_3 alone system to degrade DMP at pH 3.0 and there was only 6.93% removed in 3 min. It was reported that the

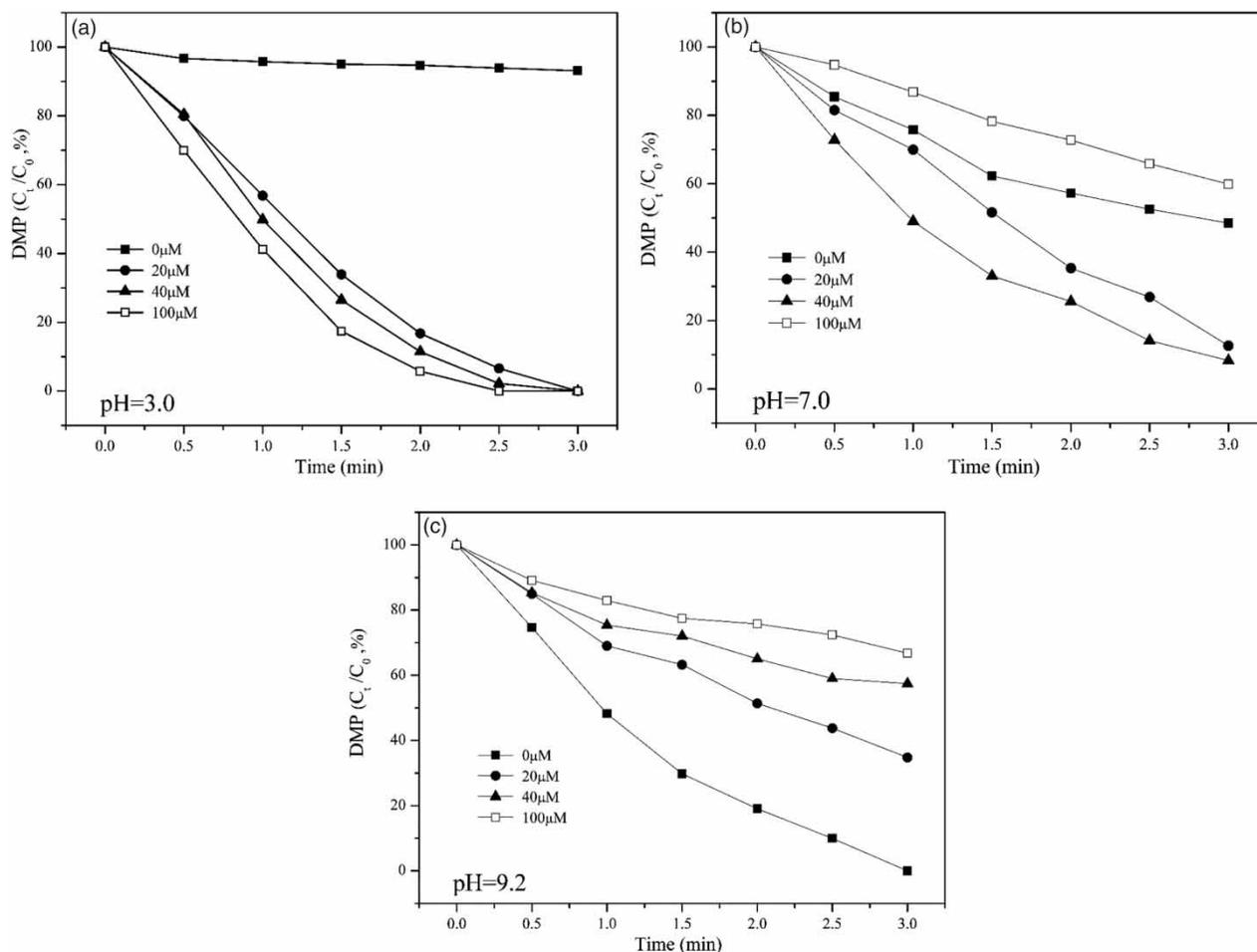


Figure 1 | Degradation of DMP at different levels of N-HA protonation (O_3 flux = 5.5 mg/(L·min), $[DMP]_0 = 1$ mg/L, $[N-HA]_0 = 0, 20, 40, 100$ μM).

degradation of DMP during the ozonation process was mainly caused by $\cdot OH$ ($K_{obs} = 2.67 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) generated from O_3 chain decomposition; however, the yield of $\cdot OH$ was very small resulting in little DMP degradation under acidic condition (Wen *et al.* 2011). The presence of N-HA significantly accelerated the degradation of DMP at pH 3.0. The degradation rate was enhanced from 6.93% to nearly 100% when N-HA concentration was increased within the range from 0 μM to 100 μM in the O_3 /N-HA system. Thus, it could be inferred that the addition of N-HA may enhance the generation of $\cdot OH$ during the O_3 decomposition, resulting in the strong enhancement of DMP degradation.

Moreover, as shown in Figure 1(b), the degradation rate of DMP in 3 min increased from 51.51% to 91.68% while the concentration of N-HA rose from 0 μM to 40 μM at pH 7.0. However, the degradation rate of DMP in 3 min

decreased to 40.1% when the dosage of N-HA was 100 μM. This revealed that under neutral condition a small amount of OH^- could enhance the decomposition of O_3 , that led to the degradation of DMP without N-HA. However, when 100 μM N-HA was added into the system, excess N-HA which had reducibility competed with DMP for $\cdot OH$ and the competition meant less DMP was removed.

In addition, the DMP degradation was significantly inhibited with the addition of different dosages of N-HA, as shown in Figure 1(c) at pH 9.2. The oxidation ability was more powerful without N-HA that caused more DMP to be removed compared to the result in Figure 1(b). It suggested that OH^- could accelerate O_3 chained decomposition and generate more $\cdot OH$.

As is known, N-HA ($pK_a = 5.96 \pm 0.05$ (Zubareva *et al.* 2007)) has protonated ($N-CH_3NH_2OH^+$) and deprotonated

(N-CH₃NHOH) forms in aqueous solution and the relative content of them is strongly dependent on the pH. The levels of N-HA protonation were 99.89%, 8.36%, and 0.06% at pH 3.0, 7.0, and 9.2, respectively. Based on the results from Figure 1, the level of N-HA protonation influenced its catalytic ability, and more N-CH₃NH₂OH⁺ may led to better degradation of DMP. In addition, the inhibition of DMP degradation was due to the excess N-HA dosage that might react with •OH generated by O₃ chained decomposition with high reaction rate constant in the O₃/N-HA system at alkaline condition.

In order to investigate the effect of N-HA on the generation of •OH in the N-HA/O₃ system, TBA was selected as the hydroxyl radical scavenger resulting from its reaction rate constant being $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ with •OH (Buxton et al. 1988) and only $1.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ with O₃ (Neta

et al. 1988). Figure 2(a) shows the degradation of DMP in the O₃ and O₃/N-HA systems with or without the presence of TBA at pH 3.0. The degradation rate of DMP in the O₃ system within 15 min was 6.93% which was much lower than that in the O₃/N-HA system. The addition of TBA significantly decreased DMP degradation rate in the O₃/N-HA system from 100% to 4.08%. Therefore, the results indicated that •OH was the main oxidant species in the O₃/N-HA system at pH 3.0 and the presence of N-HA could accelerate the generation of •OH resulting in the enhancement of DMP degradation. According to previous research, the presence of hydroxyl group (-OH) in the structure of N-HA probably enhanced the interaction between O₃ and N-HA that led to •OH being generated (Chen et al. 2015).

Figure 2(b) and 2(c) show the degradation of DMP in the O₃ and O₃/N-HA systems with or without the presence of

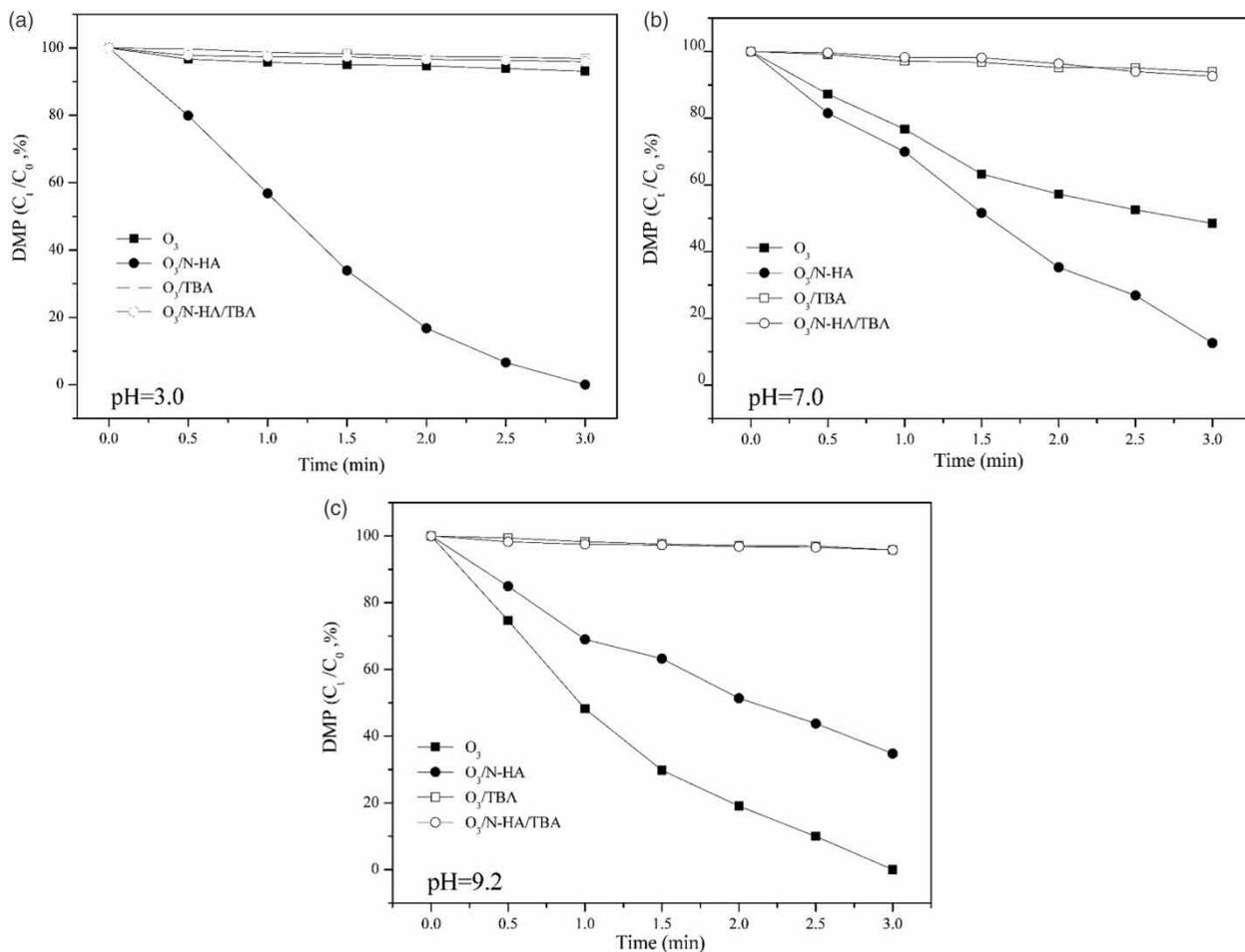


Figure 2 | Degradation of DMP with TBA (O₃ flux = 5.5 mg/(L·min), [DMP]₀ = 1 mg/L, [N-HA]₀ = 20 μM, [TBA]₀ = 25 mM).

TBA at pH 7.0 or 9.2. The degradation of DMP had the same trend in the O_3 /N-HA system with or without TBA and indicated that $\cdot OH$ was also generated during O_3 chain decomposition activated by different levels of N-HA protonation. As well, the degradation rates of DMP in the O_3 system at pH 7.0 or 9.2 were much higher than that at pH 3.0, and were 51.51% and 100%, respectively, because the rate constant of O_3 decomposition process changed at different pH (Beltran 1995).

Previous studies indicated that pH affected the reaction between amines with O_3 mainly via controlling the relative content of protonated and deprotonated amines (Hoigne et al. 1985; Buffle & von Gunten 2006). Figure 3(a)–3(c) show the O_3 decomposition with or without the presence of N-HA at pH 3.0, 7.0, and 9.2. Interestingly, the decomposition of O_3 was accelerated with the presence of N-HA in

the O_3 /N-HA system under acidic, neutral and alkaline conditions. The proportion of protonated N-HA was approximately 99.89%, 8.36%, and 0.06% at pH 3.0, 7.0, and 9.2, respectively. It could be indicated that both protonated and deprotonated N-HA could enhance the O_3 decomposition. Results presented in Figure 3 suggested that the decomposition rate of O_3 increased with more N-HA added. However, the enhancement was weaker with increased pH because more OH^- existing in the system made O_3 decompose more quickly.

It has been reported that protonated (NH_3OH^+) hardly reacted with O_3 and $\cdot OH$ compared with deprotonated HA (NH_2OH) (Broseus et al. 2009) ($k_{NH_3OH^++O_3} < 2 M^{-1} s^{-1}$, $k_{NH_2OH+O_3} = 2.1 \times 10^4 M^{-1} s^{-1}$ (Johnson et al. 2002), $k_{NH_3OH^++\cdot OH} < 5 \times 10^7 M^{-1} s^{-1}$, $k_{NH_2OH+\cdot OH} = 8.5 \times 10^9 M^{-1} s^{-1}$ (Johnson et al. 2002)). Although the structure of

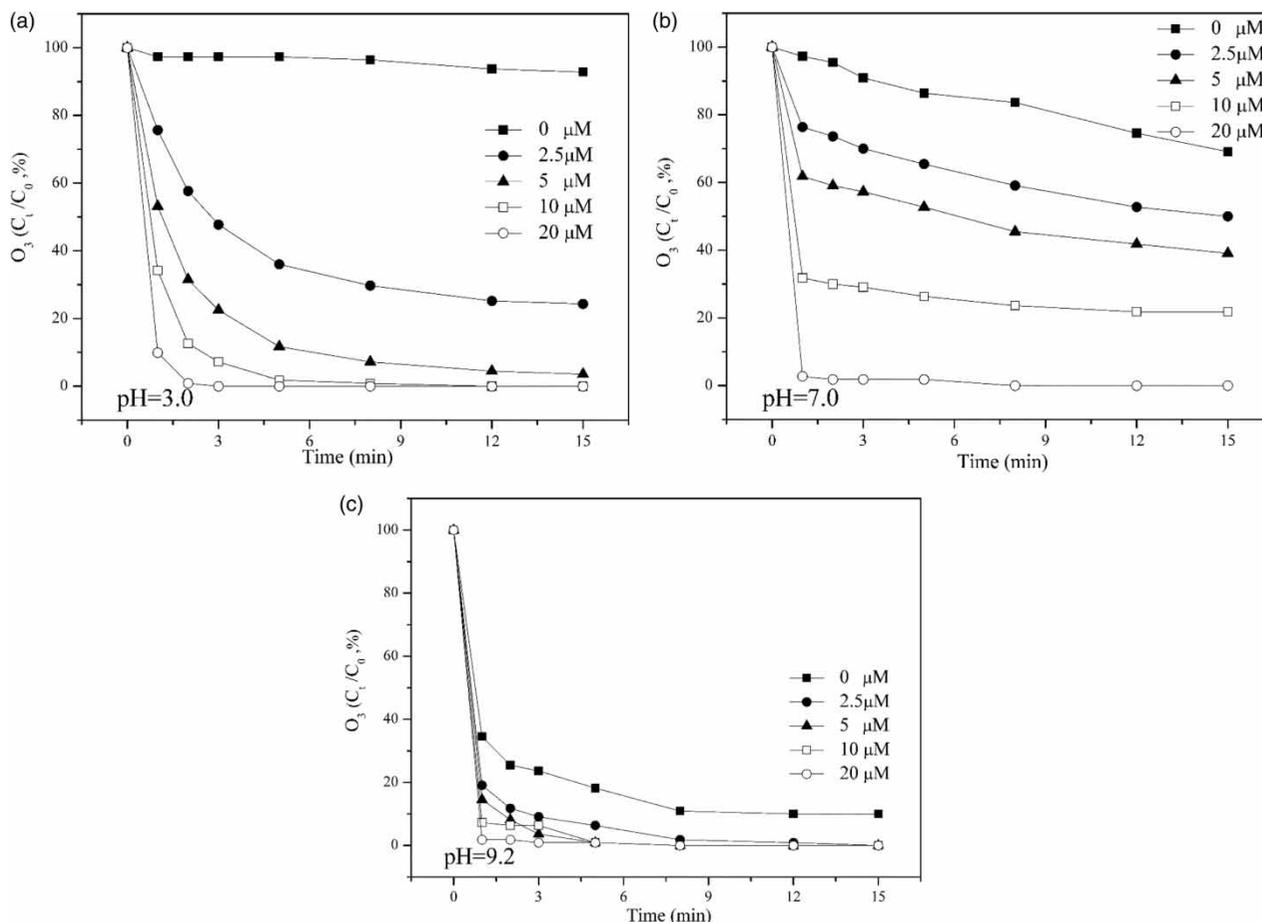


Figure 3 | Decomposition of O_3 at different level of N-HA protonation ($[O_3]_0 = 2 \text{ mg/L}$, $[DMP]_0 = 1 \text{ mg/L}$, $[N-HA]_0 = 0, 2.5, 5, 10, 20 \mu M$).

N-HA is similar to HA, its protonated state ($\text{N-CH}_3\text{NH}_2\text{OH}^+$) enhanced the O_3 decomposition improving the oxidation ability. It was guessed that protonated N-HA was involved in O_3 chain decomposition promoting the generation of $\cdot\text{OH}$, but the reaction pathway needs further study.

Based on earlier research, the presence of TBA can stop the generation of $\text{O}_2^{\cdot-}$ via the radical chain reaction, but cannot stop the direct formation of $\text{O}_2^{\cdot-}$ via the reaction between O_3 and amines (Buffle & von Gunten 2006). Therefore, the addition of TBA into the processes was studied to confirm the mechanism of the $\text{O}_3/\text{N-HA}$ system.

Figure 4 shows the effect of TBA on the O_3 decomposition at pH (a) 3.0, (b) 7.0, and (c) 9.2. With TBA introduced in the experiments without N-HA, the decomposition rate of O_3 increased by about 16.21%. TBA reacted with $\cdot\text{OH}$ that led the amount of $\cdot\text{OH}$ to lower, and the

forward reaction of O_3 chain decomposition was promoted. As well, the addition of TBA decelerated the O_3 decomposition from 96.40% to 44.14% in the $\text{O}_3/\text{N-HA}$ system at pH 3, so it suggested that catalysis ability of protonated N-HA was mainly dependent on electron transfer. The influence of TBA on the decomposition process at pH 7.0 and 9.2 could almost be ignored with or without N-HA, indicating deprotonated N-HA reacted with O_3 directly that generated $\text{O}_2^{\cdot-}$.

It has been reported that the protonated HA reacted much faster with H_2O_2 than the deprotonated form (Leitner et al. 1999) and under strongly acidic condition HA was high-level protonated that increased $\cdot\text{OH}$ production (Chen et al. 2015). Therefore, the pH might affect O_3 decomposition mainly through controlling the species distribution of N-HA.

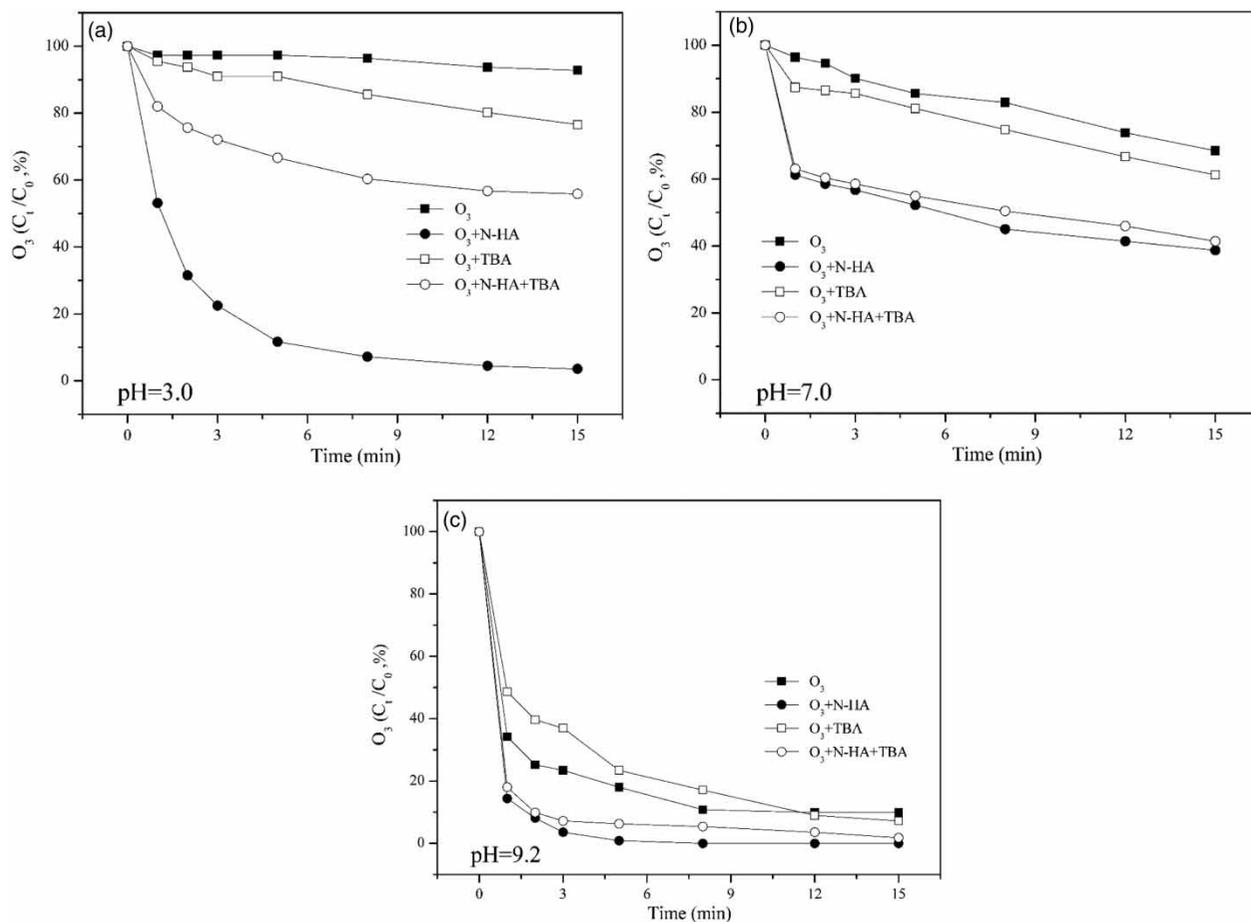
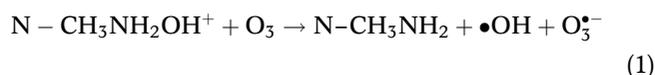
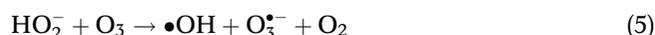


Figure 4 | Decomposition of O_3 with TBA ($[\text{O}_3]_0 = 2 \text{ mg/L}$, $[\text{DMP}]_0 = 1 \text{ mg/L}$, $[\text{N-HA}]_0 = 5 \mu\text{M}$, $[\text{TBA}]_0 = 25 \text{ mM}$).

To conclude, the results suggested that the reaction of protonated N-HA with O_3 by a direct electron transfer produced $O_3^{\bullet-}$, which was elaborated in pathway (1) below. At pH 3, the O_3 decomposition was enhanced during the whole reaction with the addition of N-HA dosage in the O_3 /N-HA system. It showed that the reaction of N-HA with O_3 at acidic pH was different from that under neutral and alkaline conditions. Due to its similar structure to HA, mentioned before, the main reactions at acidic pH are as follows:



At neutral and basic pH, as most of the N-HA was mainly deprotonated, the main reaction of N-HA and O_3 that occurred is nearly the same as other amines, as follows:



CONCLUSIONS

N-HA has a potential prospect as a promoter in the O_3 system. The addition of N-HA to the system contributed significantly to decomposition of O_3 and the generation of $\bullet OH$ at low pH. As well, the relative content of protonated and deprotonated amines was an important factor that influenced the catalytic process. In addition, the decomposition of O_3 in the presence of TBA was carried out and two possible mechanisms in the O_3 /N-HA process at different pH were proposed: (1) protonated N-HA reacted with O_3 by direct electron transfer generating $O_3^{\bullet-}$; (2) for deprotonated N-HA, the main mechanism of $\bullet OH$ generation was correlation with the formation of HO_2^- .

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