Formation and Role of H_2O_2 During Ozonation of Nitrobenzene

Liu Ke(刘可)*, *Sun Jianhong*(孙建红), *Zhou Tao*(周涛)

College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P. R. China

(Received 16 March 2014; revised 6 July 2014; accepted 20 July 2014)

Abstract: To better understand the formation of H_2O_2 in the ozonation of nitrobenzene and its role for the oxidation, a batch reactor of nitrobenzene ozonation was set up. The variables such as pH value, ozone dosage, and the presence of hydroxyl radical scavenger were investigated. The results showed that high accumulations of H_2O_2 were generally formed at low pH values and low ozone dosages. Moreover, H_2O_2 mainly formed after nitrobenzene was oxidized by hydroxyl radical during ozonation of the intermediates, such as *p*-nitrophenol, which reacted with ozone quickly in water. A small amount of additional H_2O_2 enhanced the nitrobenzene removal slightly. The kinetic study showed that nitrobenzene degradation fitted with pseudo-second-order kinetics well in the experiment. The kinetic constant values correlated linearly with the concentrations of H_2O_2 added. Thus, it is expected that the H_2O_2 formed in oxidation of nitrobenzene may initiate ozone decomposition to form hydroxyl radical and finally enhance the degradation of aromatic compounds to a certain extent.

Key words: formation of H_2O_2; ozonation of nitrobenzene; hydroxyl radical; kinetic constant values

CLC number: TU991.2 **Document code**: A **Article ID**: 1005-1120(2014)04-0445-07

1 Introduction

The products of organic compounds oxidation by ozone have been studied extensively in drinking water treatment for many years. H_2O_2 is commonly generated during ozone decay and aromatic ring or carbon double-bond cleavage by ozone, which has been previously verified as an important trace intermediate in aqueous ozone decay[1-5]. Parts of H_2O_2 will dissociate into HO_2^- and then react with ozone to produce $\cdot O_2^-$ and $\cdot O_3^-$ radicals, which thus act as a further chain carrier and finally generate hydroxyl radical (OH), the species of a known powerful oxidant ($E^0 = 2.8$ V) that reacts with organics in an unselective way in water[6-8]. Previous studies showed that H_2O_2 was also formed during the ozonation of nitrobenzene (NB), which is a relative persistent aromatic compound used in the manufacture of dyes, plastic, pesticides, explosives, and pharmaceuticals[9-12]. Kinetic studies of ozone and O_3/H_2O_2 reacting with NB were presented in Refs. [13, 14].

It is pointed that the intermediate products in NB ozonation such as nitrophenols, which react with ozone quickly, would generate H_2O_2 during subsequent reactions[9]. The effect of humic acids on NB oxidation by O_3/UV processes was investigated in which a certain concentration of humic acids was added and avoids any further degradation on NB. It was expected that an accumulation of H_2O_2 in solutions might induce chain promoting reactions to produce hydroxyl radical during the NB oxidation[12]. Additionally, the decay rates of aqueous ozone increased in the presence of aromatic organic solutes as H_2O_2 formed during the ozonation[5]. An interesting observation is that the amount of hydroxyl radical was enhanced during ozonation of 3-chlorophenol and phenol[15-16]. Since chlorine and nitro groups are electron withdrawing, the chemistry charac-

---

Foundation items: Supported by the National Natural Science Foundation of China (21407077); the Postdoctoral Science Foundation of Jiangsu Province (1002013C); the Fundamental Research Funds for the Central Universities (308201NS2012079); the Priority Academic Program Development Fund of Jiangsu Higher Education Institutions.

* **Corresponding author**: Liu Ke, Lecturer, E-mail: liuke@nuaa.edu.cn.

teristics of 3-chlorophenol are similar to nitrophenols. It can be assumed that the formation of hydroxyl radical is also enhanced during ozonation of nitrophenols. However, little attention has been paid to quantitatively describe the practical role of H_2O_2 on aromatic compounds ozonation so far, as H_2O_2 formed in oxidizing aromatic compounds by ozone.

Therefore, the objective of present work is to investigate the formation of H_2O_2 under different conditions during NB degradation by ozone. Influencing parameters such as pH, ozone dosage, and hydroxyl radical scavengers are evaluated to characterize the formation of H_2O_2. Efforts are also made to reveal the initiating reactions of H_2O_2 during NB oxidation by ozone and to provide general information on the fate of H_2O_2.

2 Materials and Methods

2.1 Materials and experimental methods

NB was purchased from Tianjin Third Factory, China (Analytical grade) without further purification. And it was dissolved in ultrapure water at a concentration of 9.76×10^{-4} mol • L^{-1} for storage. H_2O_2 with the purity of 30% was used. Ozonation experiments were carried out in a 200 mL all-glass batch reactor, shielded from laboratory lights with aluminum foil to prevent the decomposition of H_2O_2 and ozone. A 100 mL aqueous solution of NB was put into the glass and stirred using a Teflon coated magnetic bar to provide a homogeneous mixture. Before ozonation, oxygen was continuously purged into reactor until it was saturated. It was found that no NB was lost. Ozone, generated from high purity of oxygen (>99.99%) by ozone generator, was fed into the reactor at a rate of 1.3×10^{-4} mol • min^{-1} or 1.6×10^{-4} mol • min^{-1} through a porous column at the bottom just above the magnetic bar. The gas flow rate was 1.7 L • min^{-1}. After a specific time intervals, the whole reaction solution was stopped. Samples were withdrawn and analyzed for NB and H_2O_2 concentration. The pH was adjusted with phosphate buffer solution with a total phosphate concentration (C_T) of 1×10^{-3} mol • L^{-1}. All ozonation experiments were performed at 20±1 ℃. All solutions were prepared with Millipore Milli-Q 18 MΩ water. Other chemical compounds were of analytical grade.

2.2 Analytical methods

NB was extracted by hexane by 1:1 of volume and was measured by a SP-580 gas chromatograph with electron capture detector. The chromatographic conditions were set as follows: column temperature 160 ℃, detector temperature 220 ℃, injector temperature 200 ℃, and the carrier gas was nitrogen.

The concentration of H_2O_2 was determined by photometric method [17]. The dissolved ozone was determined by indigo method [18]. Before analysis of H_2O_2, the residual ozone was removed by continuously purging the solution with oxygen for 5 min. After 5 min of purging, no ozone was detected in the solution, and no significant H_2O_2 loss was found.

3 Results and Discussion

3.1 Formation of H_2O_2

H_2O_2 formation and NB evolution of remaining concentrations in dimensionless with time during the course of NB ozonation at pH 6.0 are shown in Fig. 1 (oxygen-saturated, $(O_3)_g$ dosage is 1.3×10^{-4} mol • min^{-1}, gas flow rate is 1.7 L/min, pH=6.0, $C_T=1\times10^{-3}$ mol • L^{-1}, and $T=20\pm1$ ℃). Small amounts of H_2O_2 (0.83×10^{-6} mol • L^{-1}) were formed rapidly within 1 min and the percentage of NB degradation was about 48%. After reaction for 2 min, the concentration of H_2O_2 did not increase noticeably while the percentage removal of NB reached 86%. In particular, within 6 min, when ozone gas was bubbled into the reactor continuously alone, the accumulation of H_2O_2 was at undetectable level in comparison to the ozonation of NB. Moreover, H_2O_2 formation in NB ozonation had also been identified by other researchers[12]. The mechanism of H_2O_2 formation was similar to the ozonation of phenol in water [1]. Within 5 min, the percentage degradation of NB was about 92%, and the concentration of H_2O_2 increased slowly to 1.01×10^{-6} mol • L^{-1}. However, the formation rate of

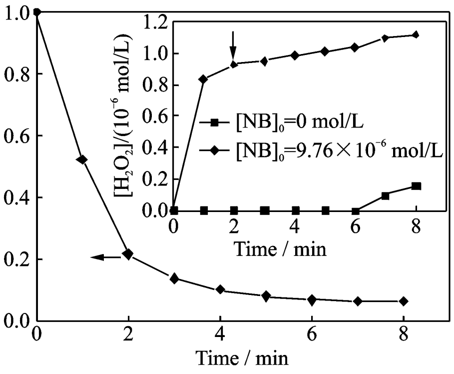

Fig. 1 NB degradation v. s. time at concentration of 9.76×10^{-6} mol • L^{-1} (Inset: H_2O_2 formation during NB ozonation)

H_2O_2 within 5 min was not rigorously proportional to the NB degradation rate during NB ozonation.

As nitro-group is electron withdrawing which diminishes the electron density of the aromatic ring, it can be deduced that direct reactions with ozone contribute little to the ozonation rate. The reaction rate constant for the oxidation of NB by molecular ozone is 0.09 L • mol^{-1} • s^{-1}[19]. On the other hand, the rate constant for the reaction of hydroxyl radical with NB is 2.9×10^9 L • mol^{-1} • s^{-1}[9]. After 1 min reaction, the concentration of ozone dissolved in solution increased, which could enhance the formation of hydroxyl radical. Then, NB was mainly degraded by hydroxyl radical oxidation, and $\cdot O_2^-$ could be formed during oxidation intermediates which acts as a further chain carrier [7, 14]. H_2O_2 formed in ozonation of NB can react with ozonation intermediates, such as organic radicals [20], glyoxal and glyoxylic acid [1], or dissociate into HO_2^- to initiate O_3 for producing hydroxyl radical in the follow minutes [6,8,21], which can decrease the concentration of H_2O_2. To get more information about the formation of H_2O_2 in the ozonation of NB, a series of experiments was performed under different conditions.

3.1.1 Effect of pH on H_2O_2 formation

Hydroxyl ion is known as a strong initiator of ozone decomposition, which also has considerable influences on H_2O_2 dissociation (pKa = 11.6), and will generate HO_2^- quickly at high pH values and finally react with ozone to form hydroxyl radical. The initial reactions of OH^- are as follows

$$O_3 + OH^- \longrightarrow HO_2^- + O_2$$
$$k_{OH^-} = 70 \cdot L \cdot mol^{-1} \cdot s^{-1} \qquad (1)$$

Thus, pH value will be an important factor in this study. Oxidation of NB by ozone and the formation of H_2O_2 at different pH values are shown in Fig. 2 (oxygen-saturated, $(O_3)_g$ dosage is 1.3×10^{-4} mol • min^{-1}, $C_T = 1\times10^{-3}$ mol • L^{-1}, $T=20\pm1$ ℃, and $[NB]_0 = 9.76\times10^{-6}$ mol • L^{-1}). At a given time, the conversion of NB increased with the increase of pH. Otherwise, the formation of H_2O_2 decreased with the increase of pH from 6 to 8. At pH 6.0, the maximum formation of H_2O_2 concentration did not reach within 8 minutes. When pH is 8.0, a high formation point of H_2O_2 concentration (0.67×10^{-6} mol • L^{-1}) was observed at 2 min, but NB was undetectable. Then the concentration of H_2O_2 slightly decreased further. At pH 8.0, the dissociation of H_2O_2 into HO_2^- was faster than the case of pH=6.0. The HO_2^- was consumed by ozone in initial reactions, which decreased the concentration of H_2O_2. As NB is a non-dissociating compound and cannot be influenced by pH [14], the effect of pH on NB degradation may be attributed to the function of free radicals. The pH effects on the formation of H_2O_2 formation can be explained that H_2O_2 dissociated into HO_2^- at high pH, and then the formed HO_2^- promoted chain reactions to form hydroxyl radical, and finally decreased the H_2O_2 amount.

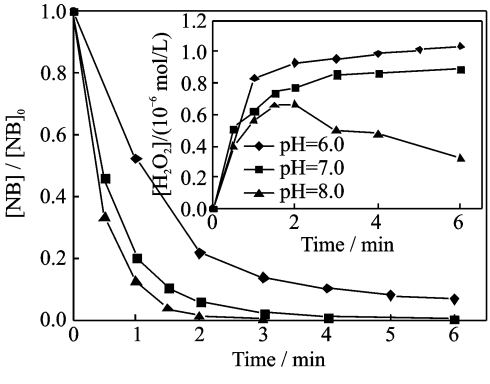

Fig. 2 Degradation of NB at different pH (Inset: H_2O_2 formation during ozonation of NB at different pH)

3.1.2 Effect of ozone dosage on H_2O_2 formation

The remaining concentration of NB in the dimensionless with time corresponding to two ozone feed rates at pH 6.0 is shown in Fig. 3 (oxygen-saturated, pH$=6.0$, $C_T=1\times10^{-3}$ mol • L^{-1}, $T=20\pm1$ ℃, and $[NB]_0=9.76\times10^{-6}$ mol • L^{-1}). At a given time, the high ozone dosage leads to high NB conversion and ozonation rate. The increase of ozone dosage mainly increased the driving force of ozone dissolution, which will increase the ozone decomposition rate to form hydroxyl radical, and enhance the conversion of NB at a given time.

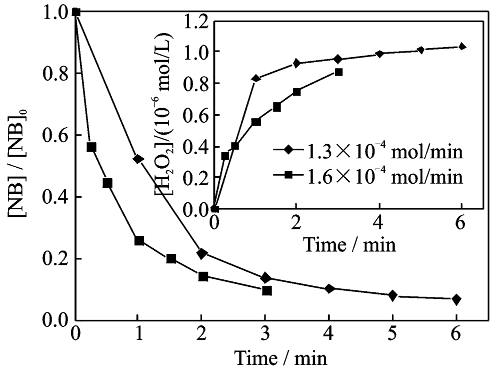

Fig. 3 Degradation of NB at two ozone dosages (Inset: H_2O_2 formation during NB ozonation at two ozone dosages)

The formation of H_2O_2 with time is also shown in Fig. 3. It can be deduced that the high NB conversion at a given time should lead to high formation of H_2O_2. But the amounts of H_2O_2 at an ozone dosage of 1.6×10^{-4} mol • min^{-1} was lower than that of 1.3×10^{-4} mol • min^{-1} within 3 min, while the conversion of NB was higher than that of 1.3×10^{-4} mol • min^{-1}. It has been investigated that the dissociation of H_2O_2 with ozone is slow at pH 6.0. Therefore, the formation of H_2O_2 will accumulate at high ozone dosage at pH 6.0. On the other hand, the concentration of H_2O_2 was lower than the products of NB oxidation by ozone at pH 6.0. Hydroxyl radical enhanced in high ozone dosage will react mostly with the products of NB.

3.1.3 Effect of hydroxyl radical scavengers on H_2O_2 formation

Formation of H_2O_2 during ozonation of NB and nitrophenol was carried out in the presence of tert-butyl alcohol (tB), a kind of hydroxyl radical scavengers which reacts very slowly with ozone (0.03 L • mol^{-1} • s^{-1}) and quickly with hydroxyl radical to terminate the free radical chain reactions (5×10^8 L • mol^{-1} • s^{-1}) [8]. Ozone is a very selective oxidant compared to hydroxyl radical, which reacts quickly with activated aromatic compounds, double bonds and deprotonated amine [22]. *p*-nitrophenol (pK $=7.2$) had been proved to be one of the intermediate products during the oxidation of NB by ozone in water. The reaction rates of phenolate ion with ozone and free hydroxyl radical were $16\pm5\times10^6$ L • mol^{-1} • s^{-1} and 7.6×10^9 L • mol^{-1} • s^{-1}, respectively[21, 23]. The effect of tB on the formation of H_2O_2 is shown in Fig. 4 (oxygen-saturated, $(O_3)_g$ dosage is 1.6×10^{-4} mol • min^{-1}, pH$=8.0$, $C_T=1\times10^{-3}$ mol • L^{-1}, and $T=20\pm1$ ℃). It can be observed that tB significantly inhibits the H_2O_2 formation during NB ozonation since NB was mainly degraded by hydroxyl radical. Contrarily, tB did not affect the H_2O_2 formation compared with NB ozonation during the ozonation of *p*-nitrophenol, and the amounts of H_2O_2 increased straightly in the presence of tB within 3 min. At pH 8.0, H_2O_2 did not initiate ozone to produce hydroxyl radical in the presence of tB, and finally H_2O_2 accumulated during the ozonation of *p*-nitrophenol. According to the mechanism of degradation of phenol by ozone, a similar series of consecutive reactions will happen in the ozonation of nitrophenol [1]. Hence, H_2O_2 was mainly produced during ozone reaction with the intermediates of NB.

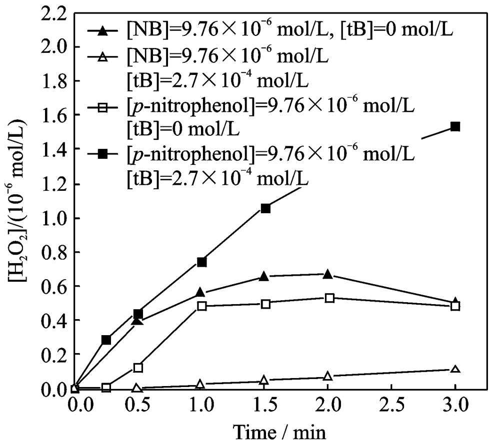

Fig. 4 Formation of H_2O_2 in the presence and absence of tB during ozonation of NB and *p*-nitrophenol

3.2 Role of H_2O_2

It had been investigated that H_2O_2 would form during the ozonation of NB. Since H_2O_2 is a strong initiator of ozone decomposition, it will produce hydroxyl radical quickly, thus accelerating the degradation of organic compounds. To investigate whether the intermediate product of H_2O_2 could enhance the degradation of NB, different amounts of H_2O_2 were added to the reactor at pH 6.0. The results are shown in Fig. 5, where dash lines denote the expected concentrations of H_2O_2, by assuming no reaction with added H_2O_2 (oxygen-saturated, $(O_3)_g$ dosage is 1.6×10^{-4} mol • min^{-1}, pH$=6.0$, $C_T=1\times10^{-3}$ mol • L^{-1}, $T=20\pm1$ ℃, and $[NB]_0=9.76\times10^{-6}$ mol • L^{-1}). On the basis of previous work, at pH values above 5, H_2O_2 strongly accelerated the decomposition of ozone [6]. In Fig. 5, after H_2O_2 is added, NB conversion is slightly improved at a given time compared to the case without the addition of H_2O_2. The amount of H_2O_2 formed is increased smoothly. It is expected that an efficient and clean source of hydroxyl radial was provided by the mixture of ozone and H_2O_2 in water, and the high powerful and unselective • OH will react with many intermediates in addition to NB [24]. On the other hand, after 0.63×10^{-6} mol • L^{-1} of H_2O_2 was added, which was supposed not to react with any agents in water, the accumulation of H_2O_2 was slightly lower than those H_2O_2 presumably formed. With the amount of H_2O_2 dose increased, the accumulation of H_2O_2 was lower and the value of H_2O_2 was lower than that presumably formed. The impact of H_2O_2 addition was explained by the fact that H_2O_2 will dissociate into HO_2^- which behaves like OH^- in water, and subsequently reacts with ozone to provide an efficient, clean source of hydroxyl radical in water. In Fig. 5, the percentage degradation of NB was also increased with the increase of added H_2O_2. Hydroxyl radical was produced right after H_2O_2 addition, which enhanced the NB degradation.

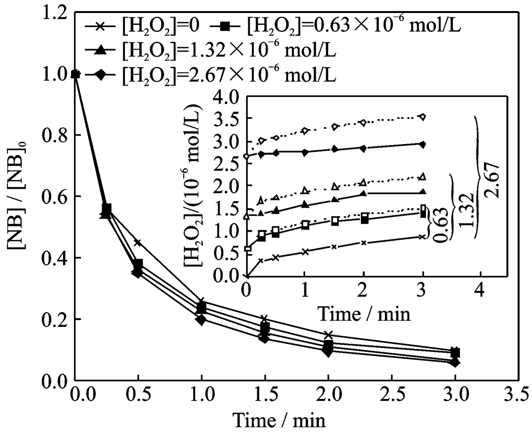

Fig. 5 Degradation of NB at different initial H_2O_2 concentrations (Insert: Accumulation of H_2O_2)

The efficiency of OH^- and HO_2^- on ozone decomposition rate can be compared by k_{OH^-} and $k_{HO_2^-}$. At pH 6.0, if $k_{OH^-}[OH^-]=k_{HO_2^-}[HO_2^-]$, the decomposition rate of ozone by HO_2^- can take place with the magnitude as same as OH^-. The concentration of H_2O_2 calculated was 0.13×10^{-6} mol • L^{-1}. However, the concentration of H_2O_2 formed at 0.25 min on oxidation of NB with initial concentration of 9.76×10^{-6} mol • L^{-1} at pH 6.0 was 0.35×10^{-6} mol • L^{-1}. It was assumed that the amounts of H_2O_2 at 0.25 min may initiate the decomposition of ozone to form hydroxyl radical.

A kinetic study was attempted to describe the reaction model in batch reactor. The time-concentration curves obtained from the oxidation experiments of NB at different H_2O_2 doses were fitted to a potential kinetic equation. In the case of NB, the oxidation rate can be described by pseudo-second-order kinetics, provided that the concentration of hydroxyl radical can be considered to be constant (Eq. 2) [25]. The pseudo-second-order kinetic constants obtained from the slope of these lines were listed in Table 1. It must be emphasized that pseudo-second-order kinetic model was selected only because it provided an effective representation of the observed trends. In fact, a kinetic model for the oxidation of NB by ozone ozone and ozone plus H_2O_2 in water was depicted in detail in Ref. [14].

$$-\gamma = kC_{\mathrm{NB}}^{2}C_{\cdot\mathrm{OH}} \cong k_{d}C_{\mathrm{NB}}^{2} \tag{2}$$

where r ($\mathrm{mol \cdot L^{-1} \cdot s^{-1}}$) is the oxidation rate of NB, k ($\mathrm{L^{2} \cdot mol^{-2} \cdot s^{-1}}$) the rate constant of NB oxidation, C_{NB} ($\mathrm{mol \cdot L^{-1}}$) the concentration of NB, $C_{\cdot\mathrm{OH}}$ ($\mathrm{mol \cdot L^{-1}}$) the concentration of ·OH , and k_d ($\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$) the rate constant of pseudo-second-order kinetic.

Table 1 Kinetic constants of NB oxidation

Added amounts of $H_2O_2/10^{-6}$ mol · L^{-1}	K_d/ 10^7 L · mol^{-1} · s^{-1}	R^2
0	1.67	0.994 5
0.63	1.96	0.999 8
1.32	2.24	0.997 6
2.67	2.69	0.997 3

In Table 1, all plots of the reciprocal of concentration of residual NB versus time were linear. All the correlation coefficients of lines were above 0.99. The values obtained for the kinetic constants at $T=20$ ℃ were increased slightly when H_2O_2 was added. Rate constants calculated at different H_2O_2 doses fitted with linear regressions. Moreover, the linear correlation coefficient between the amounts of added H_2O_2 and the kinetic constants was well correlated. With regard to the correlation of ozone decay rate and H_2O_2, it had been reported that there was a well-defined relationship between ozone decay rate and added H_2O_2[6]. It suggested that low concentrations of H_2O_2 formed in NB ozonation could initial ozone decomposition partially to produce hydroxyl radical, which will enhance the NB degradation.

It is shown that high H_2O_2 concentration inhibits the NB oxidation. When the dissolved ozone concentration is low, the initiation to produce hydroxyl radical by ozone is difficult [13]. In this experiment, the amounts of the formed H_2O_2 were lower than the concentration of ozone in the solution. The addition of H_2O_2 can initiate the decomposition of ozone. To better understand the fate of H_2O_2 during NB ozonation, the scheme of hydroxyl radical produced by H_2O_2 chain reactions is shown in Fig. 6.

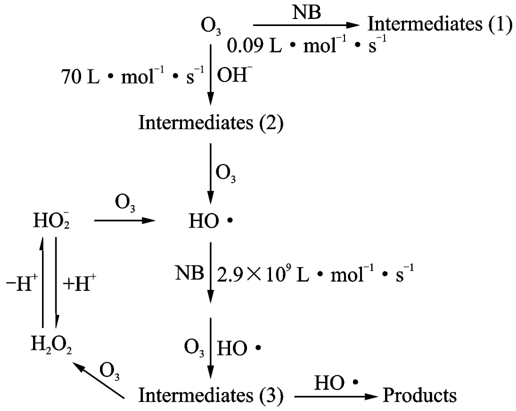

Fig. 6 Pathway of ·OH produced from the presence of intermediate product of H_2O_2

4 Conclusions

Accumulation of H_2O_2 during NB ozonation was formed mainly at low pH values ranged from pH 6—8, high NB concentration and low ozone dosage. And H_2O_2 was quickly formed after NB was oxidized by hydroxyl radical during ozonation of intermediates, such as *p*-nitrophenol, which react with ozone quickly in water. A little addition of H_2O_2 can slightly enhance the NB oxidation rate. Kinetic study showed that NB removal rate was fitted to pseudo-second-order kinetics well in the experiment. The oxidation rates increased linearly with increasing H_2O_2 addition. It verified that the intermediate product of H_2O_2 during ozonation NB would initiate ozone decomposition to form hydroxyl radical and finally enhance aromatic compounds removal.

References:

[1] Yamamoto Y, Niki E, Shiokawa H, et al. Ozonation of organic compounds. 2. ozonation of phenol in water[J]. J Org Chem, 1979, 44: 2137-2142.

[2] Almudena A, Fernando J B, Juan J P S, et al. In situ generation of hydrogen peroxide from pharmaceuticals single ozonation: A comparative study of its application on Fenton like systems[J]. J Chem Eng, 2014, 235: 46-51.

[3] Pi Y Z, Zhang L S, Wang J L. The formation and influence of hydrogen peroxide during ozonation of para-chlorophenol[J]. J Hazard Mater, 2007, 141:

707-712.

[4] García J F, Beltrán F J, Aguinaco A. Diclofenac removal from water by ozone and photolytic TiO_2 catalysed processes[J]. J Chem Tech and Bio, 2010, 85: 798-804.

[5] Pi Y, Schumacher J, Jekel M. Decomposition of aqueous ozone in the presence of aromatic organic solutes[J]. Water Res, 2005, 39: 83-88.

[6] Staehelld J, Hoigné J. Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide[J]. Environ Sci Technol, 1982, 16: 676-681.

[7] Staehelld J, Hoigné J. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions[J]. Environ Sci Technol, 1985, 19: 1206-1213.

[8] Langlais B, Reckhow D A, Brink D R. Ozone in water treatment: Application and engineering [M]. Michigan: Lweis Publishers, 1991.

[9] Beltrán F J, Encinar J M, Alonso M A. Nitroaromatic hydrocarbon ozonation in water. 1. single ozonation[J]. Ind Eng Chem Res, 1998, 37: 25-31.

[10] Zhang Y L, Dai C M, Zhou X F. Performance and mechanism of pyrite for NB removal in aqueous solution[J]. Chem Eng Sci, 2014, 111: 135-141.

[11] Wu J H, Yin W Z, Gu J J, et al. A biotic Fe^0-H_2O system for NB removal from groundwater [J]. J Chem Eng, 2013, 226: 14-21.

[12] Latifoglu A, Gurol M D. The effect of humic acids on NB oxidation by ozonation and O_3/UV processes [J]. Water Res, 2003, 37: 1879-1889.

[13] Beltrán F J, Encinar J M, Alonso M A. Nitroaromatic hydrocarbon ozonation in water. 2. combined ozonation with hydrogen peroxide or UV radiation [J]. Ind Eng Chem Res, 1998, 37: 32-40.

[14] Beltrán F J, Rivas J, Álvarez P, et al. A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: Application to phenanthrene and NB[J]. Ind Eng Chem Res, 1999, 38: 4189-4199.

[15] Han S, Ichikawa K, Utsumi H. Quantitative analysis for the enhancement of radical generation by phenols during ozonation of water[J]. Water Res, 1998, 32: 3261-3266.

[16] Utsumi H, Han Y, Ichikawa K. A kinetic study of 3-chlorophenol enhanced hydroxyl radical generation during ozonation[J]. Water Res, 2003, 37: 4924-4928.

[17] Bader H, Sturzenegger V, Hoigné J. Photometric method for the determination of low concentrations of hydrogen peroxide by the peroxidase catalyzed oxidation of N, N-diethyl-p-phenylenediamine (DPD)[J]. Water Res, 1988, 22: 1109-1115.

[18] Bader H, Hoigné, J. Determination of ozone in water by the indigo method[J]. Water Res, 1981, 15: 449-456.

[19] Hoigné J, Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water- Ⅰ Non-dissociating organic compounds[J]. Water Res, 1983, 17: 173-183.

[20] Buxton G V, Greenstock C L, Helman W P, et al. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution[J]. J Phys Chem Ref Data 1988, 17: 513-886.

[21] Neyens E, Baeyens J. A review of classic Fenton′s peroxidation as an advanced oxidation technique[J]. J Hazard Mater, 2003, B98: 33-50.

[22] Von G U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation [J]. Water Res, 2003, 37: 1443-1467.

[23] Hoigné J, Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water— Ⅱ Dissociating organic compounds [J]. Water Res, 1983, 17: 185-194.

[24] Spanggord R J, Yao D, Mill T. Kinetics of aminodinitrotoluene oxidations with ozone and hydroxyl radical[J]. Environ Sci Technol, 2000, 34: 450-454.

[25] Zazo J A, Casas J A, Mohedano A F, et al. Chemical pathway and kinetics of phenol oxidation by Fenton′s reagent[J]. Environ Sci Technol, 2005, 39: 9295-9302.

(Executive editor: Zhang Tong)