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RESEARCH ARTICLE

Degradation of nitrobenzene wastewater in an acidic environment by Ti(IV)/H_2O_2/O_3 in a rotating packed bed

Peizhen Yang[1] · Shuai Luo[2] · Youzhi Liu[1] · Weizhou Jiao[1]

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Abstract

The rotating packed bed (RPB) as a continuous flow reactor performs very well in degradation of nitrobenzene wastewater. In this study, acidic nitrobenzene wastewater was degraded using ozone (O_3) combined with hydrogen peroxide and titanium ions (Ti(IV)/H_2O_2/O_3) or using only H_2O_2/O_3 in a RPB. The degradation efficiency of nitrobenzene by Ti(IV)/H_2O_2/O_3 is roughly 16.84% higher than that by H_2O_2/O_3, and it reaches as high as 94.64% in 30 min at a H_2O_2/O_3 molar ratio of 0.48. It is also found that the degradation efficiency of nitrobenzene is significantly affected by the high gravity factor, H_2O_2/O_3 molar ratio, and Ti(IV) concentration, and it reaches a maximum at a high gravity factor of 40, a Ti(IV) concentration of 0.50 mmol/L, a pH of 4.0, a H_2O_2/O_3 molar ratio of 0.48, a liquid flow rate of 120 L/h, and an initial nitrobenzene concentration of 1.22 mmol/L. Both direct ozonation and indirect ozonation are involved in the reaction of O_3 with organic pollutants. The indirect ozonation due to the addition of different amounts of tert-butanol (·OH scavenger) in the system accounts for 84.31% of the degradation efficiency of nitrobenzene, indicating that the nitrobenzene is dominantly oxidized by ·OH generated in the RPB-Ti(IV)/H_2O_2/O_3 process. Furthermore, the possible oxidative degradation mechanisms are also proposed to better understand the role of RPB in the removal of pollutants.

Keywords Nitrobenzene · Ozone · Titanium ions · Acidic wastewater · Degradation mechanisms · Rotating packed bed

Introduction

Many toxic aromatic compounds such as nitrobenzene are widely used in explosives, pesticides, paper pulp production, and colorant industries (Zhang et al. 2014a). Nitrobenzene is frequently found in wastewater and listed as a priority pollutant by the US Environmental Protection Agency due to its strong mutagenesis and carcinogenesis in humans (Elshafei et al. 2014). The presence of nitro-groups makes nitrobenzene more stable, and thus treatment of wastewater containing toxic nitrobenzene by conventional biological methods is often inadequate to remove the pollutant completely. Although a number of technologies have been proposed to remove nitrobenzene (Yang et al. 2016), there is still a need to find a more efficient and cost-effective method for degrading nitrobenzene-containing wastewater. H_2O_2/O_3 is considered an effective treatment for different organic pollutants due to their strong oxidative capacity in an alkaline environment (Chidambara Raj and Quen 2005; Martins and Quinta-Ferreira 2011; Kordkandi and Forouzesh 2014; Kordkandi and Motlagh 2017). The decomposition of O_3 in the alkaline environment can be expressed as

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad k_1 = 70 \ mol/(L{\cdot}s) \tag{1}$$

$$O_3 + OH_2^- \rightarrow 2O_2 + {\cdot}OH \quad k_2 = 1.6 \times 10^9 \ mol/(L{\cdot}s) \tag{2}$$

Highlights
- Ti(IV)/H_2O_2/O_3 process coupled with RPB was developed to degrade acidic nitrobenzene.
- The degradation efficiency reached 94.64% with the nitrobenzene concentration of 1.22 mmol/L in 30 min.
- Direct reaction and indirect reaction coexisting in the oxidation system were confirmed.
- Indirect ozonation accounted for 84.31% in the whole oxidation process.
- The possible degradation pathways were proposed.

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✉ Weizhou Jiao
jwz0306@126.com

[1] Shanxi Province Key Laboratory of Higee-Oriented Chemical Engineering, North University of China, Taiyuan 030051, Shanxi, China

[2] Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

However, H_2O_2/O_3 has a low nitrobenzene degradation efficiency in the acidic environment because of the low amount of ·OH (Zeng et al. 2012). In order to solve this problem, the discharge standard can be met by adding alkali to neutralize the acid and then using the advanced oxidation processes (AOPs) to degrade pollutants. This, however, is achieved at the expense of increased economic costs. Homogeneous ozonation catalyzed by transition metals, such as manganic ions (Mn(II)) (Arslan et al. 2000), ferrous ions (Fe(II)) (Yao et al. 2013), and Ti(IV) (Tong et al. 2011), has emerged as a cost-effective alternative to degrade acidic wastewater. Ti(IV) is considered one of the most effective transition metals for the degradation of organic pollutants under acidic conditions (Yang et al. 2007; Lin et al. 2010). Lin et al. showed that the Ti(IV) in the acidic environment with H_2O_2 could produce multiple complexes that could catalyze O_3 to produce ·OH. In 2007, Yang et al. also reported that the high oxidative efficiency of $Ti(IV)/H_2O_2/O_3$ could be attributed to a yellow complex compound ($Ti_2O_5^{2+}$) that could initiate the chain reaction of ozone decomposition to generate ·OH. These results suggest the possible application of Ti(IV) as a promising homogeneous catalyst in the removal of organic pollutants in an acidic environment. Homogeneous catalysis can also produce ·OH to degrade organic pollutants by catalyzing O_3 in water (Ma and Graham 2000). However, most previous studies have focused on the conventional batch reactors, which have been shown to have low O_3 mass transfer efficiency and treatment capacity (Lin and Wang 2003). Thus, it is necessary to find a more efficient contactor to improve the gas-liquid mass transfer and the degradation efficiency.

Rotating packed bed (RPB) is a new efficient gas-liquid contactor that can improve the gas-liquid mass transfer and micro-mixing. For these reasons, RPB has been widely used not only in the gas-liquid contacting process but also in processes such as absorption (Mandal et al. 2004; Yi et al. 2009), distillation (Mondal et al. 2012; Luo et al. 2012; Li et al. 2014), stripping (Lin et al. 2008; Yuan et al. 2016), and wastewater treatment (Chen et al. 2005; Zeng et al. 2013; Keen et al. 2015). In recent years, RPB has also been widely used in ozonation, because it could increase the interfacial area between gas and liquid phases and decrease their transfer resistance. This allows O_3 molecules in the gas phase to easily enter into the liquid phase. Wang et al. examined the absorption of O_3 by deionized water in a RPB and found that the mass transfer coefficient of the liquid phase k_La was $1.912 \times 10^{-2} s^{-1}$, which was twice as much as that of the conventional batch reactor (Wang et al. 2008).

To the best of our knowledge, there has been no study investigating the degradation of acidic nitrobenzene wastewater using $Ti(IV)/H_2O_2/O_3$ in a RPB. In this study, we investigated the degradation of nitrobenzene through H_2O_2/O_3 catalyzed by Ti(IV), and its performance was compared with that through the classic H_2O_2/O_3 under the same conditions. In addition, the effects of high gravity factor, H_2O_2/O_3 molar ratio, liquid flow rate, and pH on the degradation efficiency were also evaluated. Finally, the intermediates formed during the degradation of nitrobenzene were determined by gas chromatography/mass spectroscopy (GC-MS), and the possible degradation pathways of nitrobenzene were proposed.

Experimental

Materials

All chemicals were of analytical grade and commercially available from Tianjin Tianli Chemical Reagent Co., Ltd. (China), without further purification. All working solutions were prepared in deionized water.

Experimental setup

Nitrobenzene was dissolved in deionized water to prepare the nitrobenzene solution with a concentration of 1.22 mmol/L. The initial pH of the solution was adjusted to 4.0 with H_2SO_4. All experiments were performed at a temperature of 25 ± 0.1 °C.

Figure 1 shows the experimental setup for the degradation of nitrobenzene. O_3 was generated from oxygen by an ozone generator (NPO10P-2, Shandong Lvbang Photoelectric Equipment Co., Ltd., China). The gas mixture of O_2 and O_3 was measured by the gas flow meter and then passed through the RPB vertically through its bottom. The nitrobenzene solution added with Ti(IV) was pumped into the RPB via a storage tank and sprayed onto the inner edge of the RPB. The gas and liquid streams were contacted in a cross-flow mode in the RPB, and then O_3 was absorbed by the liquid to react with nitrobenzene. Then, the reacted liquid flowed into the storage tank for cycling and unreacted O_3 was absorbed by KI solution. The experiments were performed at a temperature of 25 °C, a nitrobenzene concentration (C_{NB_0}) of 1.22 mmol/L, a high gravity factor (β) of 40, a pH of 4.0, a Ti(IV) molar concentration ($C_{Ti(IV)}$) of 0.50 mmol/L, a H_2O_2/O_3 molar ratio ($r_{H_2O_2/O_3}$) of 0.48, a gas flow rate (Q_G) of 75 L/h, a liquid flow rate (V_L) of 120 L/h, and a reaction time of 30 min. The device was a cross-flow RPB packed with stainless wire mesh, as shown in Table 1.

Analytical methods

A high-performance liquid chromatograph (HPLC, Dionex UltiMate 3000, USA) was used to determine the concentration

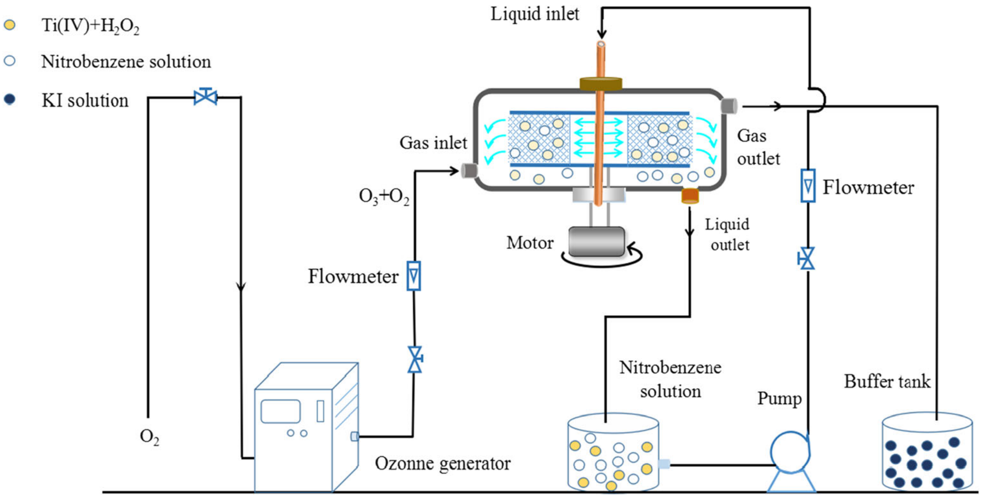


Fig. 1 Diagram of the experimental setup

of nitrobenzene. Chromatographic column was C18 reversed phase column for the 5-mL sample from the liquid outlet, where the detection wavelength was 262 nm, the methanol-water (70:30) acted as mobile phases with a flow rate of 0.9 mL/min, the column temperature was 20 °C, and the sample quantity was 20 μL. The concentration of O_3 in gas was measured by the iodometric titration method. The pH value was measured by a pH analyzer (PHS-3C, Shanghai Instrument Electric Scientific Instrument Co., Ltd., China), and the intermediate products were analyzed by GC-MS (Aglient, 5977A-7890B MSD, USA) equipped with a HP-5 ms column (30 m × 0.32 mm × 0.25 μm). The column temperature was held at 60 °C for 2 min and then increased to 300 °C at a heating rate of 10 °C/min. The samples of 1.0 L were extracted twice by dichloromethane, and then the extracted liquid was concentrated by a nitrogen gas to 1.0 mL for GC-MS. The degradation efficiency of nitrobenzene (η_B,%) was expressed as

$$\eta_B = \frac{C_{B0}-C_B}{C_{B0}} \times 100\% \tag{3}$$

where C_{B_0} is the initial concentration of nitrobenzene, mmol/L, and C_B is the concentration of nitrobenzene in the effluent solution, mmol/L.

Table 1 Specification for packing materials in rotating packed bed

Character	Parameter
Packing-materials outer diameter (mm)	75
Packing-materials inner diameter (mm)	40
Packing-materials height (mm)	75
Packing-materials density (g/cm^3)	7.9
Packing-materials surface area (m^2/m^3)	935.07
Packing-materials porosity (m^3/m^3)	0.74

Results and discussion

Effect of initial pH

The initial pH plays a key role in the Ti(IV)/H_2O_2/O_3 treatment (Lin et al. 2010). Figure 2 shows the effect of initial pH on the degradation of nitrobenzene over the pH range of 2.5–5.0. Clearly, the degradation efficiency of nitrobenzene at first increases with the increase of pH until a peak of 95.10% is reached at pH 4.0 in 30 min, after which it decreases with further increase of pH. This phenomenon can be attributed to the following two reasons:

The first reason is that H_2O_2 can act as an initiator of O_3 decomposition in an acidic environment, and a fraction of H_2O_2 is dissociated to HO_2^-, which can also act as an initiator of O_3 decomposition. The mechanism of how H_2O_2 induces O_3 to generate ·OH in the acidic environment is described in

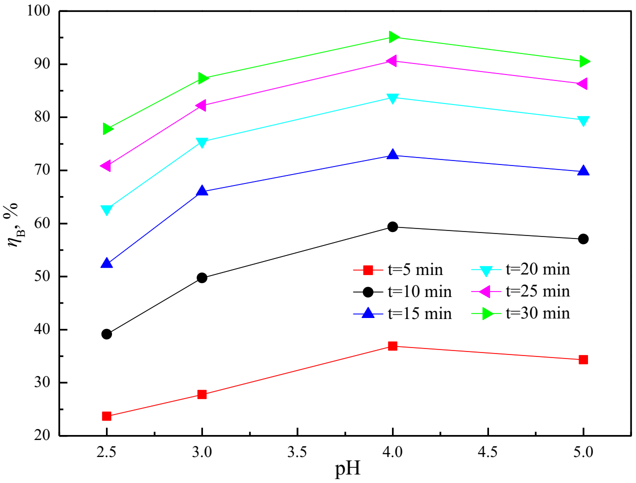


Fig. 2 Effect of initial pH on the removal efficiency of nitrobenzene (C_{NB0}=1.22 mmol/L, $r_{H_2O_2/O_3}$ =0.48, $C_{Ti(IV)}$ = 0.50 mmol/L, V_L = 120 L/h, Q_G = 75 L/h, β = 40)

Eqs. (4)–(9) (where k is the reaction rate constant) (Hoigné et al. 1985; Stefan et al. 2015).

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \quad pKa = 11.6 \tag{4}$$

$$O_3 + HO_2^- \rightarrow HO_2\cdot + O_3^-\cdot \quad k_3 = 2.2 \times 10^6 \quad mol/(L\cdot s) \tag{5}$$

$$HO_2\cdot \rightarrow O_2^- + \cdot H^+ \quad k_4 = 7.9 \times 10^5 \quad mol/(L\cdot s) \tag{6}$$

$$O_2^-\cdot + H^+ \rightarrow HO_2\cdot \quad k_5 = 5 \times 10^{10} \text{ mol}/(L\cdot s) \tag{7}$$

$$O_2^-\cdot + O_3 \rightarrow O_3^-\cdot + O_2 \quad k_6 = 1.6 \times 10^9 \text{ mol}/(L\cdot s) \tag{8}$$

$$O_3^-\cdot + H_2O \rightarrow \cdot OH + O_2 + OH^- \quad k_7 = 20\text{–}30 \text{ mol}/(L\cdot s) \tag{9}$$

Both direct ozonation (O_3 reacts directly with organic pollutants) and indirect ozonation (O_3 is decomposed to produce ·OH, which in turn reacts with organic pollutants) are involved in the reaction of O_3 with organic pollutants. Pera-Titus et al. reported that the direct ozonation was the dominating pathway at a pH below 4, and both direct ozonation and indirect ozonation were important in the pH range of 4.0–9.0 (Pera-Titus et al. 2004). Besides, as the direct ozonation between O_3 and nitrobenzene was slow (Latifoglu and Gurol 2003), the degradation efficiency of nitrobenzene was limited at a pH below 4.0.

A second possible reason is that H_2O_2 could be easily protonated and converted into more stable chemicals such as $H_3O_2^+$, which can no longer be decomposed to produce ·OH (Zhang et al. 2014b). This could explain the decrease of degradation efficiency of nitrobenzene with the increase of pH. However, it is noteworthy that the Ti(IV) could produce yellow $Ti_2O_5^{2+}$ with H_2O_2 (Eqs. 10–12), which is also an initiator of ·OH (Lin et al. 2010). The production of ·OH reaches a maximum at a pH of 4.0 (Fig. 2). Thus, the optimal pH is determined to be 4.0.

$$Ti_2O_5^{2+} + O_3 \rightarrow O_3^- \tag{10}$$

$$O_3^- + H_3O^+ \rightarrow HO_3\cdot + H_2O \tag{11}$$

$$HO_3\cdot \rightarrow O_2 + \cdot OH \tag{12}$$

Effect of high gravity factor

The high gravity factor β is a dimensionless indicator of the strength of the high gravity field, which can be defined as the ratio of the centrifugal acceleration to the gravitational acceleration (Jiao et al. 2010):

$$\beta = \frac{w^2 r}{g} = \frac{N^2 r}{900} \tag{13}$$

where w is the angular velocity of the rotating rotor, /s; r is the rotor radius, m; g is the gravitational acceleration, m^2/s; and N is the rotation speed of the rotor, r/min. These parameters could be controlled by adjusting the frequency of the converter.

The high gravity factor is proportional to the square of the rotation speed, and the high gravity field could be achieved by adjusting the rotor speed. The diffusion and interphase mass transfer of molecules are more pronounced in the high gravity field than in the conventional gravity field. The high shearing force in the high gravity field makes the mass transfer rate between gas and liquid phases one to three orders of magnitude higher than that in the conventional mass transfer equipment (Jiao et al. 2016).

Figure 3 shows the effect of high gravity factor β on the degradation of nitrobenzene ($\beta = 20$–80). It is observed that the degradation efficiency of nitrobenzene increases as the high gravity factor β increases from 20 to 60, and then decreases with further increase of the high gravity factor β to 80. The increase of high gravity factor β could enhance the mass transfer between O_3 and nitrobenzene solution due to the decrease of the size of liquid droplets and the thickness of liquid films (Jiao et al. 2016). In addition, it can also increase the O_3 mass transfer by increasing the renewal efficiency of the liquid surface. Nevertheless, the gas-liquid contact time decreases as the high gravity factor β increases, which is unfavorable for the mass transfer of O_3 and thus can explain the non-significant effect of high gravity factor β on the degradation efficiency of nitrobenzene at a high gravity factor β higher than 60. This also demonstrates that the gas-liquid contact time plays an important role in the high gravity factor β (Zeng et al. 2012). As a high rotation speed is often associated with high energy consumption, the optimal high gravity factor β is taken to be 40 based on economic considerations.

Effect of Ti(IV) concentration

The effect of initial Ti(IV) concentration (0.25–1.00 mmol/L) on the degradation efficiency of nitrobenzene is shown in

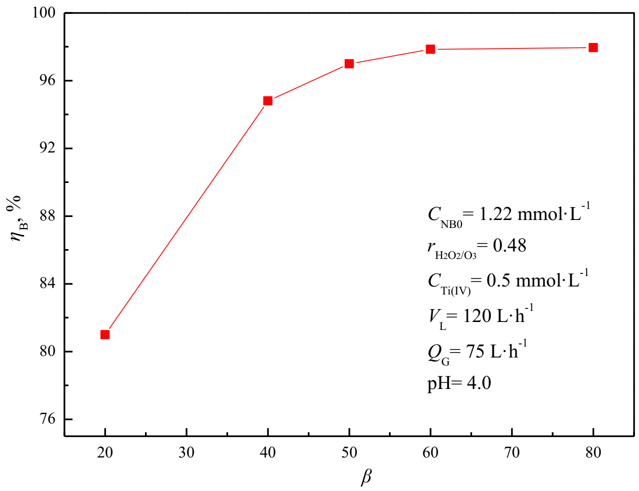


Fig. 3 Effect of high gravity factor β on the removal efficiency of nitrobenzene

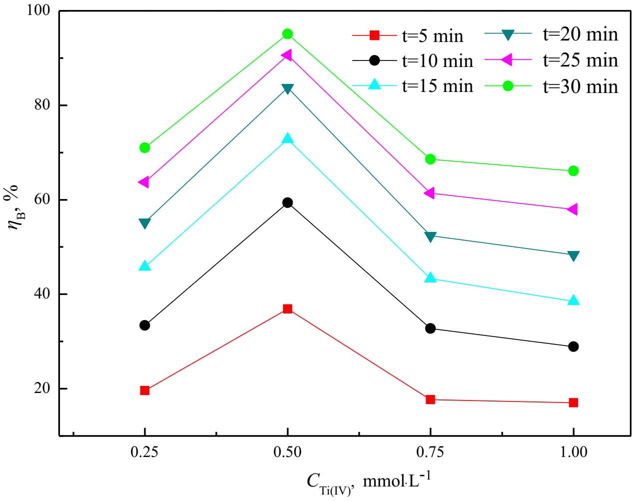


Fig. 4 Effect of Ti(IV) concentration on the removal efficiency of nitrobenzene ($C_{NB0} = 1.22$ mmol/L, $r_{H_2O_2/O_3} = 0.48$, $V_L = 120$ L/h, $Q_G = 75$ L/h, $\beta = 40$, pH = 4.0)

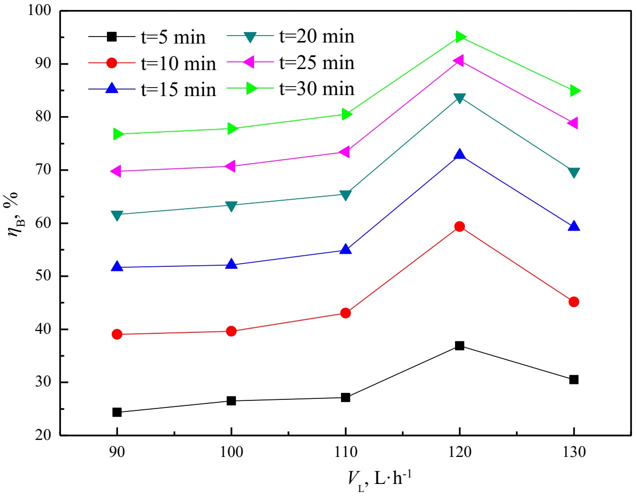


Fig. 6 Effect of liquid flow rate on the removal efficiency of nitrobenzene ($C_{NB0} = 1.22$ mmol/L, $r_{H_2O_2/O_3} = 0.48$, $C_{Ti(IV)} = 0.50$ mmol/L, $Q_G = 75$ L/h, $\beta = 40$, pH = 4.0)

Fig. 4. The degradation efficiency of nitrobenzene increases with the increase of Ti(IV) concentration until a maximum is reached at a Ti(IV) concentration of 0.5 mmol/L, after which it decreases with further increase of Ti(IV) concentration. This is because Ti(IV) can react with H_2O_2 in the system to form more $Ti_2O_5^{2+}$, which could catalyze O_3 to produce more ·OH as expressed in Eqs. (10)–(12). These results clearly reveal that Ti(IV) could improve the generation of ·OH and therefore improve the degradation efficiency of nitrobenzene. However, when the Ti(IV) concentration exceeds 0.50 mmol/L, self-extinguishing reaction occurs among ·OH through Eq. (14), and an excessive amount of H_2O_2 in the system could react with the generated ·OH through Eq. (15), leading to the decrease of the degradation efficiency of nitrobenzene (Zhang et al. 2014b).

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{14}$$

$$H_2O_2 + \cdot OH \rightarrow \cdot OOH + H_2O \tag{15}$$

In addition, the solution becomes more turbid as the Ti(IV) concentration increases, because the hydrolysis of Ti(IV) in water could generate $TiO(OH)_2$ (Yang et al. 2007):

$$Ti^{4+} + OH^- \rightarrow Ti(OH)^{3+} \tag{16}$$

$$Ti(OH)^{3+} + OH^- \rightarrow TiO^{2+} + H_2O \tag{17}$$

$$TiO^{2+} + OH^- \rightarrow TiO(OH)^+ \tag{18}$$

$$TiO(OH)^+ + OH^- \rightarrow TiO(OH)_2\downarrow \tag{19}$$

$TiO(OH)_2$ could inhibit the participation of Ti(IV) in catalytic ozonation, which can also lead to a reduction in the

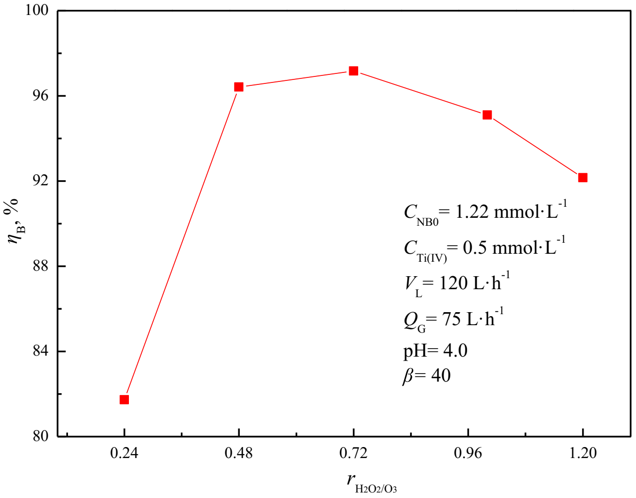


Fig. 5 Effect of the molar ratio of H_2O_2 to O_3 on the removal efficiency of nitrobenzene

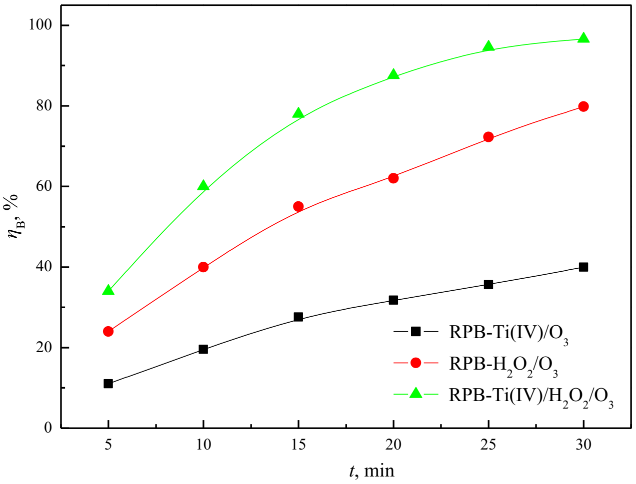


Fig. 7 Different processes on the removal efficiency of nitrobenzene ($C_{NB0} = 1.22$ mmol/L, $r_{H_2O_2/O_3} = 0.48$, $C_{Ti(IV)} = 0.50$ mmol/L, $V_L = 120$ L/h, $Q_G = 75$ L/h, $\beta = 40$, pH = 4.0)

Table 2 Comparison of different process treatment (BR/H_2O_2/O_3, RPB/H_2O_2/O_3, and RPB-Ti(IV)/H_2O_2/O_3) of acidic nitrobenzene wastewater

Nitrobenzene concentration (mmol/L)	pH	Process method	Reaction time (min)	Degradation efficiency	Investigator	Year
1.63	4	BR/H_2O_2/O_3	30	34.50%	Guo et al.	2015
1.22	4	RPB/H_2O_2/O_3	30	77.80%	This work	–
1.22	4	RPB-Ti(IV)/H_2O_2/O_3	30	94.64%	This work	–

degradation efficiency of nitrobenzene. Thus, the optimal Ti(IV) concentration is determined to be 0.50 mmol/L.

Effect of H_2O_2/O_3 molar ratio

In this study, the H_2O_2/O_3 molar ratios are 0.24, 0.48, 0.72, 1.0, and 1.2. Figure 5 shows that with the increase of the H_2O_2/O_3 molar ratio, the degradation efficiency of nitrobenzene first increases and then decreases, because H_2O_2 can catalyze the formation of ·OH from O_3 based on Eqs. (4)–(9). In addition, Ti(IV) can react with H_2O_2 to form $Ti_2O_5^{2+}$, which can also catalyze O_3 decomposition to produce ·OH (Lin et al. 2010). In case of insufficient H_2O_2, less ·OH would be produced and thus the degradation efficiency of nitrobenzene would be limited, while in case of an excessive amount of H_2O_2, it could react with the generated ·OH to produce ·OOH based on Eq. (15), which has a lower oxidation ability than ·OH (Zeng et al. 2012). Thus, the optimal H_2O_2/O_3 molar ratio is determined to be 0.48.

Effect of liquid flow rate

Figure 6 shows the effect of liquid flow rate (V_L = 90–130 L/h) on the degradation efficiency of nitrobenzene. Also, the degradation efficiency of nitrobenzene increases from 36.90 to 95.10% in 30 min with the increase of liquid flow rate from 90 to 120 L/h. This is because the contact surface area between gas and liquid phases increases per unit time with the increase of liquid flow rate. The O_3 mass transfer efficiency from the gas phase to the liquid phase and the amount of the generated ·OH increase, resulting in an increase in the degradation efficiency of nitrobenzene. However, the degradation efficiency decreases from 95.10 to 84.93% as the liquid flow rate increases from 120 to 130 L/h in 30 min, because increasing the liquid flow rate results in a decrease in the residence time and consequently a decrease in the degradation efficiency of nitrobenzene (Zeng et al. 2012). Thus, the optimal liquid flow rate is determined to be 120 L/h.

Comparison of different processes

In order to investigate the catalytic performance of different processes on O_3 under acidic conditions, several ozonation and catalytic ozonation experiments (RPB-Ti(IV)/H_2O_2/O_3, RPB-Ti(IV)/O_3, RPB/H_2O_2/O_3) were carried out.

As shown in Fig. 7, the degradation efficiency of nitrobenzene increases with the reaction time under the three conditions, but it differs significantly among different processes. At the same reaction time (30 min), the degradation efficiency of nitrobenzene by RPB-Ti(IV)/H_2O_2/O_3, RPB/H_2O_2/O_3, and RPB-Ti(IV)/O_3 is 94.64, 77.80, and only 39.74%, respectively. Clearly, RPB-Ti(IV)/H_2O_2/O_3 results in higher degradation of nitrobenzene than RPB/H_2O_2/O_3 under acidic conditions, which can be attributed to the ability of $Ti_2O_5^{2+}$ to catalyze O_3 to produce ·OH under acidic conditions. We also compared the degradation efficiency of nitrobenzene by the bubbling reactor (BR) (Guo et al. 2015) and RPB under the same conditions. The results show that the high-gravity technology can greatly improve the degradation efficiency of nitrobenzene, as shown in Table 2.

Effect of tert-butanol

In order to determine the dominant reaction for the degradation of nitrobenzene, several experiments were carried out with 0–20 ml of tert-butanol as ·OH scavenger (Liu et al. 2016). Tert-butanol may be oxidized by ·OH to some molecules or mineralized into CO_2 and H_2O. In 2013, Zeng et al.

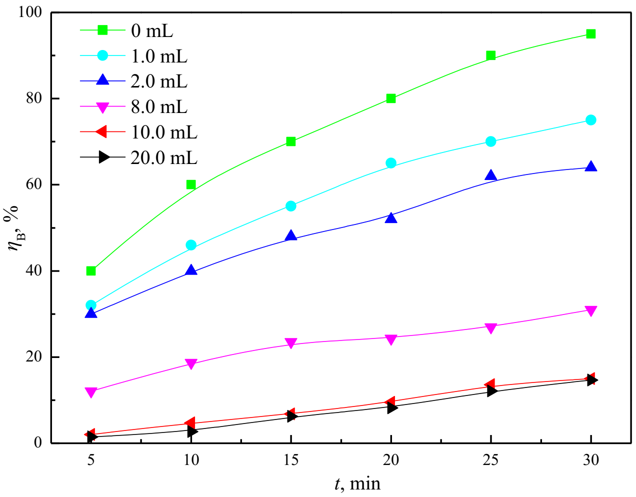


Fig. 8 Effect of tert-butanol on the removal efficiency of nitrobenzene (C_{NB0} = 1.22 mmol/L, $r_{H_2O_2/O_3}$ = 0.48, $C_{Ti(IV)}$ = 0.50 mmol/L, V_L = 120 L/h, Q_G = 75 L/h, β = 40, pH = 4.0)

Table 3 Energy requirements (kW/kg) for nitrobenzene transformation in an acidic environment by different ozonation processes, UV/O_3, BR/H_2O_2/O_3, Ultrasonic/H_2O_2/Fe^{2+}, RPB/H_2O_2/O_3 and RPB-Ti(IV)/H_2O_2/O_3

Nitrobenzene concentration (mmol/L)	pH	Process method	The moles of H_2O_2 (mmol/L)	Degradation efficiency	E_{EM} (kWh/kg)	Investigator
1.9	2.5	UV/H_2O_2	0.011	31.50%	1358.69	García Einschlag et al.
1.63	4	BR/H_2O_2/O_3	4.9	34.50%	1244.57	Guo et al.
3.00	3	Ultrasonic/H_2O_2/Fe^{2+}	0.16	20.00%	338.75	Xie et al.
1.22	4	RPB/H_2O_2/O_3	0.4	77.80%	129.52	This work
1.22	4	RPB-Ti(IV)/H_2O_2/O_3	0.4	94.64%	106.58	This work

reported that the rate constant of the reaction between O_3 and tert-butanol was 0.03 mol/(L·s) and that between ·OH and tert-butanol was 5×10^8 mol/(L·s), indicating that tert-butanol was a strong ·OH scavenger.

Figure 8 shows that with the addition of more tert-butanol into the system, the degradation efficiency of nitrobenzene is more strongly limited. The degradation efficiency of nitrobenzene with no tert-butanol (0 mL) is 94.64% in 30 min, while it decreases sharply to 15.14% with the addition of 10 mL of tert-butanol. This can be attributed to the high reaction rate of tert-butanol and ·OH, which results in the consumption of more ·OH in a short time and consequently a substantial reduction of ·OH in the solution that can inhibit the degradation of nitrobenzene.

In order to better understand the contribution of indirect ozonation and direct ozonation to the degradation efficiency of nitrobenzene, experiments were performed with higher amounts of tert-butanol. It is observed that the addition of 20 mL of tert-butanol results in a degradation efficiency of 14.85% in 30 min, which is close to that (15.14%) at a concentration of 10 mL. Thus, most ·OH in the system reacts with tert-butanol at an initial concentration of 10 mL, but the addition of more tert-butanol results in no significant decrease in the degradation efficiency of nitrobenzene, probably due to the limited amount of ·OH to be captured in the system. In this case, the degradation of nitrobenzene is mainly caused by O_3 (direct ozonation) in the system.

The degradation efficiency of nitrobenzene with no tert-butanol (0 mL) is 94.64% in 30 min under both direct ozonation and indirect ozonation in the system, and the contribution of direct ozonation to nitrobenzene degradation is 14.85%. It can be inferred that the indirect ozonation accounts for 84.31% of the degradation efficiency of nitrobenzene, indicating that ·OH is still the main active substance responsible for degrading nitrobenzene in the acidic environment.

Electrical energy calculation

For the water treatment process, the energy consumption for degrading the wastewater is an important index. Since most advance ozonation processes are electric-energy-intensive, electric energy consumption can be very useful and informative (Bircher and Bolton 2001). Recently, IUPAC put forward the "efficiency index" as an index to evaluate ozonation process wastewater treatment (Bircher and Bolton 2001; Kordkandi and Ashiri 2015). Efficiency index is the electric energy in kilowatt-hours (kWh) required to bring about the degradation of a unit mass (e.g., 1 kg) of a contaminant in polluted water or air (Bircher and Bolton 2001). In order to compare the electric energy consumption of different processes, the electric energy consumption of 1 kg of nitrobenzene is used to characterize this process. The whole electric energy consumption (E_{EM}) consists of two parts, one is ozone generation ($E_{EM/O3}$), and the other is hydrogen peroxide production ($E_{EM/H2O2}$). To calculate the theoretical energy required for different ozonation processes, we assumed an average energy requirement for 15 kWh/kg for O_3 and of 10 kWh/kg for H_2O_2 production (Rosenfeldt et al. 2006).

The electric energy consumption of ozonation process can be calculated from the simple formulas, E_{EO} (kWh/kg):

$$E_{EM/O_3}(\mathrm{kWh/kg}) = \frac{P_{O_3\mathrm{kg}}\cdot C_{O_3}\cdot Q_G\cdot t\cdot 10^{-6}}{(C_0 - C_t)\cdot V\cdot \mathrm{M}\cdot 10^{-3}} \tag{20}$$

$$E_{EM/H_2O_2}(\mathrm{kWh/kg}) = \frac{1}{(C_0 - C_t)\cdot V\cdot \mathrm{M}\cdot 10^{-3}} \times 10 \tag{21}$$

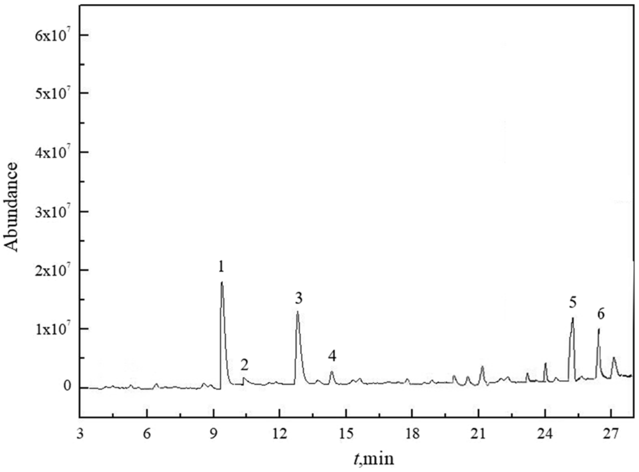


Fig. 9 GC-MS total ion chromatograms for nitrobenzene degradation in the RPB-Ti(IV)/H_2O_2/O_3 system

Table 4 Intermediate products of nitrobenzene oxidation detected by GC-MS in an acidic environment

Number	Retention time (min)	Compound identified by GC-MS	Molecular weight (m/z)	EI-MS spectrum ions (m/z)
1	9.32–10.00	Para-benzoquinone	108	26,54,82,108
2	10.53–11.00	Oxalic acid	90	29,45,46
3	12.69–13.12	Nitrobenzene	123	51,77,93,123
4	14.28–14.70	2-Nitrophenol	139	65,81,109,139
5	25.01–25.55	Catechol	110	63,64,110
6	26.31–26.80	Hydroquinone	110	53,55,81,110

The electric energy consumption of the whole nitrobenzene wastewater treatment process can be expressed as follows:

$$E_{\mathrm{EM}} = E_{\mathrm{EM}/\mathrm{O}_3} + E_{\mathrm{EM}/\mathrm{H}_2\mathrm{O}_2} \tag{22}$$

For other water treatment technologies (such as UV/H_2O_2, Ultrasonic/H_2O_2), the whole process of consumption can be expressed as follows:

$$E_{\mathrm{EM}}(\mathrm{kWh/kg}) = \frac{P\cdot t}{(C_0 - C_t)\cdot V\cdot \mathrm{M}\cdot 10^{-3}} + E_{\mathrm{EM}/\mathrm{H}_2\mathrm{O}_2} \tag{23}$$

where P is the power of an ultrasonic or ultraviolet lamp (kw), t is the reaction time (h), C_0 and C_t are the concentrations of nitrobenzene (mol/L) at the beginning of a test and at time t, respectively, V is the volume of the treated water, and M is the molar mass of the nitrobenzene (g/mol). The results of electric energy calculations are shown in Table 3 (García Einschlag et al. 2002; Xie et al. 2005).

The calculation results show that the RPB-Ti(IV)/H_2O_2/O_3 system (106.58 kWh/kg) requires the least amount of electric energy to treat the acidic nitrobenzene wastewater, compared to the RPB-H_2O_2/O_3 system (129.52 kWh/kg), the ultrasonic/H_2O_2/Fe^{2+} system (338.75 kWh/kg), the BR-H_2O_2/O_3 system (1244.57 kWh/kg), and the UV/H_2O_2 system (1358.69 kWh/kg). The experimental results show that the RPB-Ti(IV)/H_2O_2/O_3 system can improve the efficiency of acidic nitrobenzene wastewater treatment and reduce the cost of wastewater treatment.

Mechanism of nitrobenzene degradation

The experimental results suggest that the degradation of nitrobenzene can be attributed to the combined action of O_3 and ·OH. In order to better understand the mechanism of nitrobenzene degradation by O_3 and ·OH, the intermediates formed during the degradation of nitrobenzene by RPB-Ti(IV)/H_2O_2/O_3 were determined by GC-MS. Figure 9 shows total ion chromatograms for nitrobenzene degradation by GC-MS, and the intermediate products of nitrobenzene oxidation detected by GC-MS are shown in Table 4. By GC-MS analysis, 2-nitrophenol, para-benzoquinone, catechol, hydroquinone, and oxalic acid were identified to be transformation products from nitrobenzene oxidation by the RPB-Ti(IV)/H_2O_2/O_3 system. As was generally known, the concentration of intermediate products was low and unstable. Therefore, we proposed that nitrobenzene could be oxidized through two pathways from the GC-MS analysis.

Figure 10 shows that the proposed pathways of direct oxidation by O_3 consist mainly of the oxidative ring-opening reaction, molecular rearrangement, free-radical

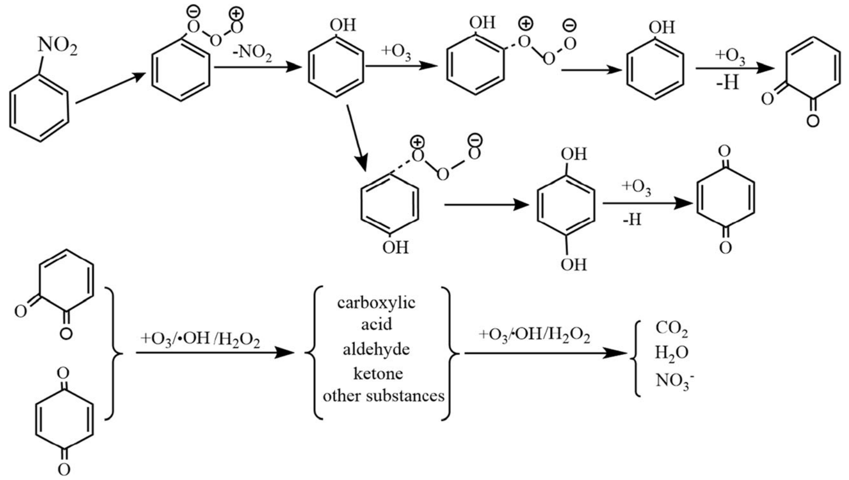
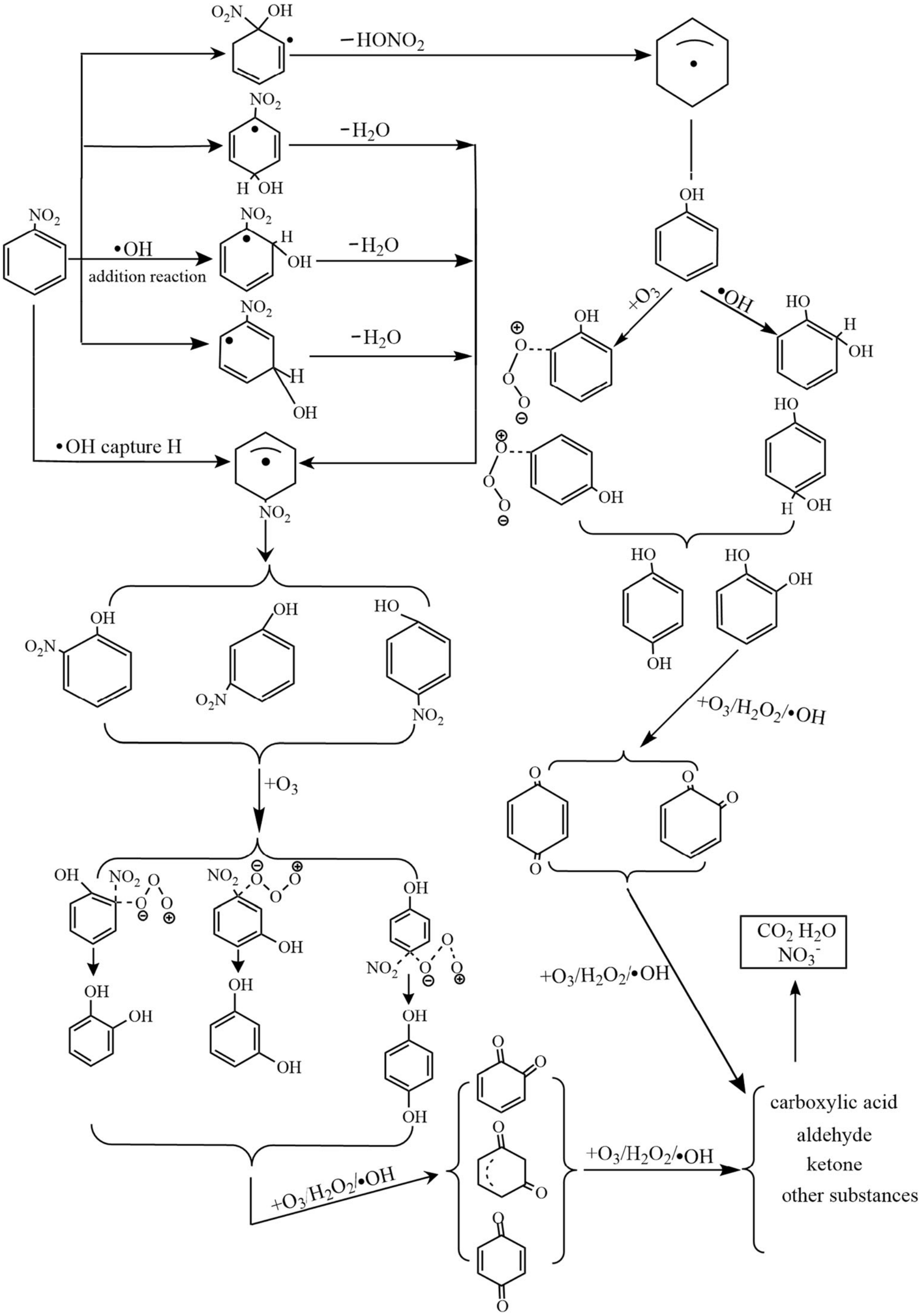


Fig. 10 Proposed pathways of direct oxidation degradation by O_3

substitution, isomerization, and mineralization. The nitro group has a strong electron withdrawing effect that allows for the attachment of carbon atoms, due to the dipole effect of O_3. O_3 is connected with the nitro group, and the carbon atoms undergo nucleophilic substitution reaction. First, oxygen atoms are bonded with carbon atoms to form unstable transition-state compounds, and the nitro group falls off from the nitrobenzene and is oxidized to nitrate. The energy required for this reaction is provided by the C-O bond release energy, and the unstable intermediate compounds are oxidized to phenols. Because the hydroxyl group is an electron-donating group, the density of the electron cloud on the benzene ring is greatly increased. According to the base effect, the positively charged oxygen atoms in the ozone molecule attack ortho-position and para-position of hydroxyl to form catechol and hydroquinone, which in turn can be oxidized to produce ortho-benzoquinone and para-benzoquinone. These quinones are easily oxidized to the

Fig. 11 Proposed pathways of indirect oxidation degradation by ·OH



open-loop structure to form maleic acid and oxalic acid, which are finally mineralized to CO_2 and H_2O (Zeng et al. 2013).

·OH has a higher oxidation capacity than O_3 (Jiao et al. 2016), and thus the possible pathways of indirect oxidation by ·OH are shown in Fig. 11. In comparison with other oxidants, ·OH has a lone pair of electrons, resulting in more efficient and selective oxidation of organic compounds. The electrophilic energy is much higher than the activation energy required for the reaction, and the reaction between ·OH and other organic matters no longer meets the inter-site positioning effect of nitro group and produces some intermediates that do not accord with the rules of location. The ·OH and nitrobenzene can undergo the addition reaction and hydrogen extraction reaction, while nitrobenzene itself can undergo denitric acid and dehydration to form phenyl and nitrophenyl radicals, which are unstable and can produce phenol and nitrophenol (Zhang et al. 2014a). Due to the electron donating effect of ·OH, the density of the electron cloud of benzene ring is greatly improved, and it will be oxidized by O_3 and ·OH to form bisphenol, which can be further oxidized to highly oxidizing quinones. The benzene ring opens to form small molecules, which are then mineralized to CO_2 and H_2O.

Conclusions

Ti(IV)/H_2O_2/O_3 was used in this study for the degradation of nitrobenzene under acidic conditions in a RPB. It is found that Ti(IV)/H_2O_2/O_3 is more effective than H_2O_2/O_3, as Ti(IV) can promote the generation of ·OH. The degradation efficiency of nitrobenzene by Ti(IV)/H_2O_2/O_3 is roughly 16.84% higher than that by H_2O_2/O_3 in RPB. The optimal degradation efficiency of nitrobenzene by Ti(IV)/H_2O_2/O_3 is obtained at an initial pH of 4.0, a high gravity factor of 40, a Ti(IV) concentration of 0.50 mmol/L, a H_2O_2/O_3 molar ratio of 0.48, a liquid flow rate of 120 L/h, and a reaction time of 30 min. It is found that the indirect oxidation accounts for 84.31% of the total oxidation process. The GC-MS results show that the intermediates of nitrobenzene oxidation are primarily phenols (phenol, catechol, resorcinol, hydroquinone, and nitrophenol) that can be further oxidized to quinones (*p*-benzoquinone, *o*-benzoquinone, and *m*-benzoquinone). The Ti(IV)/H_2O_2/O_3 method has promising applications in treating acidic nitrobenzene wastewater.

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