

# Kinetics, degradation pathway and reaction mechanism of advanced oxidation of 4-nitrophenol in water by a UV/H<sub>2</sub>O<sub>2</sub> process

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**Abstract:** Photooxidation of 4-nitrophenol (4-NP) in water by the UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process was carried out in order to investigate the kinetics and pathway of 4-NP degradation. The experimental results showed that the photodegradation of 4-NP accorded well with pseudo-first order kinetics. The effects of different parameters, such as H<sub>2</sub>O<sub>2</sub> dosage, pH value and various anion scavengers on the degradation of 4-NP have been investigated in detail. It was found that acidic conditions are more favorable to the degradation of 4-NP but many anions, such as HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, slow down the photooxidation rate of 4-NP. Hydroquinone, 1,2,4-trihydroxybenzene, 4-nitropyrogallol, and 4-nitrocatechol were tentatively identified as the intermediates of 4-NP degradation by GC/MS after samples were derivatized by *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA). A degradation pathway was proposed to account for the observed intermediates produced during 4-NP degradation by the UV/H<sub>2</sub>O<sub>2</sub> process.

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**Keywords:** UV/H<sub>2</sub>O<sub>2</sub> process; advanced oxidation processes (AOPs); 4-nitrophenol; degradation pathway; kinetics

## 1 INTRODUCTION

Organic pollution, especially organic micropollution, is nowadays known as a distinct characteristic of water pollution. A number of toxic and harmful organic micropollutants have been found not only in source water but also in drinking water. Conventional water treatment methods, for example chlorination, may result in disinfection by-products (DBPs) such as trihalomethanes (THMs).<sup>1</sup> Therefore, removal of organic micropollutants from water has become an important objective in water treatment.

In the past two decades advanced oxidation processes (AOPs) have been considered as very effective methods to destroy organic pollutants in water.<sup>2,3</sup> The hydroxyl radical, the primary oxidant in AOPs, is a strong, non-selective oxidant with a high oxidation potential of 2.8V and high rate constants, often in the order of 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.<sup>4</sup> The UV/H<sub>2</sub>O<sub>2</sub> process, an AOP, has been applied successfully to mineralize some toxic and hazardous organic micropollutants to inorganic materials or convert them to readily biodegradable intermediates.<sup>5–9</sup> Furthermore,

UV/H<sub>2</sub>O<sub>2</sub> has also been used in advanced drinking water treatment.<sup>10</sup>

4-Nitrophenol (4-NP), one of the 114 priority organic pollutants listed by the USA EPA,<sup>11</sup> is a toxic and bio-refractory compound which can damage the central nervous system, liver, kidney and blood of humans and animals. Its high stability and solubility in water are the main reasons why the degradation of the compound to non-dangerous levels is a very difficult process.<sup>12</sup> 4-NP is extensively used in the chemical industry for the manufacture of insecticides, herbicides, synthetic dyes and pharmaceuticals.<sup>13–15</sup> Therefore, 4-NP is often observed in the effluents of industrial wastewater treatment plants. A few researchers have reported the degradation of 4-NP by AOPs, including O<sub>3</sub>, UV + H<sub>2</sub>O<sub>2</sub>, Fenton reagent, photo-Fenton and electro-Fenton methods, UV + H<sub>2</sub>O<sub>2</sub> + TiO<sub>2</sub>, TiO<sub>2</sub> + UV and ultrasonic irradiation,<sup>16–22</sup> etc. However, to our knowledge, there has been little research investigating the degradation kinetics, oxidation pathway and reaction mechanism of 4-NP by the UV/H<sub>2</sub>O<sub>2</sub> process.

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In this investigation, the effects of hydrogen peroxide dosage, pH value and anions on the degradation of 4-NP have been studied. Furthermore, an attempt was made to elucidate the degradation pathway and reaction mechanism of 4-NP.

## 2 EXPERIMENTAL

### 2.1 Materials

4-Nitrophenol, hydroquinone, 4-nitrocatechol, 1,2,4-trioxylbenzene and benzoquinone were commercially purchased from Aldrich. *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) was obtained from Pierce. Ethyl ethanoate was purified by distillation. All other chemicals used in the experiments were analytical reagent grade. The water employed in all preparations was purified by a Film Tec RO TW30-4040 system, with a conductivity lower than  $5.37 \times 10^{-6} \text{ S cm}^{-1}$ . The reaction solutions were prepared by diluting 4-NP stock solution to the desired concentration. The solution pH values were adjusted with NaOH and  $\text{H}_2\text{SO}_4$  solutions.

### 2.2 Apparatus and procedure

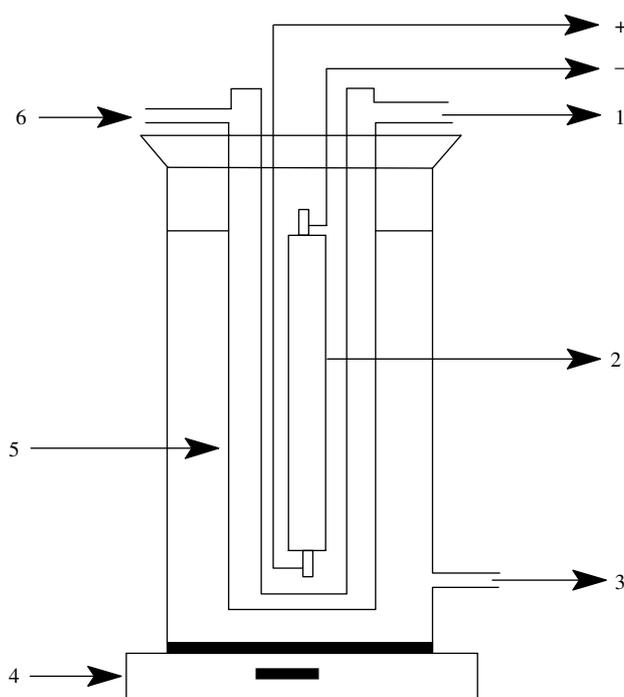
As shown in Fig 1, photoreactions were carried out in an annular glass photoreactor with a virtual volume of  $1.5 \text{ dm}^3$  (35 cm high, 7.8 cm od). A low pressure UV lamp (S2-Q-PA12, Canada R-Can Environmental Inc), with a monochromatic radiation at 254 nm and a nominal power of 14W, was housed in a double-walled quartz sleeve inside the glass reactor. The external wall of the reactor was covered with aluminum foil to improve the efficiency of photoreaction. A magnetic stirrer was placed at the bottom of the reactor to provide agitation. The photon flux (at 254 nm) entering the reactor from the UV lamp was  $3.14 \times 10^{-6} \text{ Einstein s}^{-1}$ , determined by potassium ferrioxalate actinometry.<sup>23</sup>

The reaction mixture was stirred for 10 min prior to starting the photodegradation experiments. The pH of the reaction mixture was the natural pH of dissolved 4-NP (about 5.14) except for experiments studying the effect of pH. Samples were taken at desired intervals for analysis.

### 2.3 Analysis

Quantification of the 4-NP was achieved with a Helios Alpha UV/visible spectrophotometer (Thermo Spectronic) at  $\lambda = 401 \text{ nm}$  ( $\epsilon = 19200 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>22</sup> The total organic carbon was determined by a Phoenix 8000 TOC analyzer. The concentration of hydrogen peroxide was obtained iodometrically.<sup>24</sup>

To qualitatively identify the intermediates produced during 4-NP degradation, the reaction mixture was extracted three times with  $10 \text{ cm}^3$  ethyl ethanoate at desired intervals. The extract was dried over anhydrous sodium sulfate, filtered and blown to dryness under a gentle  $\text{N}_2$  stream. Then the dried extract was dissolved in  $0.2 \text{ cm}^3$  dichloromethane for GC/MS analysis. The extract was also silylated by



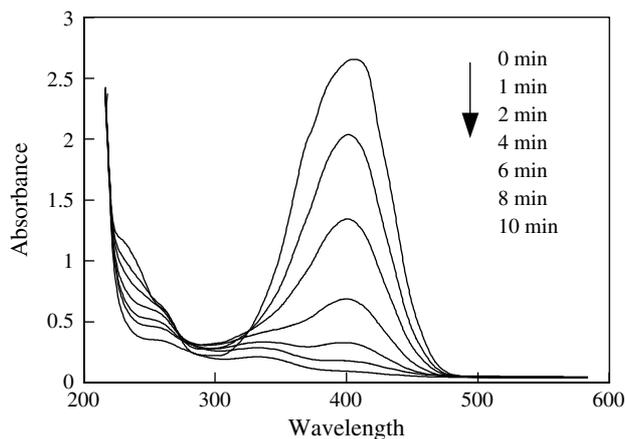
**Figure 1.** Schematic of reactor set-up 1: 1: Inlet of recycled water; 2: UV lamp; 3: sampling outlet; 4: magnetic stirrer; 5: double-walled quartz U-tube; 6: outlet of recycled water.

addition of  $50 \text{ mm}^3$  of BSTFA in a small sealed vial overnight. Under these conditions the hydroxyl groups were derivatized as trimethylsilyl ethers. A Hewlett-Packard (HP) 5890GC with a 5972 mass selective detector (MSD) operated on the scan mode was used to qualitatively identify the intermediates. The GC column used was a HP-5 fused-silica capillary column ( $50 \text{ m} \times 0.32 \text{ mm id} \times 0.17 \mu\text{m film}$ ) and the initial oven temperature was held at  $50^\circ\text{C}$  for 5 min, then programmed at a rate of  $5^\circ\text{C min}^{-1}$  up to  $250^\circ\text{C}$  and held at  $250^\circ\text{C}$  for 15 min.

## 3 RESULTS AND DISCUSSION

### 3.1 Degradation of 4-NP by the UV/ $\text{H}_2\text{O}_2$ process

When the UV irradiation or hydrogen peroxide was used alone, control experimental results showed that the concentration of 4-NP decreased slightly, which indicated that 4-NP was relatively stable during the treatment by hydrogen peroxide or UV irradiation alone. However, a significant reduction in the 4-NP concentration can be observed for the treatment by the combination of the UV irradiation and hydrogen peroxide. The absorption spectra obtained during the photodegradation of 4-NP are shown in Fig 2. This figure shows that the characteristic absorption of 4-NP disappeared rapidly and implies that 4-NP has been effectively removed from the reaction solution. As the reaction proceeded, the solution changed from colorless to orange and then gradually disappeared with prolonged reaction time, which suggested that there were some intermediates produced in the



**Figure 2.** Absorption spectra profiles during degradation of 4-NP by UV/H<sub>2</sub>O<sub>2</sub> process: [4-NP]<sub>0</sub> = 25 ppm, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9.3 mM, pH = 5.14.

photodegradation of 4-NP. The removal of 4-NP may be attributed to the hydroxylation of hydroxyl radicals through which an OH group was added to the 4-NP molecule.

### 3.2 Kinetic study

As stated above, the removal of 4-NP was attributed to the oxidation by an OH radical, which can be expressed by:



Hence, the disappearance rate of 4-NP can be obtained through the following equation:

$$-dC/dt = k_{4\text{-NP}, \bullet\text{OH}} [\bullet\text{OH}] C$$

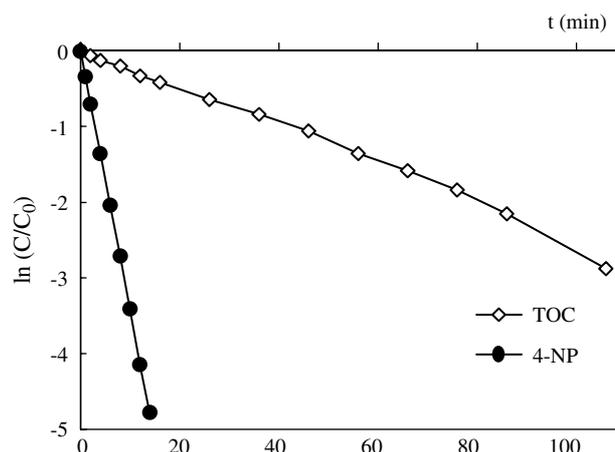
where  $C$  is the concentration of 4-NP at irradiation time  $t$  and  $k_{4\text{-NP}, \bullet\text{OH}}$  is defined as the second order rate constant of 4-NP reacting with  $\bullet\text{OH}$ . The equation can further be simplified if one takes into account that the concentration of  $\bullet\text{OH}$  is constant assuming the steady state situation for the net formation rate of these intermediates.<sup>25,26</sup> Thus, the degradation rate of 4-NP due to the combination of hydrogen peroxide and UV irradiation is finally:

$$-dC/dt = k_1 C$$

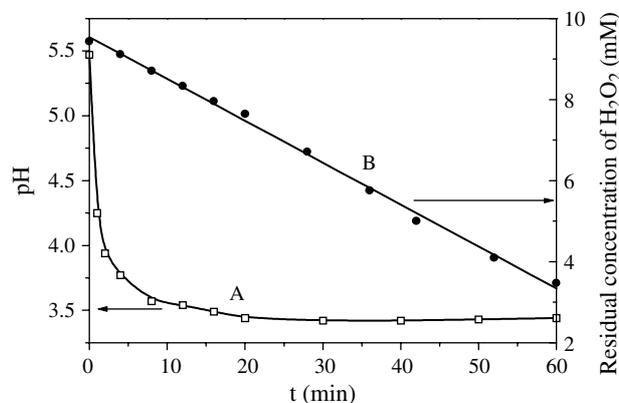
where  $k_1$  represents the product of  $k_{4\text{-NP}, \bullet\text{OH}}$  and  $[\bullet\text{OH}]$  and  $k_1$  can then be defined as a pseudo-first order rate constant. A common form of the pseudo-first order rate kinetic equation can be obtained by integrating the equation above:

$$\ln(C_t/C_0) = -k_1 t$$

where  $k_1$  (in s<sup>-1</sup>) is the pseudo-first order rate constant, and  $C_t$  and  $C_0$  are the concentrations



**Figure 3.** Profiles for the concentrations of 4-NP and TOC vs time during the experiments. Experimental conditions: [4-NP]<sub>0</sub> = 25 ppm, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9.3 mM, pH = 5.14.

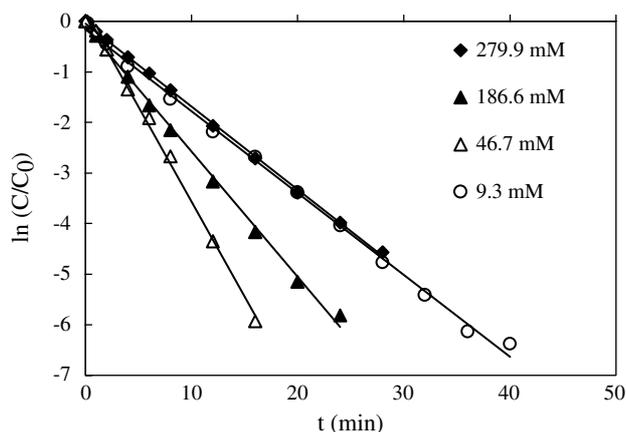


**Figure 4.** Change of solution pH and residual concentration of H<sub>2</sub>O<sub>2</sub> during the degradation of 4-NP. Experimental conditions: [4-NP]<sub>0</sub> = 25 ppm, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 9.3 mM, pH = 5.14.

at irradiation time  $t$  and initial concentration, respectively.

The experimental data indicated that more than 98% of 4-NP was decomposed within 12 min. We can conclude that 4-NP photodegradation accords with pseudo-first order kinetics and the apparent rate constant is  $7.39 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9985$ ) (see Fig 3). The reason that 4-NP disappeared so rapidly is that the hydroxyl radical has a high rate constant with 4-NP ( $k = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).<sup>19</sup> The profiles also show that the TOC was reduced dramatically with the degradation of 4-NP, but the TOC removal is much slower than the degradation rate of 4-NP (see Fig 3), which means that 4-NP is not mineralized to CO<sub>2</sub>, H<sub>2</sub>O and inorganic substrates directly but via a number of intermediates. In this study 94% of 4-NP can be mineralized completely in 106 min. The reaction mechanism of 4-NP degradation by UV/H<sub>2</sub>O<sub>2</sub> will be discussed below in detail.

The variation of pH value in the system also indicates the formation of inorganic acids and organic acids which cause the pH of the solution to drop (see Fig 4, curve A).



**Figure 5.** Effect of initial hydrogen peroxide concentration on the degradation. Experimental conditions:  $[4\text{-NP}]_0 = 50$  ppm,  $\text{pH} = 5.14$ .

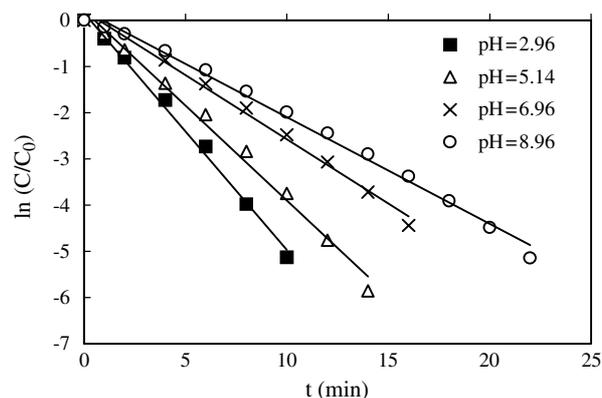
### 3.3 Effect of hydrogen peroxide concentration on photodegradation kinetics

In order to clearly learn the effects of initial concentration of hydrogen peroxide, experiments on the relationship between initial hydrogen peroxide concentration and 4-NP degradation were conducted and the profiles are shown in Fig 5. It can be observed that the disappearance rate of 4-NP is significantly increased with the increase of hydrogen peroxide concentration, but when the hydrogen peroxide concentration is higher than 46.7 mM the oxidation rate drops dramatically. Corresponding to this, the apparent rate constant is increased from  $2.70 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9972$ ) at  $C_{\text{H}_2\text{O}_2} = 9.3$  mM to  $6.25 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9970$ ) at  $C_{\text{H}_2\text{O}_2} = 46.7$  mM, however, the apparent rate constant is decreased to  $4.13 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9972$ ) at  $C_{\text{H}_2\text{O}_2} = 186.6$  mM and  $2.70 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9972$ ) at  $C_{\text{H}_2\text{O}_2} = 279.9$  mM. This result could be interpreted by the dual actions of hydrogen peroxide on the  $\cdot\text{OH}$  concentration. If the hydrogen peroxide increases to a certain concentration, more  $\cdot\text{OH}$  will be generated to accelerate the 4-NP degradation. However, when the concentration of hydrogen peroxide is higher than 46.7 mM, the scavenging effect of hydrogen peroxide on  $\cdot\text{OH}$  will become an important factor and the 4-NP oxidation rate decrease significantly. Liao and Guroi also observed this phenomenon in the oxidation of *n*-chlorobutane.<sup>27</sup>

The residual concentration of  $\text{H}_2\text{O}_2$  is also illustrated in Fig 4 (curve B) at various reaction intervals. It was found that the disappearance of hydrogen peroxide accorded with zero order kinetics and the rate was  $5.07 \times 10^{-5} \text{ M s}^{-1}$ , which reflects the fact that the primary UV light absorber is 4-NP rather than other intermediates generated during the degradation of 4-NP.

### 3.4 Effect of pH value on photodegradation kinetics

The effect of pH on the degradation of 4-NP by UV/ $\text{H}_2\text{O}_2$  is shown in Fig 6. It is obvious that the degradation rate decreases rapidly with the increase in



**Figure 6.** Effect of solution pH on the 4-NP degradation. Experimental conditions:  $[4\text{-NP}]_0 = 25$  ppm,  $[\text{H}_2\text{O}_2]_0 = 9$  mM.

the pH value, ie the apparent rate constant is reduced from  $8.56 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9946$ ) at pH 2.96 to  $3.84 \times 10^{-3} \text{ s}^{-1}$  ( $R^2 = 0.9938$ ) at pH 8.96. This is due to the fact that under strong alkali conditions the  $\text{CO}_2$  produced during the 4-NP degradation will be converted to  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , both of which have high rate constants with hydroxyl radicals ( $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively). Therefore, 4-NP degradation will be retarded with the increase of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  in the reaction solution. Furthermore, alkali conditions are favored for the dissociation of hydrogen peroxide to form  $\text{HO}_2^-$ . The ions of  $\text{HO}_2^-$  have a higher reactivity than hydrogen peroxide with hydroxyl radicals, resulting in a decrease in the number of hydroxyl radicals.<sup>28</sup> This might also lead to the reduction in the degradation rate of 4-NP. Thus it can be concluded that the photodegradation of 4-NP by the  $\text{H}_2\text{O}_2/\text{UV}$  process is more favorable in acidic pH solution than in alkaline solution.

### 3.5 Effect of scavengers on photodegradation kinetics

Anions in aquatic environments have remarkable influences on the photochemically induced degradation of organic micropollutants.  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , as the primary anions in natural water, are major scavengers of free radicals. However, some of them could generate the hydroxyl radical under certain conditions. Unfortunately, to our knowledge, the effects of scavengers on the 4-NP oxidation by UV/ $\text{H}_2\text{O}_2$  process have not been reported to date.

The effects of  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  on the degradation kinetics of 4-NP degradation are listed in Table 1. It is clear that the 4-NP degradation rates decrease significantly in the presence of  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  in comparison to that without anions. The influence of  $\text{HCO}_3^-$  is much greater than the other two anions. At  $\text{HCO}_3^- = 10$  mM, the rate constant decreased by a factor of 0.48, whereas for  $\text{NO}_3^-$  and  $\text{Cl}^-$  with the concentration of 15 mM the rate constant reduced by the factors of 0.22 and 0.29, respectively.

The detrimental effect of bicarbonate and its mechanism of scavenging hydroxyl radicals have been

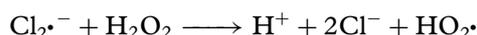
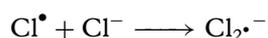
**Table 1.** Effects of anions in water on the first-order kinetic rate constants of 4-NP degradation by UV/H<sub>2</sub>O<sub>2</sub> process

Anions	$k_1$ (s <sup>-1</sup> )	$R^2$
NO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> = 0	$7.39 \times 10^{-3}$	0.9985
HCO <sub>3</sub> <sup>-</sup> = 0.5 mM	$5.18 \times 10^{-3}$	0.9995
HCO <sub>3</sub> <sup>-</sup> = 2 mM	$4.78 \times 10^{-3}$	0.9976
HCO <sub>3</sub> <sup>-</sup> = 5 mM	$4.16 \times 10^{-3}$	0.9986
HCO <sub>3</sub> <sup>-</sup> = 10 mM	$3.86 \times 10^{-3}$	0.9958
NO <sub>3</sub> <sup>-</sup> = 5 mM	$5.84 \times 10^{-3}$	0.9991
NO <sub>3</sub> <sup>-</sup> = 15 mM	$5.77 \times 10^{-3}$	0.9992
Cl <sup>-</sup> = 5 mM	$6.27 \times 10^{-3}$	0.9993
Cl <sup>-</sup> = 10 mM	$5.85 \times 10^{-3}$	0.9973
Cl <sup>-</sup> = 15 mM	$5.24 \times 10^{-3}$	0.9977

reported by several researchers.<sup>29,30</sup> Bicarbonate ions with the second-order constant of  $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  can react with hydroxyl radicals to produce carbonate radicals that will consume hydrogen peroxide. Thus it can be expected that the photodegradation of 4-NP will be reduced in the presence of bicarbonate ions.

The decrease in the 4-NP photodegradation rates was not as significant in the presence of NO<sub>3</sub><sup>-</sup> as that in the presence of HCO<sub>3</sub><sup>-</sup>. The results can be explained by the inner filter action of nitrate ions.<sup>30</sup> Nitrate can serve as an inner filter substance to reduce the photons, sheltering the photolysis of hydrogen peroxide.

The experimental results in Table 1 also show that the presence of Cl<sup>-</sup> leads to the reduction in the 4-NP degradation rate but its influence is smaller than that of the other two ions, HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. A plausible reason for the phenomena may be that the Cl<sup>-</sup> ions can react with hydroxyl radicals to form Cl<sub>2</sub>•<sup>-</sup> or ClOH•<sup>-</sup> by the following reactions:<sup>31,32</sup>



### 3.6 Degradation pathway and reaction mechanism of 4-NP

There have been some reports on the degradation mechanisms of 4-NP by AOPs. For example, in the photocatalytic oxidation of 4-NP with TiO<sub>2</sub>, 4-nitrocatechol, hydroquinone, 1,2,4-trihydroxybenzene and benzoquinone were identified as major intermediates;<sup>33</sup> however, in the degradation of 4-NP by ultrasonic irradiation and Fenton reagent, only 4-nitrocatechol, hydroquinone and benzoquinone were found to be intermediates.<sup>17,22</sup> More intermediates have been reported by Oturan *et al*<sup>19</sup> in the oxidation of 4-NP by the electro-Fenton method, including 4-nitrocatechol, hydroquinone, 1,2,4-trihydroxybenzene and benzoquinone and even some small amount of carboxylic acids, such as maleic, fumaric and oxalic acids. Thus, we can easily see that although the ways of generating •OH are different in various AOPs, the intermediates produced are similar to one another and even the distribution of these intermediates are dependent on the methods of oxidation.

The intermediates produced during 4-NP photodegradation by the UV/H<sub>2</sub>O<sub>2</sub> process are also qualitatively identified in this work by comparison of mass spectrometry with corresponding authentic standards. For the derivatives of 4-nitropyrogallol not included in GC/MS library databases, the fragment ions were assigned on the basis of the reference substance mass spectrum, where accessible.<sup>34,35</sup> MS data of intermediates are listed in Table 2. The relative concentrations of 4-NP and intermediates are expressed simply by the area of the corresponding chromatograph peak and are shown in Table 3. It is evident that the removal rate of 4-NP is very significant as the reaction proceeds. Four aromatic intermediates, ie hydroquinone, 4-nitrocatechol, 1,2,4-trihydroxybenzene and 4-nitropyrogallol, are formed rapidly and reach a maximum concentration at 6 min.

**Table 2.** GC/MS data for the intermediates during 4-NP degradation by UV/H<sub>2</sub>O<sub>2</sub> identified by BSTFA derivatization

Retention time (min)	Relative molecular mass	Predominant fragment ions (m/z)	Intermediates
23.73	254	254(M+), 239, 223, 112, 97, 73, 45	BSTFA hydroquinone
27.33	211	211(M+), 196, 166, 150, 135, 73, 45	BSTFA 4-nitrophenol
30.15	342	342(M+), 327, 254, 239, 147, 73, 45	BSTFA 1,2,4-trihydroxybenzene
33.44	299	299(M+), 284, 195, 137, 107, 73, 45	MSTFA 4-nitrocatechol
37.11	387	387(M+), 372, 342, 217, 204, 73, 45	BSTFA 4-nitropyrogallol

**Table 3.** Time course of accumulation of 4-NP intermediates produced by UV/H<sub>2</sub>O<sub>2</sub> process as measured by GC/MS

Compounds	Area			
	0 min	6 min	12 min	96 min
BSTFA 4-nitrophenol	$1.81 \times 10^8$	$6.65 \times 10^7$	$2.22 \times 10^6$	$2.14 \times 10^5$
BSTFA hydroquinone	— <sup>a</sup>	$3.49 \times 10^7$	$4.94 \times 10^5$	—
BSTFA 4-nitrocatechol	—	$5.87 \times 10^8$	$1.53 \times 10^6$	—
BSTFA 1,2,4-trihydroxybenzene	—	$7.13 \times 10^6$	$6.60 \times 10^5$	—
BSTFA 4-nitropyrogallol	—	$2.18 \times 10^5$	$1.15 \times 10^4$	—

<sup>a</sup> Not detected.

As the oxidation reaction proceeds, these intermediates gradually disappear. It can be seen from Table 2 that 4-nitrocatechol and hydroquinone are the predominant intermediates in the preliminary oxidation of 4-NP.

Based on the identification of intermediates, a possible oxidative pathway of 4-NP by the UV/H<sub>2</sub>O<sub>2</sub> process can be proposed, as shown in Fig 7. Two alternative pathways exist for the preliminary oxidation of 4-NP. In the first pathway, hydroquinone and 1,2,4-trihydroxybenzene are formed accompanied by the release of NO<sub>2</sub><sup>-</sup> and then subsequently oxidized by ring cleavage to yield small molecule compounds which do not contain nitrogen. In the second pathway, 4-nitrocatechol and 4-nitropyrogallol are formed and subsequently oxidized by ring cleavage to yield some nitrogenous compounds. Benzoquinone was identified as an intermediate by Lipczynskakochany E<sup>17</sup> in the oxidation of 4-NP by Fenton reagent. However, in the present study it was not detected by GC/MS. This may be due to the polarity of benzoquinone. It should be noted that hydroquinone is in equilibrium with benzoquinone in aqueous solution. Furthermore, hydroquinone is readily oxidized to benzoquinone in the presence of hydroxyl radicals.<sup>19</sup> Thus it can be expected that benzoquinone may be an intermediate during 4-NP degradation by the UV/H<sub>2</sub>O<sub>2</sub>.

Hydroxylated compounds of 4-NP will be formed when an hydroxyl radical attacks different positions in the benzene ring, leading to different oxidation pathways. The *ortho*- and *para*-positions of 4-NP are liable to attack by the electrophilic reagent <sup>•</sup>OH in the presence of the electron-donor group -OH in the benzene ring.

The interaction of <sup>•</sup>OH radicals with 4-NP initiates reactions to produce hydroxylated products through denitration or an H-abstraction reaction. 4-NP will be readily oxidized to hydroquinone with a simultaneous elimination of the nitro group because the -NO<sub>2</sub> group is easily removed. 1,2,4-Trihydroxybenzene is also formed with the further oxidation of hydroquinone, followed by ring cleavage and eventual mineralization. 4-Nitrocatechol (4-NC) is also identified as a primary intermediate in the system. It is hypothesized that 4-NC was formed by the substitution reaction of hydroxyl radical at the *ortho* position of 4-NP. 4-NC can be converted to 4-nitropyrogallol, which is also tentatively identified as one of the intermediates during 4-NP oxidation. It should be pointed out that 4-NC may be a parent compound to form 1,2,4-trihydroxybenzene. The formation of 1,2,4-trihydroxybenzene is similar to that of hydroquinone, ie the position of the nitro group of 4-NC is another object maybe attacked by hydroxyl radicals.

As shown in Fig 7, 4-NP is oxidized to polyhydroxybenzenes, especially the hydroxylated compounds whose hydroxyl groups are adjacent to each other in the preliminary oxidation stage of 4-NP. It is well known that the C-C bonds between

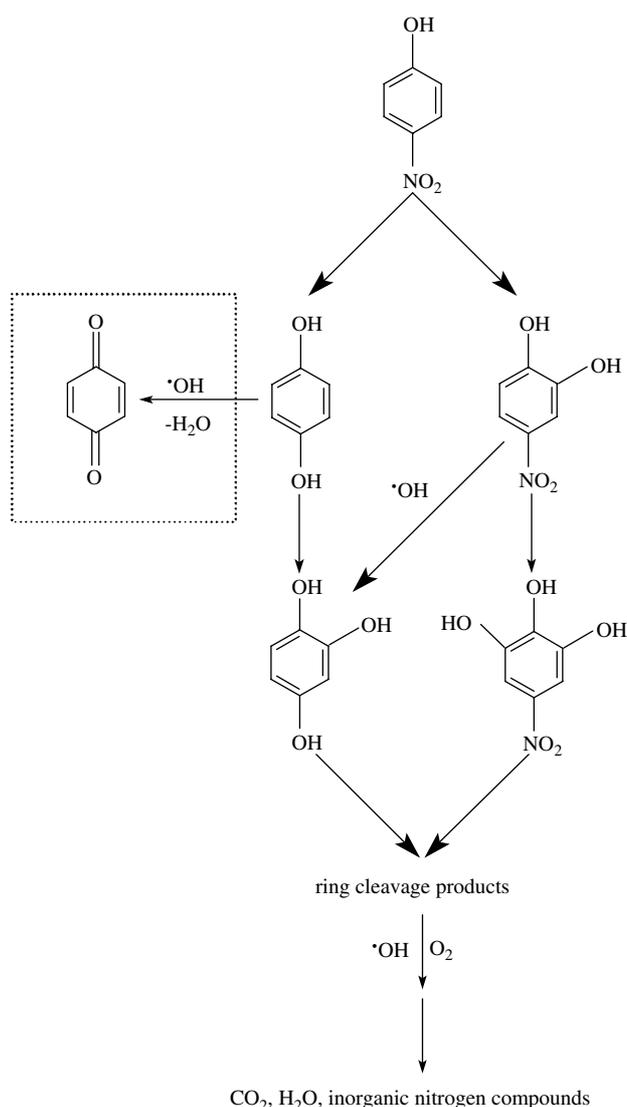


Figure 7. Pathways of 4-NP degradation by UV/H<sub>2</sub>O<sub>2</sub> process.

the adjacent hydroxyl groups are readily oxidized. As illustrated by the change of TOC concentration, the intermediates would be further degraded through the ring cleavage of polyhydroxy-aromatic compounds to form some secondary intermediates, such as aldehydes, ketones and carboxylic acids and so on until complete mineralization is achieved.

#### 4 CONCLUSION

Photodegradation of 4-NP by the H<sub>2</sub>O<sub>2</sub> process accords well with pseudo-first order kinetics; more than 98% of 4-NP can be removed within 12 min and the TOC removal is up to 94% within 106 min. Appropriate addition of hydrogen peroxide can enhance the 4-NP degradation, whereas excessive hydrogen peroxide retards the degradation rate. The 4-NP degradation rate is significantly reduced in the presence of some hydroxyl radical scavengers, including HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. The mechanisms of 4-NP degradation by the UV/H<sub>2</sub>O<sub>2</sub> process could

be summarized as (a) the *ortho*- and (b) the *para*-position of 4-NP substituted by the electrophilic reagent OH to form polyhydroxy-benzenes and (c) the ring-cleavage of polyhydroxy-aromatic compounds to produce some small molecule intermediates. Complete mineralization of 4-NP would ultimately take place.

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