# Direct photolysis of nitroaromatic compounds in aqueous solutions

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**Abstract:** The direct photolysis of nitrobenzene and nitrophenols in aqueous solutions irradiated by polychromatic light were investigated. Several aromatic intermediates were identified as three nitrophenol isomers, nitrohydroquinone, nitrosobenzene, nitrocatechol, catechol and phenol. Nitrite and nitrate ions were also detected in the irradiated solution indicating direct photolysis of nitrobenzene or nitrophenols. The degradation of nitrobenzene and nitrophenols and the formation of three nitrophenol isomers were observed to follow zero-order kinetics. The quantum yields for nitrobenzene and nitrophenols removal are about $10^{-3}$ and $10^{-3}$—$10^{-4}$ respectively. The mechanism for nitrobenzene degradation was suggested to follow mainly nitro-nitrite intramolecular arrangement.

**Keywords:** photodegradation; photolysis; nitrobenzene, nitrophenols

## Introduction

Nitroaromatic compounds such as nitrobenzene(NB) and nitrophenols(NPs) are presented in industrial effluents from production of dyestuffs, pesticides and various intermediate products for organic synthesis. NB and NPs are considered as priority toxic pollutants by the United States of America Environmental Protection(EPA) and Public Health Service (USEPA, 1985; ATSDR, 1990). Purification of wastewaters contaminated with aromatic compounds is difficult since this class is usually resistant to microbial degradation(O'Connor, 1989). Recently, UV-based advanced oxidation technologies have attracted more and more interests because of their effective mineralization of organic pollutants. However, so far, there only a few reports deal with direct photolysis of NB and NPs in aqueous solution by UV light. Simmons and Zepp (Simmons, 1986) studied the kinetic behaviour of the direct photolysis of nitroaromatic compounds, including NB, in water using a merry-go-round reactor equipped with a 450 W mercury lamp. The reaction quantum yield and the rate constant for nitrobenzene decomposition at 313 nm were reported as $(2.9 \pm 1.0) \times 10^{-5}$ and $5.2 \times 10^{-3}$ $d^{-1}$, respectively. Among the nitroaromatic compounds investigated in their work, NB in water was the most difficult to be degraded by direct photolysis. Lipczynska-Kochany (Lipczynska-Kochany, 1992) did not observe any degradation of NB and NPs during study on the direct photolysis of the aqueous solutions irradiated by the UV-Vis polychromatic light using a 150 W mercury-xenon lamp. Alif et al. investigated the direct photolysis aqueous solutions of p-nitrophenol(p-NP)(irradiated at 365 nm; Alif, 1987), m-nitrophenol (m-NP) (irradiated at 254 and 365 nm respectively; Alif, 1990) and o-nitrophenol (o-NP) (irradiated at 254 and 365 nm respectively; Alif, 1991). The quantum yields for the photo-transformation of these three nitrophenol isomers were reported as around $10^{-6}$—$10^{-5}$ in the pH range of 2—8. Hydroquinone(HQ), benzoquinone (BQ), catechol (CC), nitrocatechol (NC), nitrohydroquinone (NHQ), resorcinol and p-(or o-) nitrosophenol (NSP) have been detected as the photoproducts. In the present work, particular attention has been focused on the detailed studies of the photochemical behaviours of nitrobenzene, as well as nitrophenols in aqueous solutions irradiated by polychromatic light. The main photoproducts were identified, the quantum yields for the degradation of these compounds were estimated and

mechanism to account for NB photodegradation were suggested. More detailed studies on the direct photolysis of nitroaromatic compounds in aqueous solution will be helpful for understanding the photochemical degradation of this class of pollutants in environmental decontamination.

## 1 Experimental

### 1.1 Materials

Ferrioxalate ( $K_3 Fe (C_2 O_4)_3 \cdot 3H_2 O$ ) was prepared according to the method mentioned by Cavert et al.(Calvert, 1966). Water used in the experiment was made by passing distilled water through an ultra-pure water system (milli-Q plus 185, Millipore) with 18.2 M$\Omega$/cm followed by passing through the activated carbon. All the chemicals are obtained as commercial grade and used as received.

### 1.2 Photochemical reaction procedures

Before running an experiment, the tank of a batch reactor, named Rayox reactor(30 L, 1 kW medium pressure mercury lamp, Calgon Carbon Corporation of Markham, Ontario, Canada) was cleaned first using tap water(twice) followed once by distilled water. After cleaning, the tank was filled with the water first up to 20 L in the Rayox reactor. The previously prepared sample solutions were transferred into the tank from the access port on the top of the tank, mixing the solution for at least 10 min stirring at rotation rate 500 r/ min, and finally filling with water to 26 L for the Rayox II, then keeping the mixture for another 10 min. Approximately 5—10 ml of the sample solution was taken as a zero-sample just before switching on the UV lamp, followed by turning on the lamp. During irradiation, 5—10 ml of irradiated sample was withdrawn at regular intervals. The collected samples were directly used for analysis. All collected samples were stored in a refrigerator and analysed as quickly as possible after collection.

### 1.3 Incident photo flux

The determination of the incident photon flux for the Rayox reactor was carried out using a liquid-phase chemical actinometer ferrioxalate in a dark room. The ferrioxalate (0.15 mol/L, 26 L) solution was acidified by adding concentrated $H_2 SO_4$ to 0.05 mol/L.

Since the ferrioxalate solution was irradiated by polychromatic light from a 1 kW medium pressure mercury lamp, it is important to have a modified quantum yield($\Phi_m$) for ferrioxalate photolysis at various wavelengths. $\Phi_m$ was estimated by the published values of $\Phi$ at the various

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wavelengths as shown in Table 1 ( Murov, 1993 ). The quantum yield does show a dependence on wavelength above 300 nm with 0.15 mol/L ferrioxalate solution. It is noted from Table 1 that most of the modified quantum yielding with values > 1 fall into the wavelength range from 200 to 450 nm. Although there is emission from the lamp for wavelengths > 450 nm, the absorbance of the ferrioxalate solution in the range > 450 nm is so small that hardly any of this light is absorbed. Thus, almost all of the contribution of the photon flux for the formation of $Fe^{2+}$ can be approximated in the wavelength range 200 to 450 nm. A plot of the quantum yield versus wavelength was fit to a 4th order polynomial and the regression equation for this fit is given as follows:

$$\Phi_m = A + B_1\lambda + B_2\lambda^2 + B_3\lambda^3 + B_4\lambda^4, \qquad (1)$$

where $\lambda$ is the wavelength (nm); $A = 0.347 \pm 1.166$, $B_1 = -(0.032 \pm 0.015)$, $B_2 = (1.664 \pm 0.726) \times 10^{-4}$, $B_3 = -(3.673 \pm 1.505) \times 10^{-7}$, $B_4 = (2.844 \pm 1.146) \times 10^{-10}$, $R^2$(square of correlation coefficient) = 0.9906.

A modified distribution of the quantum yields, $\Phi_m$, at the wavelengths from 200 to 450 nm can be obtained from the Equation (1). Thus, a "weighted average" quantum yield $\Phi_{ave}$ for the $Fe^{2+}$ generation can be obtained as $\Phi_{ave} = 1.184$ using Equation (2):

$$\Phi_{ave} = \frac{\sum_{200}^{450} E_\lambda \Phi_m}{\sum_{200}^{450} E_\lambda}, \qquad (2)$$

where $E_\lambda$ is the known relatively incident photon flux of lamp at certain wavelength. Making a plot of $Z = (AV_2 V_3)/(\varepsilon d \Phi_m V_1)$ versus $t$ (s), a linear fit with a correlation coefficient of 0.9994 was obtained as:

$$Z = (5.38 \pm 0.02) \times 10^{-4} t . \qquad (3)$$

In this case, the modified photon flux $G_{o(m)}$ entering the Rayox II reactor from the UV lamp can be obtained from the slope of this plot as follows:

$$G_{o(m)} = (5.38 \pm 0.02) \times 10^{-4} (\text{Einstein s}^{-1}). \quad (4)$$

Thus, the total photon fluxes for the 200 to 300 nm and 200 to 400 nm ranges are obtained as follows:

$$G_{o(200-300)} = G_{o(m)} \times 0.494$$
$$= (2.66 \pm 0.01) \times 10^{-4} (\text{Einstein s}^{-1}), (5)$$
$$G_{o(200-400)} = G_{o(m)} \times 0.818$$
$$= (4.40 \pm 0.02) \times 10^{-4} (\text{Einstein s}^{-1}). (6)$$

Where 0.494 and 0.818 are the fractions of light emitted in the ranges of 200 to 300 nm and 200 to 400 nm, respectively.

Table 1   Quantum yields of $Fe^{2+}$ production at various wavelengths(Murov, 1993)

| $\lambda$, nm | 254 | 297/302 | 313 | 326 | 334 | 341 | 358 | 361/366 | 405 | 436 | 468 | 480 | 502 | 577/579 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Phi_{(Fe^{2+})}$ | 1.25 | 1.24 | 1.24 | 1.23 | 1.23 | 1.22 | 1.25 | 1.21 | 1.14 | 1.01 | 0.91 | 0.93 | 0.90 | 0.013 |

## 1.4 Analysis

Analysis of nitrobenzene and of the aromatic intermediates produced was carried out using HPLC(LC-10A series HPLC system, Shimadzu, Japan) coupled with a reverse-phase column packed with $C_{18}$ groups(STR ODS-II, 4.6 mm × 15 cm). Detection was performed by an UV-Vis photodiode array detector(SPD-M10Avp) at 210, 245, 254, 280 and 350 nm simultaneously. The mobile phase was acetonitrile/water(33/67), acidified with $H_3PO_4$ to pH 2.5 to elute acid compounds in their undissociated forms and to avoid peak tailing. The flow rate was adjusted to 1.2 ml/ min. Samples were injected using the auto-sampler and simultaneously recording the chromatogram using the PC computer program. Identification of the samples and other aromatic intermediates was performed by comparison of their chromatography retention times with those of authentic standard chemicals.

Photo-produced aliphatic and inorganic intermediates, such as formic acid, oxalic acid, maleic acid, nitrite and nitrate ions, were determined using HPLC coupled with a conductivity detector and an anion exchange column packed with quaternary ammonium groups. The mobile phase was a 10 mmol/L $NaH_2PO_4$ solution adjusted to pH 3.5 with $H_3PO_4$; the flow rate was 1.2 ml/min; CDD and the column were kept at 40℃. All of the inorganic and aliphatic intermediates were identified by comparison of their retention times with those of the commercial compounds.

## 2 Results and discussion

### 2.1 Photochemical behaviour and kinetic study
#### 2.1.1 Degradation of nitrobenzene and intermediates

The UV-Vis spectrum of aqueous nitrobenzene shows that nitrobenzene absorbs light strongly for $\lambda < 320$ nm; therefore it has the potential to undergo direct photolysis in aqueous solutions. In fact, a slight degradation of nitrobenzene has been observed during the direct photolysis process under the experimental conditions.

In both air-saturated and nitrogen-saturated solutions, o-nitrophenol ( o-NP ), m-nitrophenol ( m-NP ), p-nitrophenol ( p-NP ), phenol ( PhOH ), nitrohydroquinone ( NHQ ), nitrocatechol( NC ) and catechol( CC ) were detected as the main aromatic intermediates during irradiation. In addition, nitrosobenzene(NSB) and benzoquinone(BQ) were also observed in the irradiated NB solution. Fig. 1a shows the direct photodegradation of 0.519 mmol/L nitrobenzene in air-saturated solution and the production of the aromatic intermediates. After 120 min irradiation, about 30% of NB is degraded. The production of all the identified aromatic intermediates increases almost linearly with irradiation time in the studied range. NPs, NHQ and PhOH appear after about 10 min irradiation. Among them, the accumulation of phenol and NHQ are slow and last over 120 min irradiation after their formation. NC and CC appear only after 60 min irradiation and their chemical yields remain at trace levels throughout the whole process, indicating that they are secondary products mostly generated from NPs, which has been confirmed by the direct photolysis of NPs described later, alternatively may be generated from PhOH. Other unidentified chromatographic peaks were also observed at earlier retention times ( < 2.0 min ), especially a peak that increases significantly with irradiation time at a retention time of about 2 min, which may indicate the presence of other hydrophilic aromatics, such as hydroquinone, dihydroxybenzenes or trihydroxybenzenes ( Minero, 1994 ). The distribution of the chemical yields follows the order o-NP > p-NP > m-NP > PhOH > NHQ > CC > NC over 100 min irradiation. The ratio for the three nitrophenol isomers is: o-NP:p-NP:m-NP = 3.6:2.4:1.0 at 20 min irradiation and 1.6 : 1.4 : 1.0 at 120 min irradiation, respectively.
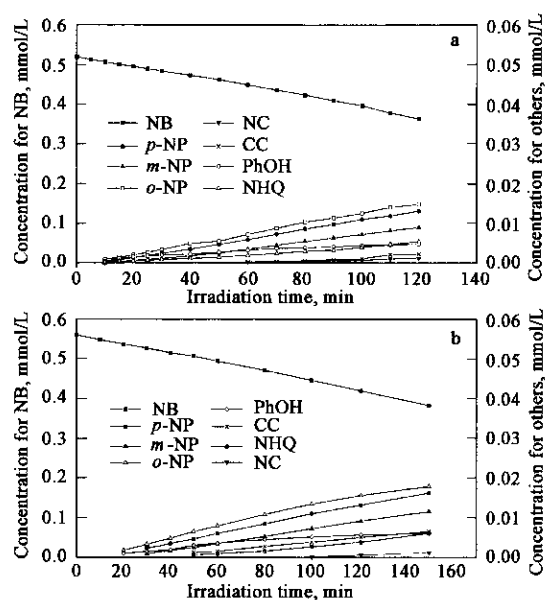
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Fig.1　Time profiles in the direct photolysis of nitrobenzene and produced aromatic intermediates
a. air-saturated solution; b. nitrogen-saturated solution

The direct photolysis of a 0.560 mmol/L nitrobenzene in nitrogen-saturated solution has also been investigated. Fig. 1b shows the curves for NB degradation and the formation of aromatic intermediates during irradiation. Around 25% of NB is degraded over 120 min irradiation. Similar to the air-saturated solution, all of the identified aromatic intermediates are generated linearly with irradiation time, but most of them appear after a longer irradiation time ( ~ 20 min irradiation) in contrast to the case for the aerated solution. These facts indicate that oxygen may be involved in the degradation of nitrobenzene in air-saturated solution. The distribution of the chemical yields for these aromatic intermediates in nitrogen-saturated solution follows the order $o$-NP > $p$-NP > $m$-NP $\geqslant$ PhOH > CC > NHQ > NC over 120 min irradiation, which is almost in the same order as that in aerated solution. The ratio of the chemical yields for NPs is from $o$-NP : $p$-NP : $m$-NP = 3.5 : 2.5 : 1.0 at 30 min irradiation to 1.7 : 1.4 : 1.0 at 120 min irradiation, which is in good agreement with those of the aerated solutions, indicating the isomer composition does not change whether in air-saturated or nitrogen-saturated solution.

Nitrate and nitrite ions were detected as the predominant inorganic intermediates during the direct photolysis of NB in air-saturated solution. Fig. 2 shows that nitrite ion appears immediately after irradiation has begun, whereas nitrate ion appears somewhat later after about 10 min irradiation. These facts indicate direct denitration of NB during irradiation. Both nitrate and nitrite ions increase linearly with the irradiation time, indicating that the nitro-group is released from the nitrobenzene ring into the solution. The distribution of nitrate and nitrite follows the order nitrite > nitrate for the whole process. This can be explained by the released nitro group forming $NO_2^-$ at first, followed by conversion into $NO_3^-$ by oxidation of oxygen in the solution. It was also observed that the pH gradually decreased with irradiation time, which is attributed to the generation of $HNO_2$ and $HNO_3$ during the irradiation of the NB solution. Besides nitrate and nitrite, trace amounts of maleic acid have also been observed after ~ 50 min irradiation and remains almost constant up to 120

min irradiation, implying that some of the nitrobenzene rings cleave into aliphatic compounds during the direct photolysis of nitrobenzene.
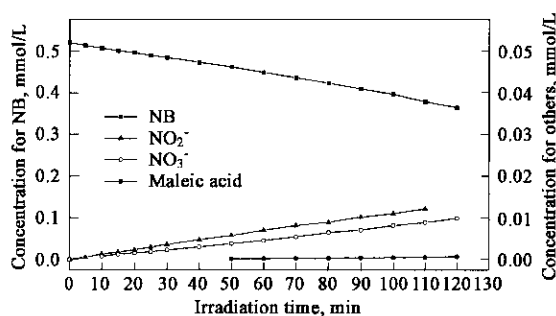


Fig.2　Time profiles in the direct photolysis of nitrobenzene and produced inorganic nitrogen species in air-saturated solution

### 2.1.2　Degradation of nitrophenols and intermediates

Direct photolysis of each of the three nitrophenol isomers in air-saturated aqueous solutions was studied. As shown in Fig. 3a and 3b, complete decomposition of $o$-NP ( > 99.5% ) and $p$-NP( > 99.8% ) is achieved after around 80 min and 60 min irradiation respectively, whereas only about 47.7% of $m$-NP is decomposed at 80 min irradiation ( Fig. 3c). This means that $m$-NP is more difficult to be removed than $o$-NP and $p$-NP under experimental conditions.
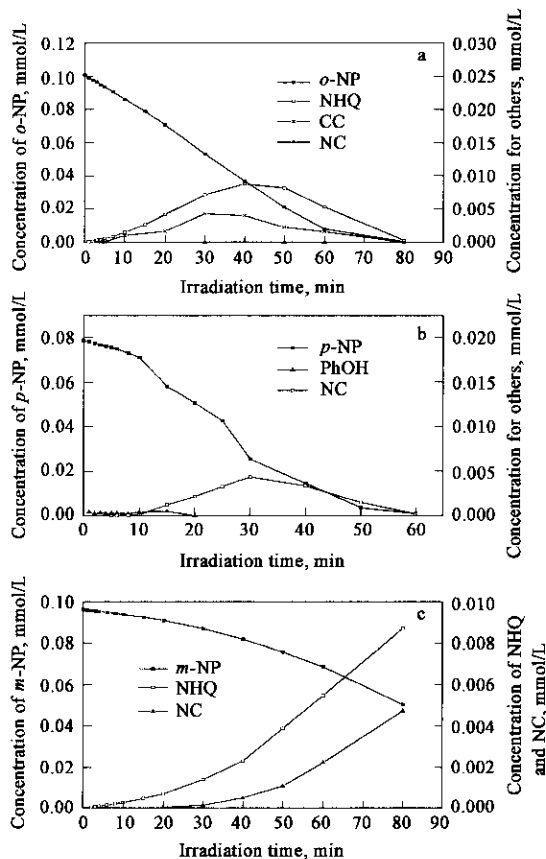


Fig.3　Time profiles in the direct photolysis of nitrophenols and produced aromatic intermediates in air-saturated solutions
a. $o$-nitrophenol; b. $p$-nitrophenol; c. $m$-nitrophenol

For the $o$-NP degradation, three aromatic intermediates were identified as NHQ, CC and NC. Among them, NHQ and CC are the predominant aromatic intermediates. The chemical yields for their formation follow the order NHQ > CC

≫NC in the whole process. NHQ appears very rapidly after starting irradiation and reaches maximum chemical yield of 25.7% of the initial o-NP concentration after 40 min irradiation and is almost completely degraded after ~ 80 min irradiation. CC is produced after about 5 min irradiation and reaches the maximum chemical yield ~ 4.2% of the initial o-NP concentration at ~ 30 min irradiation, and its complete decay is achieved at ~ 80 min irradiation. NC has been detected only at a trace level during the irradiation process. Nitrite and nitrate ions were observed during irradiation of the o-NP solution. They are considered to be results from the denitration of o-NP. Both the nitrite and nitrate ions increase almost linearly with same rate over the whole process. The total inorganic nitrogen, IN ( $NO_2^-$ + $NO_3^-$ ), accounts for 43.6% of the initial o-NP concentration at ~ 80 min irradiation corresponding to ~ 99.5% of o-NP removal, indicating that almost half of nitrogen which was not detected in this work remains in the form of organic nitrogen(aromatic or aliphatic ) in the irradiated solution. One of these undetected nitrogen-containing organic compounds probably is o-nitrosophenol which has been detected with the highest yield during the direct photolysis of o-NP in acidic solution at 254 nm by Alif et al. (Alif, 1991). In addition, the nitrite ion may also decompose under irradiation of UV light according to the following reactions(Alif, 1990):

$$NO_2^- + h\nu \rightarrow O^- + NO ,\qquad (7)$$

$$O^- + H_2O \rightarrow \cdot OH + OH^- ,\qquad (8)$$
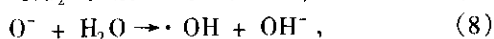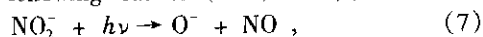
which might be another reason for low concentration of inorganic nitrogen detected in the irradiated solution.

For the p-NP degradation, NC and PhOH are only aromatic intermediates detected in the irradiated solution. After ~ 5 min irradiation, NC begins to appear and achieve a maximum yield of 4.4% of the initial p-NP concentration at 30 min irradiation. It is completely decomposed after 60 min irradiation. PhOH appears rapidly after starting irradiation, but maintains at a trace level in the whole process and disappears after ~ 20 min irradiation. The presence of PhOH is considered to be the result of direct denitration of p-NP. It was observed that nitrite and nitrate ions are produced immediately after irradiation of p-NP solution. After 60 min irradiation, both nitrite and nitrate ions reach their chemical yields of 16.1% and 16.3% of the initial p-NP concentration respectively, corresponding to > 99.7% of p-NP decomposition. IN is only 32.4% of the initial p-NP concentration at 60 min irradiation, which means nearly 67.6% of nitrogen still exists in solution without identification. Most of them are believed to be nitroaromatic compounds.

For the m-NP degradation, only NHQ and NC were detected as aromatic intermediates in the irradiated solution. NHQ is produced immediately when irradiation is begun, and its chemical yield reaches 26.9% of the initial m-NP concentration at 80 min irradiation. NC begins to appear after 20 min irradiation and rises to 4.9% of the initial m-NP concentration. Nitroresorcinol and resorcinol, which have been reported during direct photolysis of m-NP at 254 nm by Alif et al. (Alif, 1990), were not detected in this work. The rates of production for both NHQ and NC follow the order NHQ > NC during the irradiation. The detected inorganic intermediates are mainly nitrite and nitrate ions in irradiated m-NP solution. Both the nitrite and nitrate ions appear rapidly after the irradiation begins and increase almost with identical rates over the whole process. Both of them achieve

their chemical yields of ~ 4.9% of the initial m-NP concentration at 80 min irradiation, corresponding to 47.7% of m-NP degradation, which indicates that most of nitrogen remains in the form of organic compounds containing nitrogen in the investigated solution.

The produced intermediates and their chemical yields for the direct photolysis of the three nitrophenol isomers are summarized in Table 2. From this table and earlier discussions, it can be concluded that both o-NP and m-NP are responsible for most of the NHQ production during direct photolysis of NB.

**Table 2** Chemical yields for identified intermediates produced by direct photolysis of NPs ( ~ 0.1 mmol/L ) aqueous solutions after 15 min irradiation

| Identified intermediates | Yields, % [a] | | |
|---|---|---|---|
| | o-NP | p-NP | m-NP |
| Nitrohydroquinone | 7.8 | – | 1.4 |
| Nitrocatechol | < 0.1 | 1.2 | < 0.1 |
| Catechol | 1.3 | – | – |
| Phenol | – | 0.5 | – |
| $NO_2^-$ | 3.0 | 6.9 | 0.6 |
| $NO_3^-$ | 2.3 | 2.4 | 0.4 |
| $C_2O_4^{2-}$ | 5.9 | 9.7 | 1.6 |
| Maleic acid | 0.1 | 0.4 | < 0.1 |
| Formic acid | 0.4 | 2.4 | < 0.1 |

Note: [a] Yield ( % ) = 100[NPs]/[NPs]$_0$

All three nitrophenol isomers are responsible for the production of nitrocatechol during direct photolysis of NB, but their contributions follow the order p-NP > m-NP ≫ o-NP. o-NP is responsible for most of the CC production during direct photolysis of NB. p-NP is responsible for most of the phenol production during direct photolysis of NB. Each of the NPs decays follows zero-order kinetics. All of the three isomers are responsible for the formation of nitrite and nitrate ions, and the denitration follows the order p-NP > o-NP > m-NP based on the chemical yield of $NO_2^-$ .

### 2.1.3 Kinetics and quantum yield

The degradation NB and NPs was found to follow zero-order kinetics in the early stages. Table 3 and Table 4 show the rates and the quantum yields for NB and NPs decay in the early stages, respectively. The fractions of light absorbed by NB and NPs ( $F_x$ ) in the range 200—400 nm can be calculated from the sum of the light absorbed by nitrobenzene at each wavelength divided by the incident photon flux in 200—400 nm wavelength range by following equation:

$$F(x) = \frac{\sum_{200}^{400} f(\lambda, x) E(\lambda)}{\sum_{200}^{400} E(\lambda)},\qquad (9)$$

where $f(\lambda, x)$ is the fraction of monochromatic light absorbed by NB and/or NPs at certain wavelength, $\lambda$, and concentrations of NB and/or NPs, $x$(in mol/L); while $E(\lambda)$ is the known incident photon flux of lamp at certain wavelength.

**Table 3** The rates and quantum yields for NB decay in the direct photolysis of nitrobenzene at various initial concentrations of NB

| [NB]$_0$, mmol/L | Rate, mol/(L·s) | $\Phi_{NB}$ |
|---|---|---|
| 0.104 (air) | $(1.63 \pm 0.03) \times 10^{-8}$ | $(1.22 \pm 0.04) \times 10^{-3}$ |
| 0.519 (air) | $(1.94 \pm 0.04) \times 10^{-8}$ | $(1.19 \pm 0.01) \times 10^{-3}$ |
| 1.007 (air) | $(2.56 \pm 0.02) \times 10^{-8}$ | $(1.57 \pm 0.01) \times 10^{-3}$ |
| 0.560 ($N_2$) | $(1.77 \pm 0.04) \times 10^{-8}$ | $(1.09 \pm 0.02) \times 10^{-3}$ |

The quantum yields( $\Phi_{NB}$ ) for NB and/or NPs decay are evaluated based on the following equation and corrected by $F$:

$$\Phi_{NB} = \frac{dx}{dt} \frac{V}{FG_{o(200-400)}}, \qquad (10)$$

where $V$ is the initial irradiation volume(26 L), $G_{o(200-400)} = (4.40 \pm 0.02) \times 10^{-4}$ (Einstein s$^{-1}$), is the incident photon

flux in the wavelength range from 200 to 400 nm, $F$ is the light fraction absorbed by NB and/or NPs in the wavelength range from 200 to 400 nm.

**Table 4  Initial rates($r_{NPs}$) and quantum yields for NPs degradation by direct photolysis**

| Species | $[NPs]_0$, mmol/L | $r_{NPs}$, mol/(L·s) | $\Phi_{NPs}$ | $\Phi$ |
|---|---|---|---|---|
| o-NP | 0.101 | $(2.45 \pm 0.03) \times 10^{-8}$ | $(1.44 \pm 0.02) \times 10^{-3}$ | $7.8 \times 10^{-4}$(Alif, 1991) |
| p-NP | 0.098 | $(1.35 \pm 0.05) \times 10^{-8}$ | $(7.94 \pm 0.26) \times 10^{-4}$ | $6.0 \times 10^{-4}$(Alif, 1991) |
| m-NP | 0.096 | $(4.19 \pm 0.01) \times 10^{-9}$ | $(2.47 \pm 0.02) \times 10^{-4}$ | $7.6 \times 10^{-5}$(Alif, 1990) |

In the calculations of the rates and quantum yields for NB and/or NPs decomposition, only those concentrations corresponding to < 10% of NB and/or NPs decomposition were employed in order to avoid influence on the light absorption for NB and/or NPs from products and other side reactions during the photolysis processes.

It can be seen from Table 3 that the rate for NB decay is around $10^{-8}$ mol/(L·s) for both air-saturated and nitrogen-saturated solutions. The NB decay rate increases slightly with the initial concentration of NB under the air-saturated solutions. The differences between the decay rate air-saturated and nitrogen-saturated solutions are insignificant, which implies that the presence of oxygen has less contribution to the NB decay in air-saturated solutions. By referring the values of ($\Phi$NB for NB decay for both air-saturated and nitrogen-saturated NB solutions as shown in Table 3, it can be observed that in the range of the investigated concentrations, the quantum yield for NB decay is very low, it does not appear to increase significantly with the initial concentration of NB, and the difference between the air-saturated solution and the nitrogen-saturated solution is insignificant(the value for the deaerated solution is only approximately 10% less than the value for the aerated solution). Lower quantum yield for NB decay arises from the consequence of an inefficient yield of NB triplets and rapid deactivation of these triplets(Hurley, 1966):

$$C_6H_5NO_2^{*(T)} \rightarrow C_6H_5NO_2$$
$$k_d \sim 10^9 \text{ s}^{-1} \text{ radiationless decay.} \qquad (11)$$
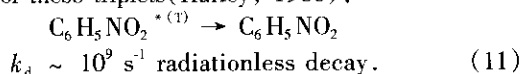
The fact that the absence of a significant influence of oxygen on the quantum yield for NB decay confirms the short

lifetime of the exited triplet state involved. Hurley *et al*. (Hurley, 1966) have estimated that the oxygen quenches the triplet state of NB with high constant.

$$C_6H_5NO_2^{*(T)} + O_2 \rightarrow C_6H_5NO_2$$
$$k_q \sim 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ oxygen quenching.} \qquad (12)$$
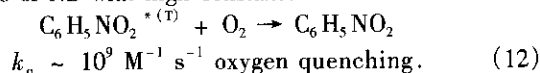
In addition, it was also observed that the formation of three nitrophenol isomers, as well as the formation of nitrite and nitrate ions also follow zero-order kinetics during direct photolysis of NB in aqueous solution over investigated irradiation time( ~ 150 min). The quantum yields for the formation of NPs, nitrite ion and nitrate ion in the range of 200—400 nm are calculated based on the following equations:

$$\Phi_{NPs} = \frac{d[NPs]}{dt} \frac{V}{F_{ave} G_{o(200-400)}}, \qquad (13)$$

$$\Phi_{NOx^-} = \frac{d[NOx^-]}{dt} \frac{V}{F_{ave} G_{o(200-400)}} \quad (x = 2 \text{ or } 3), (14)$$

where $V$ is the initial irradiation volume(26 L), $G_o = (4.40 \pm 0.02) \times 10^{-4}$ (Einstein s$^{-1}$) is the incident photon flux and $F_{ave}$ is the average light fraction absorbed by NB from 200—400 nm for the investigated NB decay curve. Since only those concentrations which are less than 10% of NB decay were used and the NB can be regarded as the only solute absorbing light during the irradiation, under this limiting condition, the $F_{ave}$ has an insignificant error and can be regarded as a constant. As seen from Table 5, both the rate and the initial quantum yield for the NPs formation increase following the order o-NP > p-NP > m-NP.

Obviously , from Table 5 , both formation rate and

**Table 5  The rates and quantum yields for NPs formation and inorganic acids at initial stage during the direct photolysis of NB aqueous solutions by polychromatic light**

| NPs | Rate, mol/(L·s) | $F_{ave}$ | $\Phi_{NPs}$(200—400 nm) |
|---|---|---|---|
| o-NP (air)[a] | $(2.21 \pm 0.03) \times 10^{-9}$ | $0.9398 \pm 0.0016$ (air) | $(1.38 \pm 0.01) \times 10^{-4}$ |
| o-NP (N$^2$)[b] | $(2.31 \pm 0.02) \times 10^{-9}$ | $0.9435 \pm 0.0020$ (N$_2$) | $(1.44 \pm 0.01) \times 10^{-4}$ |
| p-NP (air) | $(1.95 \pm 0.04) \times 10^{-9}$ | – | $(1.22 \pm 0.02) \times 10^{-4}$ |
| p-NP (N$_2$) | $(1.92 \pm 0.02) \times 10^{-9}$ | | $(1.20 \pm 0.01) \times 10^{-4}$ |
| m-NP (air) | $(1.04 \pm 0.02) \times 10^{-9}$ | – | $(6.50 \pm 0.07) \times 10^{-5}$ |
| m-NP (N$_2$) | $(9.82 \pm 0.01) \times 10^{-10}$ | | $(6.14 \pm 0.02) \times 10^{-5}$ |
| NO$_2^-$ | $(1.97 \pm 0.02) \times 10^{-9}$ | $0.9398 \pm 0.0016$ | $(1.23 \pm 0.01) \times 10^{-4}$ |
| NO$_3^-$ | $(1.26 \pm 0.02) \times 10^{-9}$ | – | $(7.90 \pm 0.08) \times 10^{-5}$ |

Notes: [a]$[NB]_{o(air)} = 0.519$ mmol/L; [b]$[NB]_{o(N_2)} = 0.560$ mmol/L
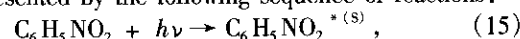
quantum yield of nitrite formation is larger than that of nitrate indicating that the nitro group is released first from the NB ring, followed by the conversion of nitrite to nitrate. However, the total rate(for aerated solution) for NPs and IN formation in air-saturated solution is evaluated as 8.43 × $10^{-9}$ mol/(L·s) which is only ~ 43% of the NB decay rate ($1.94 \times 10^{-8}$ mol/(L·s). The rest ( ~ 57%) of the intermediates during this period are attributed to PhOH, NHQ and unidentified intermediates such as dimers ( Hurley, 1966 ), polyhydroxy aromatic compounds, as well as experimental errors.
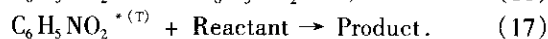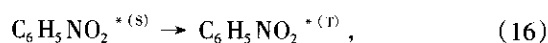
Table 4 shows that the rates for the NPs decay follow the order o-NP ≥ p-NP > m-NP under experimental

conditions, and the quantum yields for NPs decay also follow the order o-NP > p-NP > m-NP. The quantum yields for all of the NPs decay obtained from this work are larger than those obtained by Alif *et al*. (Alif, 1990; 1991) at 254 nm (pH = 2.2), which may attributed to different conditions used in the experiment.

## 2.2  Mechanisms

Under irradiation of UV light, nitrobenzene is associated with the n-π$^*$ change-transfer(CT) triplet state which arise from an inter-system crossing from an n-π$^*$ singlet to an n-π$^*$ (Hurley, 1966). The excitation process of nitrobenzene can be represented by the following sequence of reactions:

$$C_6H_5NO_2 + h\nu \rightarrow C_6H_5NO_2^{*(S)}, \qquad (15)$$

$$C_6H_5NO_2^{*(S)} \rightarrow C_6H_5NO_2^{*(T)}, \tag{16}$$

$$C_6H_5NO_2^{*(T)} + \text{Reactant} \rightarrow \text{Product}. \tag{17}$$

### 2.2.1 Formation of nitrophenols and benzoquinone

The formation of nitrophenols and benzoquinone in the irradiated solutions by the direct photolysis of nitrobenzene can be explained by a nitro-nitrite rearrangement ( Chow, 1982; Morrison, 1969 ). This mechanism involves the formation of aromatic nitrite, and is considered as an intramolecular rearrangement. A well-known evidence for the nitro-nitrite rearrangement in aromatic compounds was given by Chapman et al. in their study on 9-nitroanthracene (Chapman, 1966).
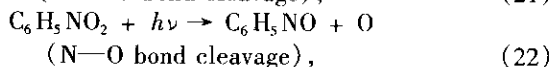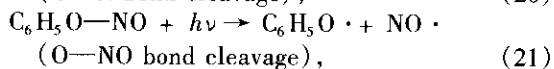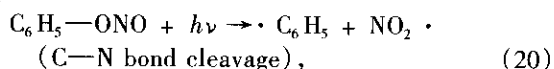


$$(18)$$
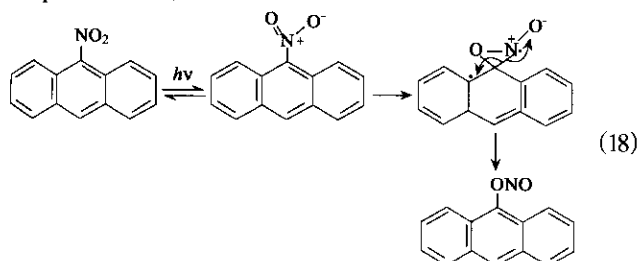
They suggested that because the plane of the nitro group is almost at right angles to the plane of the anthracene ring leading to nonconjugation, an overlap of a nonbonding p orbital of oxygen in the nitro group(out of plane nitro group) with the adjacent orbital of the aromatic ring leads to the formation of an oxaziridine ring which collapses to the nitrite.

By analogy, nitrobenzene is expected to undergo similar conversion more easily than the 9-nitroanthracene by the intramolecular arrangement, which is supported by the result obtained by Sinha et al. ( Sinha, 1990 ) that in small nitroaromatic ring systems, the nitro group is more strongly involved in the electronic transition from benzene to the nitro group than in large nitroaromatic ring systems.



$$(19)$$
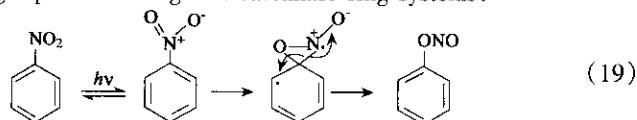
Subsequent reaction is related to the ArO-NO bond cleavage. It can be supported by the results reported by Galloway et al. ( Galloway, 1993 ). They used vacuum-ultraviolet photoionization molecular-beam mass spectrometry to study the pathways and kinetic energy releases in the primary process of photodissociation of nitrobenzene at wavelengths between 220 to 320 nm. They found that nitrobenzene undergoes three primary photodissociation pathways under irradiation of UV light by the following reactions:

$$C_6H_5 - ONO + h\nu \rightarrow \cdot C_6H_5 + NO_2 \cdot$$
$$(C - N \text{ bond cleavage}), \tag{20}$$

$$C_6H_5O - NO + h\nu \rightarrow C_6H_5O \cdot + NO \cdot$$
$$(O - NO \text{ bond cleavage}), \tag{21}$$

$$C_6H_5NO_2 + h\nu \rightarrow C_6H_5NO + O$$
$$(N - O \text{ bond cleavage}), \tag{22}$$

and reported that the kinetic energy releases for the cleavage of the bonds are in the order of $O - NO(0.86 \pm 0.20 \text{ eV}) > N - O(0.11 \pm 0.04 \text{ eV}) > C - N(0.087 \pm 0.022 \text{ eV})$. After $O - NO$ cleaving, it is possible to form BQ and dimmers subsequently.

BQ has been detected in irradiated solution and dimers may correspond to part of "miss" intermediates in the irradiated solution in which the detected intermediates are only ~ 15% to 30% of the NB decay. Chapman et al.

( Chapman, 1966 ) have also demonstrated the 10, 10'-bianthrone and anthraquinone to be the products during photolysis of 9-nitroanthracene.

Another pathway of $C_6H_5ON - O$ bond cleavage will lead to form nitrophenols in the irradiated solution is shown in following reaction( The formation of p-NP and m-NP has the same processes as o-NP).



$$(22)$$
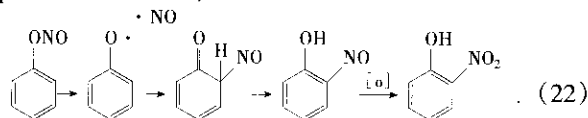
This mechanism is supported by the results obtained by Jones et al. ( Jones, 1969 ) that direct photolysis of 4-nitroanisole leads to form corresponding nitrosophenol and nitrophenol.

### 2.2.2 Formation of nitrosobenzene

Nitrosobenzene has been detected qualitatively in the irradiated solutions. Many reports have shown the presence of aromatic nitroso compounds during photolysis of the aromatic nitro compounds in organic solvents( Chow, 1982; Morrison, 1969 ). Wubbels and Letsinger ( Wubbels, 1974 ) have suggested that 3-chloro-4-nitrosophenol ( Cl-$C_6H_4$-NO) is an intermediate during direct photolysis of NB in concentrated aqueous HCl solution. Alif et al. ( Alif, 1990; 1991 ) have observed the generation of corresponding nitrosophenols during direct photolysis of m-NP and o-NP and p-NP in aqueous solutions.

By analogy, the mechanism for NSB generation in the irradiated NB solution can be explained by the N—O bond cleavage of the nitro group in NB ring. This cleavage is possible in the view of kinetic energy release as mentioned early( Galloway, 1993 ). One of the N—O bond cleavage mechanisms is shown following reaction( Morrison, 1969):



$$(24)$$
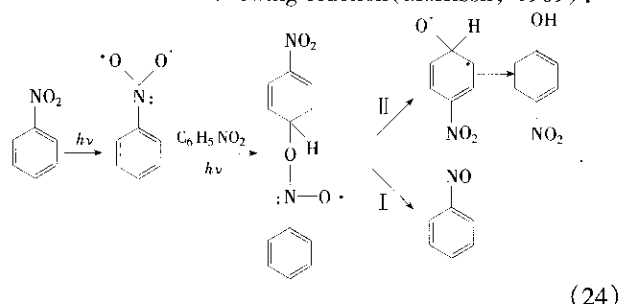
Two nitrobenzenes first form dimer followed by N—O bond cleavage to form nitrosobenzene via pathway I and/or form nitrophenols via pathway II .

Another possible pathway to form NSB via N—O bond cleavage and to lead finally the formation of p-NP is shown in the following reaction ( m-NP and o-NP are formed in the same way):



$$(25)$$
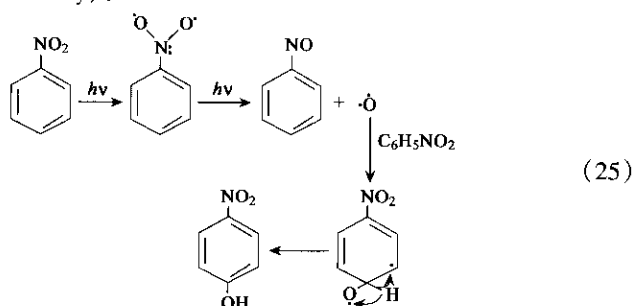
In Reaction ( 25 ), two NB molecules generate one molecule nitrophenol, which may be one of the reasons for less percentage of detected intermediates in the irradiated solutions.

### 2.2.3 Formation of phenol and nitrite ion

The presence of phenol and nitrite ions has been observed with higher yield in the irradiation solutions during irradiation. The formation of phenol has also been observed during direct photolysis of the solutions containing nitrophenols by Alif *et al*. (Alif, 1987; 1990; 1991). From the experimental observation, the differences between the formation rates between NPs and nitrite ion are insignificant. This fact may indicate that the formation of the phenol is the result of denitration of nitrobenzene rather than of nitrophenols. Heterolytic mechanisms were proposed for the phototransformation of 3-nitrophenol (Alif, 1990), 2-nitrophenol(Alif, 1991), 3-chlorophenol(Boule, 1982) and chlorobenzene(Boule, 1984) have proposed a mechanism for the formation of dihydroxybenzenes such as resorcinol and catechol. By analogy, it was assumed that the formation of phenol and nitrite ion in experimental conditions is considered as an attack of '' O on the excited singlet state at the position occupied by the nitro group leading to C—N bond cleavage, although this cleavage does not favour to the kinetic energy release (Galloway, 1993). However, under UV light irradiation, the excited state of NB is not stable, and it is expected that the C—N bond is weaker at excited state than at ground state, which will be in favour of hydrolysis. Thus, the C—N bond would be cleaved by $H_2O$ attack resulting in generating phenol and nitrite ion:
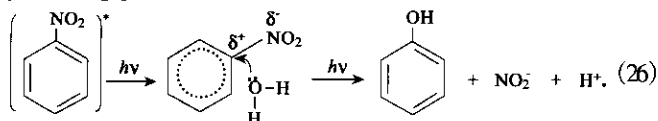


### 2.2.4 Formation of nitrohydroquinone, nitrocatechol and catechol

The NHQ and NC are considered to be generated mainly from *o*-NP and *p*-NP, respectively, following similar mechanism as in Reactions (23), (24) and (25), whereas the CC is generated mainly from *o*-NP following similar mechanism described in Reaction (26).

### 2.2.5 Other possible mechanisms

The fact that the chemical yields for three nitrophenol isomers follow the order *o*-NP $\geqslant$ *p*-MP > *m*-NP in the experimental conditions may indicate that · OH radical was involved in the photochemical process because this order is a typical result of free radical substitution reaction which have been confirmed by many reports (Hurley, 1966; Bhatia, 1975; Eberhardt, 1973; Fendler, 1968). On the other hand, NC, NHQ and CC, which were observed in the experiments, are mostly possible to be arisen from · OH radical attack. One of the possible resources to generate ·OH radicals is via the direct photolysis of water by the small output of the lamp in the < 200 nm range(Zafiriou, 1984; Cabelli, 1997).

$$H_2O + h\nu \ (< 200 \text{ nm}) \longrightarrow \cdot OH + \cdot H \ . \quad (27)$$
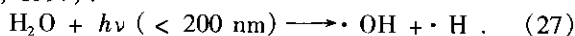
Assuming the generation of · OH radicals in the system is true, the possible reaction pathways will involve · OH radical to add on the nitrobenzene ring leading to a series of reactions.

## 3 Conclusions

Photodegradation of NB and NPs in aqueous solutions irradiated by polychromatic light follows zero-order kinetics. The quantum yields of NB and NPs decay are very low, which means that this method is not effective for the treatment wastewater contaminated by this class of pollutants. Many aromatic intermediates are produced during photolysis of NB.

*o*-NP, *p*-NP and *m*-NP are primary predominant intermediates produced from photolysis of NB, whereas NHQ, NC and CC are considered as secondary main products. It has been confirmed by direct photolysis of each nitrophenol isomer that NHQ and CC are produced mainly from *o*-NP, whereas NC is produced mainly from *p*-NP during photolysis of NB. Nitrite and nitrate ions were detected at early irradiation stage indicating direct denitration of NB. The formation of the three nitrophenol isomers also follows zero-order kinetics. The results show that the direct photolysis of NB in aqueous solution is a complex process. Relevant mechanisms have been suggested in this work.

## References:

Alif A, Boule P, Lemaire J, 1987. Photochemical behavior of 4-nitrophenol in aqueous solution[J]. Chemosphere, 16(10-12): 2213—2223.

Alif A, Boule P, Lemaire J, 1990. Photochemistry and environment: XII. phototransformation of 3-3itrophenol in aqueous solution [J]. J Phtochem Photobiol A: Chem, 50(3): 331—342.

Alif A, Pilichowski J F, Boule P, 1991. Photochemistry and environment XIV: photo-transformation of nitrophenol induced by excitation of nitrite and nitrate ions[J]. J Photochem Photobiol A: Chem, 59(3): 357—367.

ATSDR(Agency for Toxic Substances and Disease Registry), 1990. Toxicological profile for nitrobenzene[Z]. TP-90-19, USA.

Bhatia K, 1975. Hydroxyl radical induced oxidation of nitrobenzene[J]. J Phys Chem, 79(10): 1032—1038.

Boule P, Guyon C, Lemaire J, 1982. Photochemistry and environment: IV. Photochemical behaviour of monochlorophenols in dilute aqueous solution[J]. Chemosphere, 11(12): 1179—1188.

Boule P, Guyon C, Lemaire J, 1984. Photochemistry and environment: VI. Direct phototransformation of chlorophenols and interactions with phenol on UV exposure in aqueous solution[J]. Toxicol Environ Chem, 7: 97—110.

Cabelli D E, 1997. Peroxyl radicals(Alfassi Z B ed.)[M]. Chichester: John Wiley & Sons. 407.

Calvert J G, Pitts Jr J N, 1966. Photochemistry[M]. John Wiley & Sons. 784.

Chapman O L, Heckert D C, Reasoner J W *et al*., 1966. Photochemical studies on 9-nitroanthracene[J]. J Am Chem Soc, 88(23): 5550—5554.

Chow Y L, 1982. Supplement F: The chemistry of amino, nitroso and nitro compounds and their derivatives, Part 1(Patai S ed.)[M]. Chichester: John Wiley & Sons. 181.

Eberhardt M K, Yoshida M, 1973. Radiation-induced homolytic aromatic substitution. I. Hydroxylation of nitrobenzene, chlorobenzene, and toluene [J]. J Phys Chem, 77(5): 589—597.

Fendler J H, Gasowski G L, 1968. Radiation-induced hydroxylation of nitrobenzene in dilute aqueous solution[J]. J Organ Chem, 33(5): 1865—1868.

Galloway D B, Bartz J A, Huey L G *et al*., 1993. Pathways and kinetic energy disposal in the photodissociation of nitrobenzene[J]. J Chem Phys, 98(3): 2107—2114.

Hurley R, Testa A C, 1966. Photochemical $n \rightarrow \pi^*$ excitation of nitrobenzene [J]. J Am Chem Soc, 88(19): 4330—4332.

Jones L B, Kudma J C, Foster J P, 1969. Photochemically induced reactions of 4-nitroanisole[J]. Tetrahedron Lett, 10(38): 3263—3265.

Lipczynska-Kochany E, 1992. Degradation of nitrobenzene and nitrophenols in homogeneous aqueous solution: Direct photolysis versus photolysis in the presence of hydrogen peroxide and the Fenton reagent[J]. Water Poll Res J Canada, 27(1): 97—122.

Minero C, Pelizzetti E, Piccinini P *et al*., 1994. Photocatalyzed transformation of nitrobenzene on $TiO_2$ and ZnO[J]. Chemosphere, 28(6): 1229—1244.

Morrison H A, 1969. The chemistry of the nitro and nitroso groups, Part 1(Feuer H ed.)[M]. NY: John Wiley & Sons. 165.

Murov S L, Carmichael I, Hug G L, 1993. Handbook of photochemistry[M]. NY: Marcel Dekker Inc. 299.

O' Connor O A, Young I. Y, 1989. Toxicity and anaerobic biodegradibility of substituted phenols under methanogenic conditions [J]. Environ Toxicol Chem, 8: 853—862.

Simmons M S, Zepp R G, 1986. Influence of humic substances on photolysis of nitroaromatic compounds in aqueous systems[J]. Wat Res, 20(7): 899 —904.

Sinha H K, Yates K, 1990. Ground- and excited-state dipole moments of some nitroaromatics: Evidence for extensive charge transfer in twisted nitrobenzene systems[J]. J Chem Phys, 93(10): 7085—7093.

Wubbels G G, Letsinger R I., 1974. Photoreactions of nitrobenzene and monosubstituted nitrobenzenes with hydrochloric acid: Evidence concerning the reaction mechanism[J]. J Am Chem Soc, 96(21): 6698—6706.

USEPA, 1985. Health and environmental effects profile for nitrophenols [S]. Cincinnati, OH, USA.

Zafiriou O C, Joussot-Dubien J, Zepp R G *et al*., 1984. Photochemistry of natural waters[J]. Environ Sci Technol, 18: 358A—371A.