Photooxidative degradation of 4-nitrophenol (4-NP) in UV/H$_2$O$_2$ process: Influence of operational parameters and reaction mechanism

N. Daneshvar [a,*], M.A. Behnajady [b,1], Y. Zorriyeh Asghar [b,2]

[a] *Water and Wastewater Treatment Research Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz,*
CP 51664, Tabriz, Islamic Republic of Iran
[b] *Department of Applied Chemistry, Islamic Azad University, Tabriz Branch, Tabriz, Islamic Republic of Iran*

Abstract

The photooxidative degradation of 4-nitrophenol (4-NP) was studied in the UV/H$_2$O$_2$ process. The effects of applied H$_2$O$_2$ dose, initial 4-NP concentration and UV light intensity have been studied. Degradation was complete in 13 min and follows apparent first-order kinetics. The removal efficiency of 4-NP depends on the operational parameters and increases as the initial concentration of H$_2$O$_2$ and light intensity are increased but it decreases when the initial concentration of 4-NP is increased. From HPLC analysis, major intermediate products were hydroxyl derivatives of 4-NP as a result of photooxidative hydroxylation.
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1. Introduction

Nitrophenols are some of the most refractory pollutants, which can be present in industrial wastewater. In particular, 4-nitrophenol and its derivatives result from the production processes of pesticides, herbicides [1] and synthetic dyes [2].

These pollutants have high toxicity and carcinogenic character. They have caused considerably damage to the ecosystem and human health. They are notified as potential toxic compounds by United States Environmental Protection Agency (USEPA) and their maximum allowable concentrations in water ranged from 1 to 20 ppb [2].

The conventional approach in industrial wastewater treatment is by chemical–physical processes: adsorption, stripping, chemical oxidation. All these processes can guarantee high removal efficiencies, but the first two have the main disadvantage that they do not provide a real degradation of the compounds but only their transfer from a diluted to a concentrated stream to be disposed on the other hand, chemical oxidation could produce intermediates characterized by a toxicity level similar to the original substance [3].

Photooxidative degradation plays an important role in the degradation of these pollutants into the components that are nontoxic and safe for human health. In other words, photooxidative degradation is a system, which operates at room temperature and being used for the purification of polluted water and decomposition of toxic organic pollutants. These processes are based on the generation of the highly reactive hydroxyl radical capable of unselectively react with most of organic and inorganic substances present in drinking water and wastewaters. Homogenous advanced oxidation process employing hydrogen peroxide with UV light has been found to be very effective in the degradation of organic compounds [4–6]. This process involves the production of hydroxyl radicals ($^\bullet$OH) that are extremely reactive and strong oxidizing agent ($E^0 = 2.8$ V) capable of mineralizing organic contaminants. Reaction of hydroxyl radicals generated in the presence of an organic substrate may occur via one of the three general pathways: (1) hydrogen abstraction; (2) electrophilic addition; (3) electron transfer [7]. The UV/H$_2$O$_2$ process in comparison to other methods of water treatment has additional

* Corresponding author. Tel.: +98 411 5255825/3393146;
fax: +98 411 3340191.
E-mail addresses: nezam_daneshvar@yahoo.com (N. Daneshvar),
behnajady@iaut.ac.ir (M.A. Behnajady), zorriyeh@yahoo.com
(Y. Zorriyeh Asghar).
1 Tel.: +98 411 3320198; fax: +98 411 3313922.
2 Tel.: +98 411 3316464.

advantages such as no formation of sludge during the treatment and high removal rates of chemical oxygen demand (COD) [8].

Many studies were published on the degradation of organic pollutants, in particular phenols and nitrophenols, in water. In this study 4-NP was chosen as a model compound. It is one of the 114 organic pollutants listed in EPA and its maximum allowed concentration is 20 ppb. Dieckmann and Gray [1] have reported direct and sensitized photocatalysis degradation of 4-NP in TiO_2 slurries. Chen and Ray [9] have reported kinetics and influence of operational parameters at photocatalysis degradation of 4-NP in the presence of TiO_2. In this work, homogenous photooxidative degradation of 4-NP, with particular emphasis on the operational parameters, intermediate identification and reaction mechanism have been studied.

2. Experimental

2.1. Materials

4-Nitrophenol (4-NP) was obtained from Fluka. The hydrogen peroxide solution (30%), NaCl, $NaHCO_3$, and Na_2CO_3 were purchased from Merck (Germany). Solutions were prepared by dissolving the requisite quantity of the 4-NP in double distilled water.

2.2. Photoreactor

All experiments were carried out in a batch photoreactor. The radiation source was a low pressure mercury UV lamp emitting at 254 nm (15 W, UV-C, manufactured by Philips, Holland) which was placed above a batch photoreactor of 0.5 l volume [4]. The light intensity was measured by a Lux-UV-IR meter (Leybold Co.). Changing the distance between the lamp and the surface of the solution would vary the light intensity. In each experiment, 200 ml of the 4-NP solution of nearly constant concentration ($20\,mg\,l^{-1}$) and variable concentration of hydrogen peroxide (from 50 to $1400\,mg\,l^{-1}$) was transferred to Pyrex reactor. Then the lamp was switched on to initiate the reaction. During irradiation, the solution was agitated in a constant rate. At certain reaction intervals, 2 ml of sample was withdrawn and the concentration of 4-NP was determined by means of a spectrophotometer.
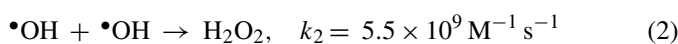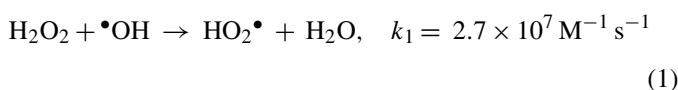
2.3. Analysis

The degradation of 4-NP was measured with UV–vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 317 nm. A calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. High-performance liquid chromatograms were recorded on an HPLC (Perkin-Elmer Series 200). A Spheri-5 RP-18 column with dimension of $220\,mm \times 4.6\,mm$ and with $5\,\mu m$ particle size and UV–vis detector with the wavelength set at 210 nm were used. The mobile phase was a mixture of methanol–water (H_3PO_4 5 Mm) 35/65 (v/v) at a flow rate of $1\,ml\,min^{-1}$. The light intensity in the center of the photoreactor was measured by a Lux-UV-IR meter (Leybold Co.).

3. Results and discussion

3.1. Effect of the initial concentration of H_2O_2

The degradation efficiency versus irradiation time at different initial concentrations of H_2O_2 has been summarized in Fig. 1. The degradation efficiency increases with increasing of H_2O_2 concentration from 50 to $1400\,mg\,l^{-1}$. The enhancement of 4-NP removal percent in this course is due to an increase in the hydroxyl radical concentration. The removal percent decreases with increasing initial concentration of H_2O_2 above $700\,mg\,l^{-1}$. This is reasonable because, when H_2O_2 is used in excess, hydroxyl radical efficiently reacts with H_2O_2 and produces $HO_2^{\bullet}$ (Eq. (1)), also $^{\bullet}OH$ radicals generated at high concentration, dimerize to H_2O_2 (Eq. (2)). As a result, there is a critical hydrogen peroxide concentration for the removal of 4-NP in UV/H_2O_2 process. At this favorable concentration the rate of photooxidation is maximized [10]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O, \quad k_1 = 2.7 \times 10^7\,M^{-1}\,s^{-1} \tag{1}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2, \quad k_2 = 5.5 \times 10^9\,M^{-1}\,s^{-1} \tag{2}$$

The critical effect of H_2O_2 in UV/H_2O_2 process was shown in our previous work [5] and other researchers [11].

The semi-logarithmic graphs of the concentration of 4-NP in the presence of different concentrations of H_2O_2 versus irradiation time yield straight lines, which confirm the pseudo-first-order kinetic for degradation of 4-NP in this process. The pseudo-first-order rate constant (k_{ap}) was shown in Fig. 2 as a function of initial concentration of H_2O_2. The results showed k_{ap} increases with increasing H_2O_2 concentration but above an optimum value increasing of H_2O_2 concentration retards the reaction.

Mineralization of 4-NP in this process was studied by COD reduction. COD values have been related to the total concentration of organics in the solution. Results show 60% COD reduction of 4-NP with initial concentration of $20\,mg\,l^{-1}$ in the presence of $700\,mg\,l^{-1}$ H_2O_2, at 150 min irradiation under $28.5\,W\,m^{-2}$ UV light intensity. The persistence of a constant
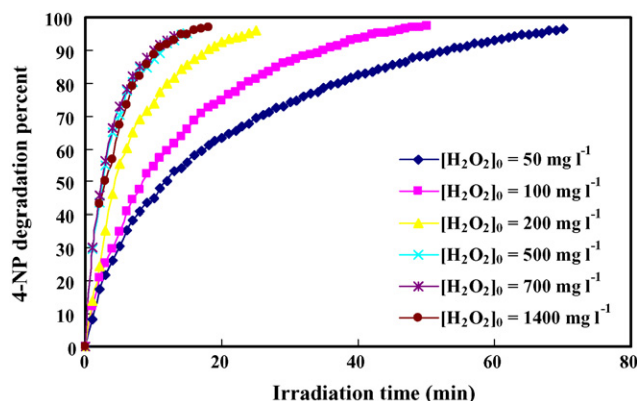
Fig. 1. Effect of initial concentration of hydrogen peroxide in photooxidative degradation of 4-NP. $[4\text{-NP}]_0 = 20\,mg\,l^{-1}$, $I_0 = 28.5\,W\,m^{-2}$, and pH 4.8.
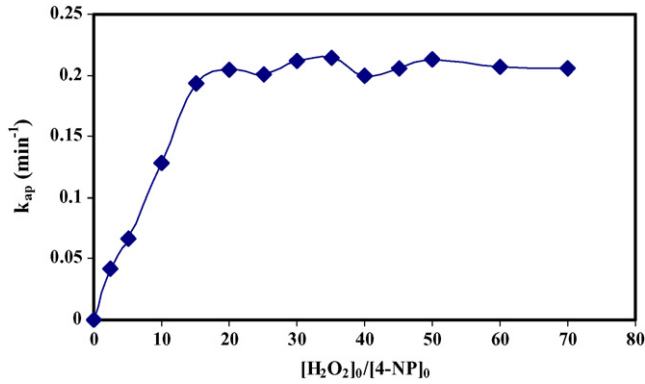
Fig. 2. First-order degradation rate constant of 4-NP as a function of H_2O_2 initial concentration. For experimental details refer to Fig. 1.

level of COD suggests that the accumulated of dead-end products are resistant to degradation by the UV/H_2O_2 process.

3.2. Effect of the initial concentration of 4-NP

Figs. 3 and 4 show the effect of initial 4-NP concentration on the degradation percent and pseudo-first-order rate constant (k_{ap}), respectively. Although the complete removal of $5 \, mg \, l^{-1}$
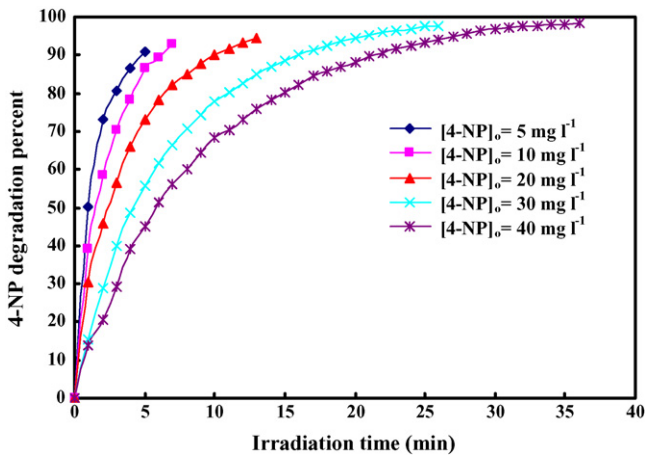

Fig. 3. Effect of initial concentration of 4-NP in photooxidative degradation of 4-NP. $[H_2O_2]_0 = 700 \, mg \, l^{-1}$, $I_0 = 28.5 \, W \, m^{-2}$, and pH 4.8.
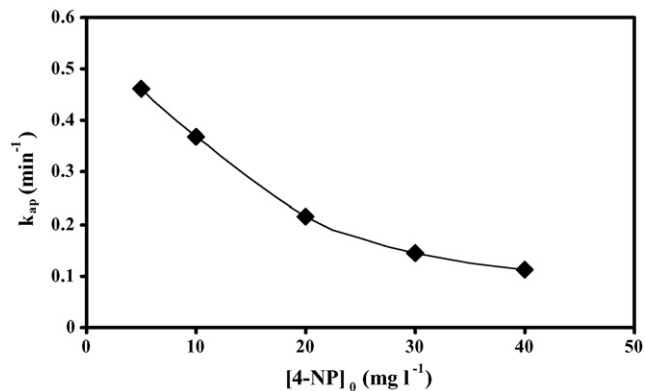

Fig. 4. First-order degradation rate constant of 4-NP as a function of 4-NP initial concentration. For experimental details refer to Fig. 3.
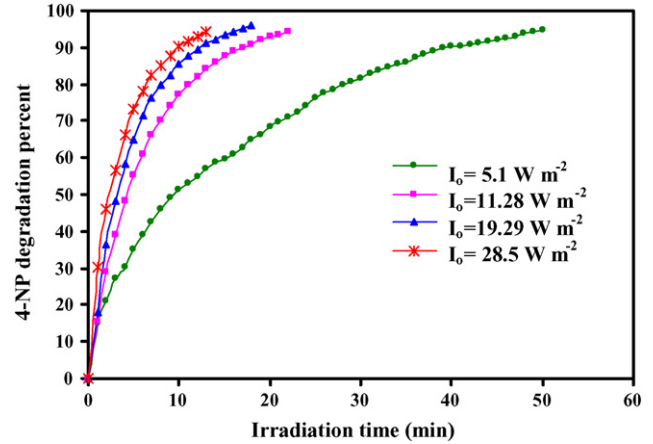

Fig. 5. Effect of the light intensity in photooxidative degradation of 4-NP. $[H_2O_2]_0 = 700 \, mg \, l^{-1}$, $[4\text{-}NP]_0 = 20 \, mg \, l^{-1}$, and pH 4.8.

4-NP was possible after 5 min of irradiation, the removal time with an increasing initial 4-NP concentration to $40 \, mg \, l^{-1}$, increased to 36 min. This can be explained by considering that, the molar extinction coefficient of the 4-NP at $\lambda < 260 \, nm$ is very high, so that a rise in its concentration induces an inner filter effect. Consequently, the solution becomes more and more impermeable to UV radiation. Also, at higher concentrations of 4-NP, higher intermediates are formed. These intermediates are also highly reactive towards hydroxyl radicals. Thus, 4-NP and its intermediates compete effectively for hydroxyl radicals, reducing the removal efficiency [12].

3.3. Effect of the UV light intensity

The effect of the UV light intensity on the degradation percent of 4-NP was shown in Figs. 5 and 6. The results showed that the removal percent steadily increased with increasing the light intensity. The results also showed that the UV light intensity plays an important role in degradation of 4-NP. This is due to effective role of light intensity in the formation of high amounts of $^\bullet OH$ from H_2O_2 in the solution, which can be used for decolorization and degradation of 4-NP (Eq. (3)). The almost linear relation between removal percent and light intensity shows that
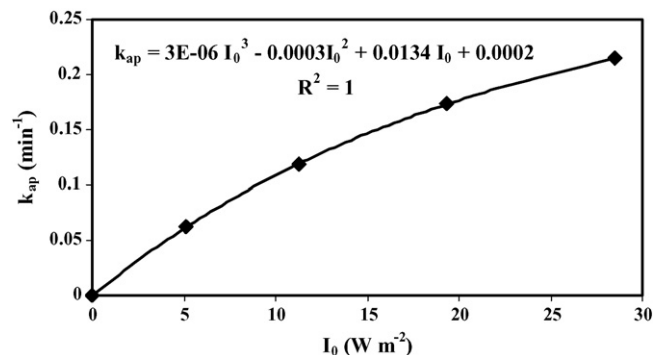

Fig. 6. First-order degradation rate constant of 4-NP as a function of light intensity. For experimental details refer to Fig. 5.
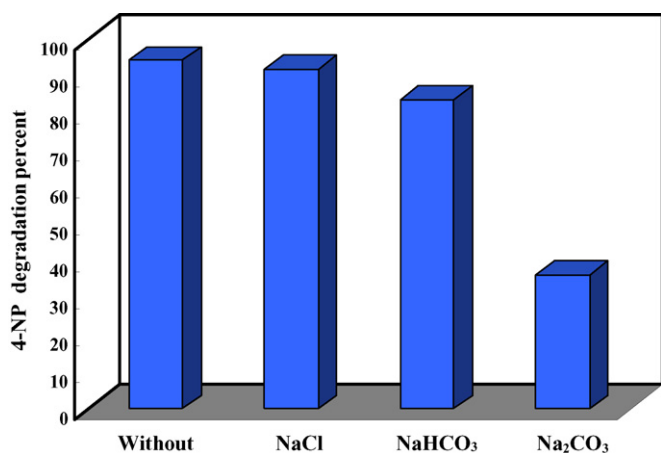
Fig. 7. Effects of NaCl, NaHCO$_3$ and Na$_2$CO$_3$ on the 4-NP degradation percent in UV/H$_2$O$_2$ process. [H$_2$O$_2$]$_0$ = 700 mg l^{-1}, [4-NP]$_0$ = 20 mg l^{-1}, pH 4.8, I_0 = 28.5 W m^{-2}, and [Salts]$_0$ = 1 g l^{-1}.

UV light intensity used in this work is in the low region.

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH \tag{3}$$

3.4. Effect of salts on degradation of 4-NP

The effects of addition other chemicals such as NaCl, NaHCO$_3$ and Na$_2$CO$_3$ (1 g l^{-1}) on the photodegradation rate of 4-NP was shown in Fig. 7. Na$_2$CO$_3$ strongly retard the removal rate and only 36.4% of degradation was observed. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers by the following reactions [13]:

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + {}^{-}OH \tag{4}$$

$$HCO_3^{-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \tag{5}$$
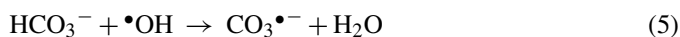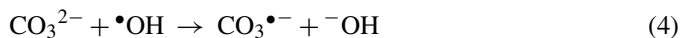
Addition of NaCl does not affect the removal rate significantly. The small decrease in the removal efficiency is due to the hydroxyl radical scavenging effect of chloride ion by the following reactions [8]:

$$Cl^- + {}^{\bullet}OH \rightarrow HOCl^{\bullet-} \tag{6}$$

$$HOCl^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O \tag{7}$$
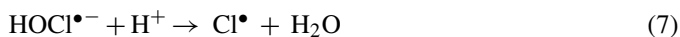
3.5. Intermediate identification and reaction mechanism

HPLC chromatogram analysis of the solutions at different irradiation times revealed the presence of several intermediates. The intermediates were identified by comparison with retention time of standard solutions of intermediates products. The main intermediates were hydroquinone and 4-nitrocathecol. As we described in previous section hydroxyl radicals are reactive species in UV/H$_2$O$_2$ process. Reaction of hydroxyl radicals with aromatic groups occurs via electrophilic addition. In the presence of 4-NP hydroxyl radicals may enter in the ortho position to form 4-nitrocatechol (4-NC). Based on information, the reaction pathway shown in Scheme 1 has been proposed for the photooxidative degradation of 4-NP. 4-NC will react further with hydroxyl radical to form 1,2,4-benzenetriol (1,2,4-BT). Further reaction of the primary intermediates with hydroxyl radicals lead to ring opening and formation of oxygenated aliphatic compounds and eventual producing mineralization products. The ring opening of 1,2,4-BT is very rapid such that no detectable amount of 1,2,4-BT accumulates in the solution. Direct attack of the hydroxyl radicals to nitrogroup position can be cause to formation of hydroquinone (HQ). HQ similar to 4-NC react with hydroxyl radical to form 1,2,4-BT. The degradation of 4-NP to form 4-NC and HQ and also further reaction with hydroxyl radical to form 1,2,4-BT is similar to the degradation pathway proposed for the photocatalytic degradation of 4-NP in UV/TiO$_2$ process. Other ways to formation of hydroquinone such as leaving of nitrogroup and heterolytic photohydrolysis of 4-NP with formation of HNO$_2$ were supposed with other researchers [14].
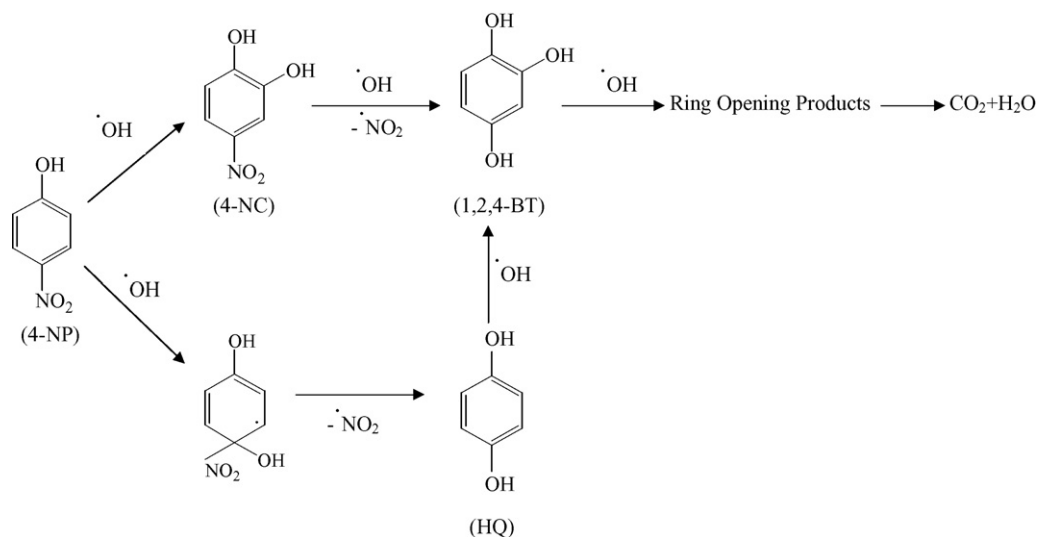
Scheme 1.

4. Conclusions

UV/H_2O_2 process can be used for complete degradation of 4-NP. The semi-logarithmic graphs of the concentration of 4-NP versus irradiation time were linear suggesting pseudo-first-order reaction. The results indicate that the removal efficiency is a function of light intensity, H_2O_2 and 4-NP concentrations, so that decreases as the initial concentration of 4-NP is increased but it increases with increasing the amount of H_2O_2 until an optimum value and then slightly decreases. Between k_{ap} and light intensity was a linear relation which demonstrates UV light intensity used in this work is in the low region. The intermediates formed in the photooxidative courses were identified by HPLC. The main intermediates of photooxidative degradation of 4-NP in UV/H_2O_2 process were hydroquinone and 4-nitrocathecol.

Acknowledgements

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