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The heterogeneous photocatalytic degradation, intermediates and mineralization for the aqueous solution of cresols and nitrophenols

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Abstract

This investigation was initiated to study the heterogeneous photocatalytic reactions of cresols and nitrophenols with ultraviolet light/titanium dioxide (UV/TiO₂) system. The experimental parts consisted of pH effect, determination of intermediates and mineralization. At pH 7 and a concentration of 0.1 mM, cresols and nitrophenols nearly disappeared after 2.5 h of reaction time. Under various pH levels, the pseudo first order rate constants of Langmuir–Hinshelwood model was found satisfactory. From the results of GC/MS analysis, most intermediate products were hydroxyl derivatives of parent compounds as a result of photocatalyzed hydroxylation. In the mineralization of *o*-nitrophenol, about 89.6% of the compounds were mineralized in 9 h of reaction time with initial formation of nitrite and nitrate ions, indicating denitration followed by subsequent degradation. © 1998 Elsevier Science B.V.

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1. Introduction

Many toxic and harmful pollutants directly or indirectly enter water bodies, soil and atmosphere. This is due to an ever increasing deterioration of environment quality and is

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threatening to human health and safety. In the scheme of pollution abatement, the effective elimination of these organic pollutants becomes an essential priority.

Traditional wastewater treatment techniques include activated carbon adsorption, chemical oxidation, biological treatment, etc. However, in each technique, there are limitations and disadvantages. For instance, activated carbon adsorption only involves phase transfer of pollutants without decomposition but induces another pollution problem. Chemical oxidation is unable to mineralize all organic substances and is only economically suitable for the removal of pollutants in high concentrations. For biological treatment, the drawbacks to be considered are the slow reaction rates, disposal of sludges and control of proper pH and temperature.

Regarding the serious pollution problems, one of the most important tasks is the removal of pollutants of low concentration from water. Photocatalytic process has the following advantages [1]:

1. Complete oxidation of organic pollutants within a few hours.
2. Without production of polycyclized products.
3. Highly active and cheap catalyst adaptable to specially designed reactor system.
4. Oxidation of pollutants in ppb range.

Terzian et al. [2] studied the effect of pH on photocatalytic reaction of *m*-cresol with ultraviolet (UV) light and titanium dioxide (TiO_2) (Degussa P-25). The decomposition rates ranked as $\text{pH } 12 > 6.5 > 3$, i.e. such oxidation process was faster under alkaline conditions. However, there was no explanation provided in the study. D'Oliveira et al. [3] used UV light with the wavelength above 340 nm to treat *m*-chlorophenol by TiO_2 suspension. The results indicated that the reaction rate increased as the pH value increased at the $\text{pH} > \text{p}K_a$ of *m*-chlorophenol and there was no significant change of reaction rate in the range of pH 3.5–9. Auguliaro et al. [4] explored how pH value affected the photocatalytic reaction of phenol. It was indicated that the reaction rate increased with the increased pH at $\text{pH} > 10$, while the highest oxidation rate was occurred at pH 3 in the range of pH 3 to 10. Lu et al. [5] used UV light and TiO_2 of anatase crystal to treat $77.8 \mu\text{M}$ *o*-chlorophenol. Under the experimental conditions, the removal rate decreased with the increased pH. That is, the removal rates followed the order of $\text{pH } 3 > 5 > 7 > 9 > 11$. The study of Auguliaro et al. [6] indicated that the photocatalytic reaction rate of nitrophenol decreased as pH value increased. However, the study of Palmisano et al. [7] demonstrated that the reaction rate of nitrophenol increased in the alkaline range. From all the descriptions above, the effect of pH on the decomposition of organic compounds in photocatalytic system showed the complicated results. Therefore, this study tried to manipulate the pH controlling factor and to explore the effect on the decomposition of cresol and nitrophenol isomers. Moreover, the intermediates production and mineralization of photocatalytic degradation were also investigated.

In the present investigation, a specially designed batch reactor of glass construction was used to study the heterogeneous UV/ TiO_2 catalyzed oxidation of cresols and nitrophenols in water. The main factor for study was the effect of pH and to compare its influence on different isomers through kinetic studies under various conditions together with the monitoring of intermediates to postulate possible mechanisms. Finally, the degree of mineralization of nitrophenol was determined from the concentrations of

released nitrite and nitrate ions to survey the completeness of mineralization of organic substances.

2. Experimental

2.1. Experimental apparatus

The cylindrical batch reactor (13 cm ID \times 30 cm H) equipped with a UV light source (365 nm, BLE-6T365, Spectronic) inside a jacketed quartz tube (7 cm OD \times 27 cm H) with cooling water circulation in the centre of the reactor was arranged. A magnetic stirring device was used to keep TiO₂ (Degussa P-25) in suspension. A pH controller was installed to control constant pH during reaction.

2.2. pH Effect

Under different pH values and the following operating conditions: TiO₂ = 2 g/l, stirring speed = 650 rpm, temperature = 25°C, light intensity = 1.5 mW/cm², sampling intervals were set at 0, 10, 20, 40, 60, 80, 100, 120 and 150 min, respectively. For each sample, a 15-ml solution was placed in a teflon centrifuge tube for clarification with high speed centrifuging, followed by filtration with 0.2 μ m nitrocellulose filter paper. About 5 ml of initial filtrate was rejected to avoid interference from adsorbed phenolics. The next portion of 10 ml was stored in a brown glass bottle for analysis by HPLC (Hitachi L6000).

2.3. Determination of intermediates

By considering the detection limit of instruments, the initial concentration of reactants was raised to 0.75 mM with the same amount of TiO₂ as above and controlled pH at 7. The reaction time for cresols was 8 h with sampling intervals at 0, 2, 4, 6 and 8 h respectively; for nitrophenols, the reaction time was 12 h with sampling at 0, 3, 6, 9 and 12 h. The volume of each sample was 20 ml, to be centrifuged and extracted three times with 20 ml of ethyl ether. The extract was stored in a 40-ml brown glass bottle for concentration by blowing a stream of nitrogen gas to 0.5 ml, which was then stored in a 1-ml vial for analysis by GC/MS(HP 5890II + HP 5989B).

2.4. Mineralization

The reaction of *o*-nitrophenol took place at pH 7 for 9 h with sampling at 0, 0.5, 1, 2, 3, 4, 5, 7 and 9 h, respectively. The concentrations of nitrite and nitrate ions were analyzed immediately after sampling with a spectrophotometer [8]. Residual nitrophenol was analyzed by HPLC and residual organic carbon by TOC (Dohrmann DC-180).

3. Results and discussion

3.1. pH Effect

Table 1 shows the removal ratio of *o*-, *m*-, *p*-cresols and nitrophenols with initial concentration of 0.1 mM under different pH values after 2.5 h of photocatalytic reaction. The differences in removal ratio between the best and worst conditions are 26, 40 and 51%, respectively for the three isomers of cresol, while those of nitrophenol are 7, 12 and 12%, respectively under different pH values. It is indicated that the decomposition of both cresols and nitrophenols is affected by pH, and such effect is more significant on cresol.

According to the Langmuir–Hinshelwood model: $r = kKC/(1 + KC)$ [4,9], the rate equation can be simplified to a pseudo first order equation: $\ln C_0/C = k't$, where C_0 = initial concentration, C = concentration at time t , k' = pseudo first order rate constant. By plotting $\ln C_0/C$ vs. t , a good linear relation is observed. The slopes, k' , from these plots are listed in Table 2. Generally speaking, the decomposition of cresols and nitrophenols treated with UV/TiO₂ process is pretty good under neutral and weak alkaline conditions.

The surface functional groups of TiO₂ in water may be TiOH₂⁺, TiOH and TiO⁻, and the p*H*_{zpc} of TiO₂ is one of the important factors determining the distribution of surface functional groups. At p*H* > p*H*_{zpc}, TiO⁻ is the predominant species, while TiOH₂⁺ plays the role as p*H* < p*H*_{zpc}. The state of the chemical species presented in water is also affected by p*H*, and is closely related to the dissociation constant of the species. When p*H* is lower than the p*K*_a of the species, it primarily presents in molecular state. On the contrary, it exists as ionic state at p*H* greater than the p*K*_a. The p*H*_{zpc} of TiO₂ used in this study is about 6.6 and the p*K*_a's of cresols and nitrophenols are 10.01–10.2 and 7.15–8.28, respectively. Under neutral and weak alkaline conditions, TiO⁻ is the predominant species for TiO₂ and molecular state is the primary species for phenolic compounds. Both of them may combine by hydrogen bonding easily and thus elevate the amount of adsorption and enhance the decomposition rate. As to the *o*- and *p*-nitrophenols, it shows good decomposition effect even under acidic condition. The rate limiting step might be the free radical formation mechanism instead of the surface adsorption mechanism described earlier. Hydroxyl-free radicals are generated by the reactions of light-excited holes with H₂O/OH⁻. The other source of hydroxyl-free

Table 1
The removal ratio (%) of cresols and nitrophenols under different pH

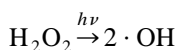
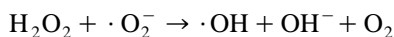
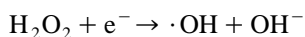
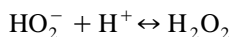
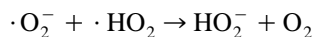
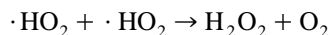
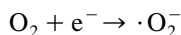
| | pH 3 | pH 5 | pH 7 | pH 9 | pH 11 |
|-----------------------|------|------|------|------|-------|
| <i>o</i> -cresol | 81 | 91 | 98 | 95 | 59 |
| <i>m</i> -cresol | 63 | 79 | 88 | 81 | 37 |
| <i>p</i> -cresol | 70 | 75 | 93 | 96 | 95 |
| <i>o</i> -nitrophenol | 96 | 92 | 98 | 98 | 91 |
| <i>m</i> -nitrophenol | 82 | 84 | 92 | 94 | 90 |
| <i>p</i> -nitrophenol | 84 | 72 | 82 | 82 | 84 |

Table 2

List of pseudo first order rate constants k' (min^{-1}) for cresols and nitrophenols at different pH

| | pH 3 | pH 5 | pH 7 | pH 9 | pH 11 |
|-----------------------|-------|-------|-------|-------|-------|
| <i>o</i> -cresol | 0.012 | 0.019 | 0.025 | 0.02 | 0.006 |
| <i>m</i> -cresol | 0.007 | 0.01 | 0.014 | 0.011 | 0.003 |
| <i>p</i> -cresol | 0.008 | 0.01 | 0.017 | 0.021 | 0.02 |
| <i>o</i> -nitrophenol | 0.021 | 0.016 | 0.023 | 0.023 | 0.016 |
| <i>m</i> -nitrophenol | 0.011 | 0.012 | 0.018 | 0.019 | 0.015 |
| <i>p</i> -nitrophenol | 0.012 | 0.008 | 0.012 | 0.012 | 0.013 |

radicals might come from the hydrogen peroxide which generated in the following chain reactions [10]:



At the pH values lower than the $\text{p}K_{\text{a}}$ (4.88) of $\cdot\text{HO}_2$, the amount of $\cdot\text{HO}_2$ increases, thus, enhances the sequential reactions and the $\cdot\text{OH}$ production. Many literature [10,11] have proved that the hydroxyl-free radicals are the primary active species in the photocatalytic reaction. Thus, the formation of $\cdot\text{OH}$ is beneficial to increase the reaction rate.

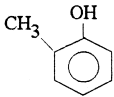
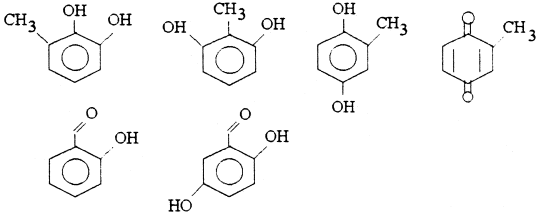
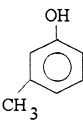
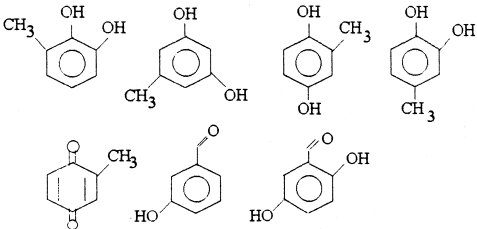
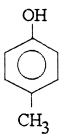
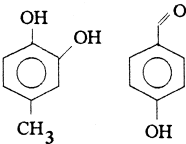
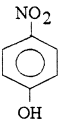
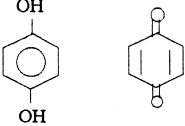
As the reaction rates varied with pH for cresols at $\text{pH} < 9$, the order is *o*->*p*->*m*-cresols, but above pH 9, the order changes to *p*->*o*->*m*-cresols. According to Terzian et al. [2], the lower limit of quantum yields for cresol isomers at initial pH 3 in the photocatalytic system of 365 nm UV/TiO₂ was in the order of *p*->*o*->*m*-isomers with respective quantum yield of 0.0096, 0.0076, and 0.001 being close to our findings at constant pH during reaction. Between pH 3 to 11, the order of k' is *o*->*m*->*p*-nitrophenols. Palmisano et al. [7] and Dieckmann et al. [12] respectively used TiO₂ catalyst and found the order of rate constant for photodegradation was *p*->*o*->*m*-nitrophenols. By comparing their results with ours, we could not obtain similar findings, probably due to the difference of TiO₂ structure, since they used anatase with pH_{zpc} between 1–3, while ours is Degussa P-25 with pH_{zpc} around 6.6. The difference in isoelectric points could affect reaction mechanisms which deserves further studies.

3.2. Intermediates

By GC/MS analysis, the intermediates product from photocatalytic degradation of cresols and nitrophenols are listed in Table 3. For *o*-cresol, 3-methyl-1,2-benzenediol,

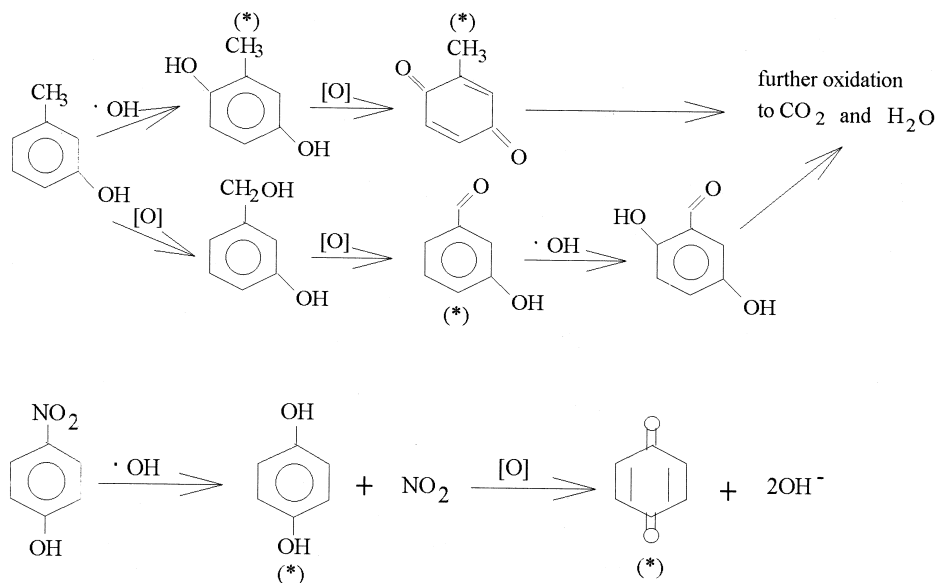
Table 3

Intermediate products identified in the photocatalytic reactions of cresols and nitrophenols

| reactant | intermediate products |
|---|---|
|  |  |
|  |  |
|  |  |
|  |  |

2-methyl-1,3-benzenediol, methyl-hydroquinone, 2-methyl-*p*-benzoquinone, 2-hydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde were found. For *m*-cresol, 3-methyl-1,2-benzenediol, 3,5-dihydroxytoluene, methyl-hydroquinone, 4-methyl-1,2-benzenediol, 2-methyl-*p*-benzoquinone, 3-hydroxybenzaldehyde and 2,5-dihydroxybenzaldehyde were detected. For *p*-cresol, 4-methyl-1,2-benzenediol and 4-hydroxybenzaldehyde were specified. For *p*-nitrophenol, hydroquinone and *p*-benzoquinone were identified. No intermediate product was found for both *o*- and *m*-nitrophenols.

The presence of these intermediates from cresols and nitrophenols indicates the attachment of a hydroxyl group to the benzene ring as a result of hydroxylation. In



(*) : Isolated intermediate product

[O] : $\text{OH}\cdot$ or $\text{O}_2\cdot$

Fig. 1. The possible postulation of reaction paths for *m*-cresol and *p*-nitrophenol.

addition, the products of aldehydes from cresols are an indication of the conversion of methyl group to alcohols and by further oxidation to aldehydes.

Using the examples of *m*-cresol and *p*-nitrophenol, the possible postulation of reaction paths are shown as Fig. 1. There are two possibilities for the oxidation of *m*-cresol. The OH radicals attach the benzene ring to form methyl-hydroquinone and further oxidation by peroxy radicals to produce 2-methyl-*p*-benzoquinone. Another possibility might begin through the oxidation of the methyl group to form alcohol and then aldehyde, followed by the attachment of OH radical to the benzene ring to form 2,5-dihydroxybenzaldehyde. Further oxidation of these two intermediates would lead to the formation of carbon dioxide and water.

The photocatalytic oxidation of nitrophenol starts from the attachment of OH radical to the benzene ring, with the release of the nitrite ion to form hydroquinone, which reacts with peroxy radical to be oxidized to *p*-benzoquinone.

In the hydroxylation process, the *ortho* site between OH and CH_3 functional groups of *m*-cresol is more difficult to react with hydroxyl-free radicals, thus, there are only three sites exposed for reaction to take place. Therefore, the decomposition rates of *o*- and *p*-cresol are faster. The other reaction mechanism considered here is the oxidation of methyl group. The side by side functional groups of OH and CH_3 of *o*-cresol possess stronger attraction so that the oxidation reaction is relatively difficult to happen.

However, the reaction rate of *o*-cresol was not observed to slow down in this study. Thus, the hydroxylation mechanism might be the major reaction path. The reaction mechanism of nitrophenol decomposition is induced by bond breaking of NO₃ functional group. Theoretically, *m*-nitrophenol is more difficult to decompose than the other two isomers. But the results in this study did not show it. There was no intermediate detected for *o*- and *m*-nitrophenols, and two intermediates were detected for *p*-nitrophenol. It is proposed that there might be some other dominant reaction paths in this process.

3.3. Degree of mineralization

Using *o*-nitrophenol at pH 7, the initial concentration of *o*-nitrophenol is 0.1 mM corresponding to 0.6 mM of carbon for mineralization in 9 h. Complete decomposition of *o*-nitrophenol appears in 4 h (Fig. 2). The result of TOC shows a faster reaction rate at the initial stage with 39% degradation, but turns sluggish after 5 h and more so, towards a later stage. This is probably due to the resistance of intermediates against photo-oxidation or the increased dilution of the concentration. The total removal in TOC reached 89.6% at the conclusion of the reaction, and more time will be required to complete mineralization.

The mass balance based on the total carbon concentration in the system can be represented by:

$$C_T = (o-NP)_t + (Int)_t + (CO_2)_t$$

where $(Int)_t = (TOC)_t - (o-NP)_t$; C_T = total carbon concentration in the system; $(o-NP)_t$ = carbon concentration in *o*-nitrophenol at time t ; $(Int)_t$ = carbon concentration in

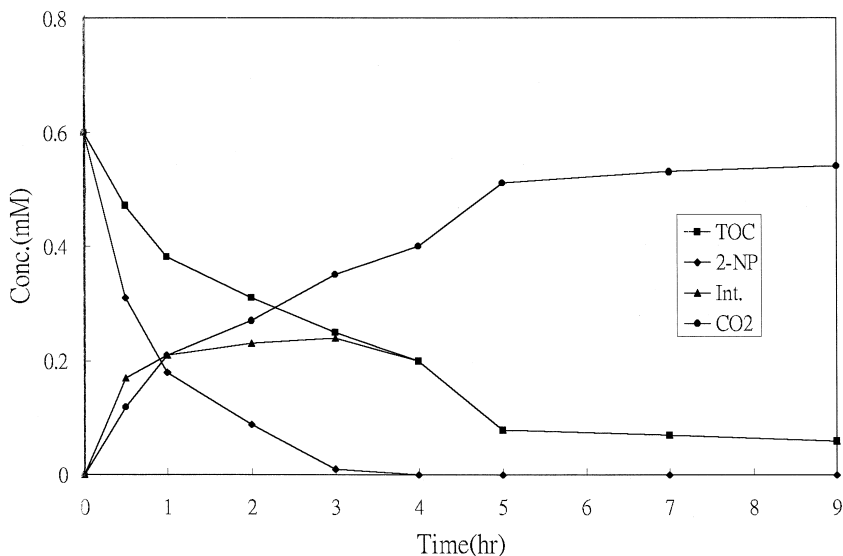


Fig. 2. Concentration changes of *o*-NP, Int, CO₂ and TOC vs. time in mineralization of *o*-nitrophenol. (initial total carbon = 0.6 mM, TiO₂ = 2 g/l, light intensity = 1.5 mW/cm², temperature = 25°C, pH = 7).

the intermediate at time t ; $(\text{CO}_2)_t$ = carbon concentration in carbon dioxide at time t ; $(\text{TOC})_t$ = carbon concentration found in TOC at time t .

Fig. 2 shows the variation of these values with respect to time change. The amount of intermediates reaches a maximum around 3 h with nearly complete decomposition of *o*-nitrophenol while TOC decreases by 50%. After this period, TOC changes slowly, since these intermediates are resistant to photolysis. The formation of carbon dioxide increases rapidly at the beginning and reaches a maximum around 7 h and later changes slowly.

Fig. 3 shows the concentration changes of *o*-nitrophenol intermediate, nitrite, nitrate and (nitrite + nitrate) ions. The nitrite concentration quickly reaches a maximum around 3 h and then decreases rapidly and vanishes in 5 h. For nitrate ions, it is found that the concentration increases in two stages, after 2 h of reaction it reaches a maximum and remains steady. A further increase appears again in 4 h and then flattens. After 4 h, the nitrate ion concentration increases in contrast to the decrease of nitrite ion concentration, while the sum of these two ion concentrations also decreases, indicating that not all nitrite ions convert to nitrate. In addition, the maximum of the sum of nitrate and nitrite ion concentrations is not more than 50% of theoretical value, probably due to the formation of ammonium ion. Most likely, after 9 h of reaction there still remains 10% of intermediates not completely oxidized and containing nitrogen. The evolution of nitrogen gas is another possibility or a combination of all possibilities in affecting the measurement of total nitrogen.

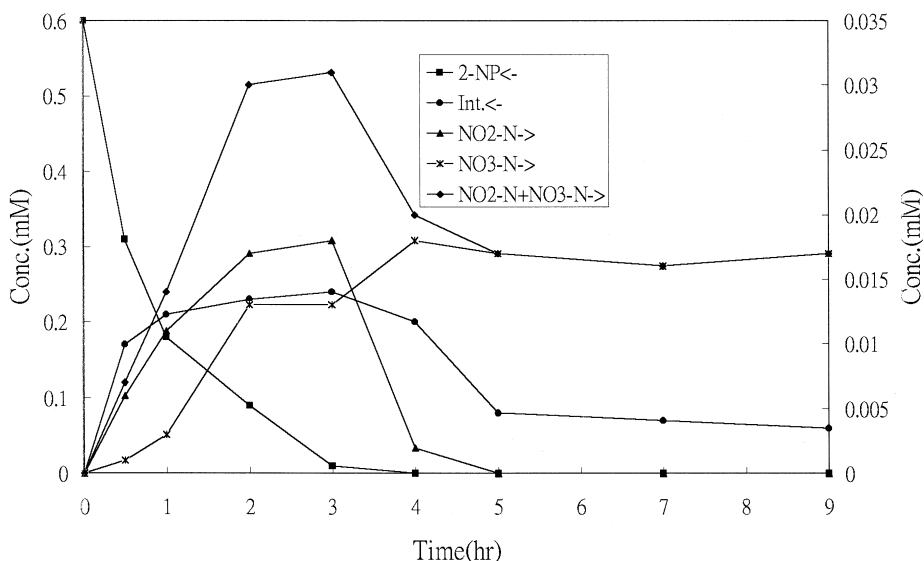


Fig. 3. Concentration changes of *o*-NP, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, and $(\text{NO}_2 + \text{NO}_3)$ vs. time in mineralization of *o*-nitrophenol. (initial total carbon = 0.6 mM, TiO_2 = 2 g/l, light intensity = 1.5 mW/cm^2 , temperature = 25°C, pH = 7).

4. Conclusions

(1) The decomposition of cresols and nitrophenols by UV/TiO₂ photocatalytic reactions is considered satisfactory. At pH 7, removal ratios exceed 90% for 0.1 mM of these compounds, but complete elimination may need 4–5 h of reaction time.

(2) The reactions are influenced by pH values, which affect less for nitrophenols. In the present studies, pH 7 is found optimal for decomposition by photocatalytic process.

(3) For the effect of isomeric structures in cresols, the order of reaction rates for pH below 9 is *o*->*p*->*m*-cresols, above pH 9, the order is *p*->*o*->*m*-cresols. For nitrophenol series with pH 3–11, the order is *o*->*m*->*p*- nitrophenols.

(4) Under different pH values, the photocatalytic reactions of cresols and nitrophenols are found to be pseudo first order kinetics conforming Langmuir–Hinshelwood model.

(5) The intermediate products from the degradation of cresols and nitrophenols are identified by GC/MS analysis as hydroxy derivatives of the parent compounds, indicating that hydroxylation is involved in the photocatalytic decomposition process.

(6) In 9 h of reaction time, the degree of mineralization of *o*-nitrophenol reaches 89.6%. The formation of nitrite and nitrate ions at the beginning of the reaction shows denitration of nitrophenol followed by subsequent series of reactions.

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