

TiO₂-Mediated Photodegradation of Aqueous Trinitrophenol Irradiated by an Artificial Light Source

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Abstract TiO₂-mediated photodegradation is widely reported to degrade recalcitrant pollutants such as nitrophenolics. This paper investigated the TiO₂-mediated photodegradation of trinitrophenol (TNP) in aqueous solution irradiated by an artificial light source. About 28.4 % TNP degradation was attained over 450 min from an initial TNP concentration of 1,000 mg L⁻¹. Ionic chromatographic analysis further revealed the evolution of nitrite and nitrate anions and an unknown intermediate *X* during the photodegradation process. The trends of nitrite and nitrate anions indicate that the photodegradation process produced nitrite at first, which subsequently turned to nitrate in the presence of oxygen. The removal rate of COD was far slower than that of TNP, inferring the photodegradation reaction gradually mineralized the parent pollutants. The photodegradation of TNP could not proceed under anaerobic condition, presumably a result of oxygen deficiency that disabled the denitration process. Because of the volumetric loss of the test solution, follow-up irradiations were performed after addition of supplementary water. This follow-up irradiation period revealed that direct photolysis, i.e., irradiation in the absence of TiO₂

photocatalysts, could not photodegrade TNP but gradually diminish the component *X*.

Keywords Titanium dioxide · Trinitrophenol · Photocatalysis · Direct photolysis

1 Introduction

Nitrophenolic compounds are widely used in a range of industrial productions including dyes, pesticides, explosives, and pharmacies, and occur very often in the relative effluents. They are irritant and toxic towards plants, microorganisms, animals, and human beings, and are rated by US EPA as priority pollutants with a restricted concentration below 10 ng l⁻¹ in natural water bodies (Shen et al. 2009a, 2009b). Hence, proper treatment must be adopted to prevent nitrophenolics from reaching the downstream watercourses. A copious of literatures have focused on the degradation of nitrophenolic compounds, including absorption (Ganigar et al. 2010; Mohan et al. 2011), bio-treatment (Nipper et al. 2004; Dai et al. 2009; Ghosh et al. 2010), and chemical oxidation such as Fenton process (Dulova et al. 2011; Sun et al. 2011), catalytic wet air oxidation (Morales-Torres et al. 2010; Lai et al. 2011), photolytic degradation (Zhao et al. 2010) and photocatalytical oxidation (Yang et al. 2010; Chai et al. 2011; Zhai et al. 2013; Nezamzadeh-Ejehieh and Khorsandi 2014). Efficacies of the above treatments, however, are usually not sufficient because the nitrophenolics are chemically stable due to their electron-withdrawing nitro groups (Shen

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et al. 2009a, 2009b; Dulova et al. 2011). For an instance, biological treatments of nitrophenolics are hindered by a slow reaction rate, difficulty to find suitable microorganisms, and a limited treatment capacity (Dai et al. 2009; Shen et al. 2009a, b).

Photocatalytic degradation, as one of the advanced oxidation processes (AOPs), has recently been reported to deal with those recalcitrant pollutants. It is usually mediated by semiconductor photocatalysts, e.g., ZnO (Vora et al. 2005), Zn/MgO (Ali et al. 2013), Ag/AgBr/BiOBr (Li et al. 2013), Cu₂O (Zhai et al. 2013), Al₂O₃/CaO (Imtiaz et al. 2013), Ag/ZnO (Divband et al. 2013), and TiO₂ (Mele et al. 2007; Luo et al. 2009; Yang et al. 2010; Chai et al. 2011). TiO₂-mediated photocatalytic degradation has reportedly been able to completely destruct p-nitrophenol using sunlight as the light source (Herrera-Melián et al. 2001). In principle, photocatalytic degradation begins with excitation of a semiconductor that absorbs an incident photon. This excites an electron from the valence band into the conduction band and leaves behind a positive hole. The electron and hole, if not rejoin, may initiate the formation of hydroxyl radicals that destruct organic compounds. Since a photocatalytic process may freely utilize sunlight and air to degrade organic pollutants, it presumably outperforms other AOPs such as ozonation and Fenton processes which usually cost chemicals. If solar irradiation is not available an artificial light source may be a supplement.

A representative of the nitrophenolic family, trinitrophenol (TNP) is particularly of interest for research with respect to its chemical stability arising from the multi-nitro groups. Trinitrophenol features a low octanol-water partition coefficient ($K_{ow}=40$), high mobility and little biodegradability in the groundwater (Tan et al. 2006). In this research, we investigated the efficacy of photocatalytic degradation of TNP using an artificial light source, expecting to find some clues for industrial application.

2 Materials and Methods

2.1 Chemicals and Reagents

All TNP solution were prepared using 2,4,6-trinitrophenol (>98 %) purchased from Sigma-Aldrich (Shanghai, China). P25 TiO₂ photocatalysts were purchased from Degussa (Germany). Nitrogen (>99.99 %) was released from a cylinder to build an anaerobic

environment during the photoreaction. The reagents used for chemical oxygen demand (COD) test included potassium dichromate (>99 %), silver sulfate (99.7 %), and concentrated sulfuric acid (>95 %). They were purchased from Chengdu Kelong Chemical Ltd. (China). Double distilled water was used in this research.

2.2 Experimental Setup

Figure 1 shows the reaction apparatus. A high-pressure mercury UV lamp (150 W, Beijing Zhongruida Light Source Company, China) with a quartz jacket stands coaxially in the center of a cylinder. The irradiation of this lamp has a center wavelength of 365 nm according to the specification provided by its manufacturer. Cooling water circulated in an outer jacket coating the cylinder and kept the temperature of the reaction solution below 36 °C over the experimental period. Air or nitrogen was bubbled into the solution to build aerobic or anaerobic condition as needed.

2.3 Photodegradation with Fresh Solutions

At the beginning of photodegradation, the cylinder was charged with TNP solution (800 ml at 1000 mg l⁻¹). With vigorous stirring, TiO₂ fine particles (0.2 g) were dispersed into the solution to obtain a suspension. After 20 min allowing absorption to reach equilibrium, the UV lamp was turned on and time logged. Aliquots of

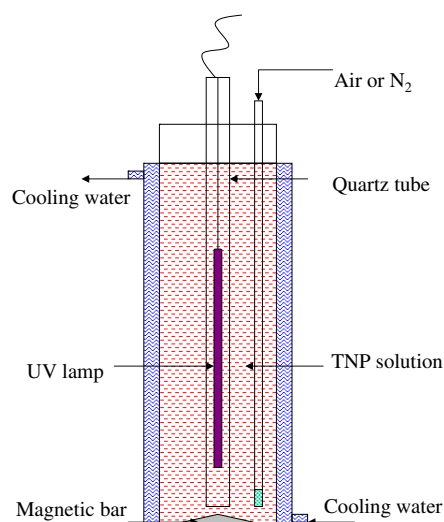


Fig. 1 Apparatus used for photodegradation reaction in this research

mixture were taken from the cylinder according to a preset time schedule and filtered through a 0.22- μm polytetrafluoroethylene (PTFE) filter prior to analysis. The photodegradation reaction was studied under either aerobic or anaerobic condition. Each experiment is repeated twice.

A control experiment was also performed to understand the adsorption of TNP by TiO_2 photocatalysts. In this experiment, a same procedure as mentioned above was adopted except that the UV lamp was turned off. This experiment went up to 360 min, suggesting no appreciable adsorption of TNP by the photocatalysts used.

2.4 Follow-Up Irradiation with the Remaining Solution

After the above photodegradation period, the volume of the reaction solution was substantially reduced due to repeated sampling and slight evaporation. This forced the irradiation process to abort though the target organic substances were not destroyed completely, as was indicated by the colorful appearance of the remaining solution. To check if the pollutants could be further converted, a follow-up irradiation experiment was performed under aerobic condition using either of the following strategies.

(A) In the presence of TiO_2 photocatalysts

Supplementary water was added into the remaining solution to gain a total volume of 800 ml and irradiation resumed.

(B) In the absence of TiO_2 photocatalysts

The TiO_2 photocatalysts in the remaining solution were removed via filtration through a 0.22- μm PTFE filter. Supplementary water was then added into the clear filtrate to regain a total volume of 800 ml and irradiation resumed.

2.5 Analytical Methods

The UV/Vis spectra of reaction solution were recorded using an ultraviolet-visible spectrophotometer (Model 759, Alpler, China). The progress of photodegradation reaction was also tracked using ion chromatography, which was carried out on an NJ-SA-4A column (250×4.6 mm) using a solution of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ as the mobile phase. The ion chromatographic analysis could examine the evolution of NO_2^- and NO_3^- , and the

change of TNP concentration. COD tests were performed through standard oxidation process using $\text{K}_2\text{Cr}_2\text{O}_7$ as the oxidant in the presence of Ag_2SO_4 under a concentrated H_2SO_4 environment. The dissolved oxygen (DO) concentration in the solution was measured by using a DO meter (JPB-607A, Leici, China).

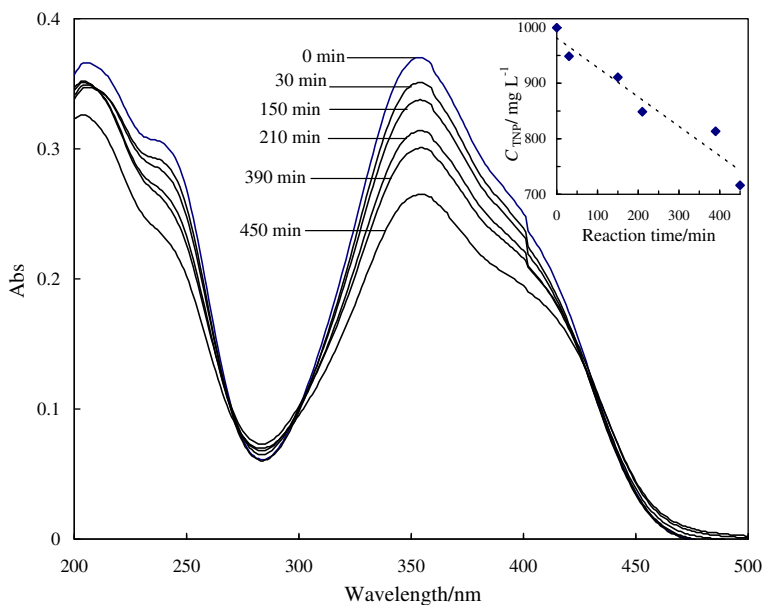
3 Results and Discussions

3.1 TiO_2 -Mediated Photodegradation of TNP under Aerobic or Anaerobic Condition

During the aerobic photodegradation reaction, the test solution was sampled at different times for analysis. Figure 2 shows the UV/VIS spectra between 200 and 500 nm of samples ($t=0, 30, 150, 210, 390,$ and 450 min). The trend of the spectra illustrates the progress of photodegradation along with the reaction time, indicating a gradual degradation of TNP. The absorbance at 355 nm is correlated to the TNP concentration that is plotted in the inset of Fig. 2. In this research about 28.4 % TNP degradation was attained over 450 min from an initial concentration of $1,000 \text{ mg L}^{-1}$. The low efficiency of TNP photodegradation has also been reported by Katsoni et al. who obtained 13 % degradation over 120 min from an initial TNP concentration of 270 mg L^{-1} (Katsoni et al. 2011). The authors, however, reported that 100 and 80 % conversion were achieved in 120 min from TNP concentrations of 64 and 144 mg L^{-1} , respectively. Imtiaz et al. also obtained a 100 % TNP photodegradation in 15 min from an initial TNP concentration of 15 mg L^{-1} (Imtiaz et al. 2013). These studies demonstrate that photodegradation is more applicable for a TNP-contained effluent of low concentration than for the one of high concentration.

Figure 3 shows the chromatograms of the reaction solution sampled at different time over the photodegradation period. The trend of the chromatograms reveals the evolution of NO_2^- (R_t 3.3 min), NO_3^- (R_t 4.7 min), and an unidentified component X (R_t 11.3 min) along with the degradation of TNP (R_t 9.2 min). Their concentrations versus reaction time are plotted in Fig. 4. NO_3^- evolved steadily with ascending tendency over the degradation time while NO_2^- saw an ascendancy period and subsequently a level off. These observations suggest that the denitration of TNP first generated nitrite ions, which were subsequently oxidized to nitrate ions under aerobic condition. The level

Fig. 2 UV/VIS spectra of reaction solution sampled at different time under aerobic condition. *Inset* is the trend of TNP concentration



off of nitrite concentration might arise from equilibrium of the two trends, i.e., generation of nitrite ions (resulting from denitration) and their consumption (resulting from oxidation). In fact, the nitrate/nitrite anions evolved from the transformation of nitroaromatics may backward influence the photodegradation of the parent nitroaromatics, but this effect remains controversial (Kavitha et al. 2005). Figure 4 also shows that TNP abated along with irradiation going on, which agreed well with the gradual attenuation of absorbance at

355 nm as shown in Fig. 2. In the same time, the concentration of component *X* increased steadily, indicating a constant formation of this intermediate. The tendency of mineralization of TNP was indicated by the change of COD in Fig. 4, which decreased along with the reaction time. The decrease of COD, however, was left far behind that of TNP. This infers that photodegradation reaction did not lead to mineralisation of TNP immediately but generated organic intermediates such as component *X*. The produced intermediates still contributed to COD and

Fig. 3 Chromatograms of test solution sampled during aerobic photodegradation reaction. The *top chromatogram* is a reference

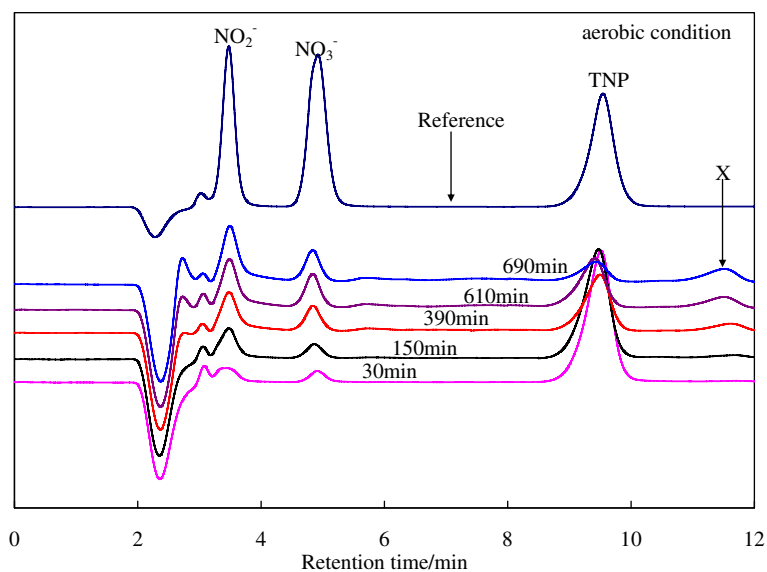
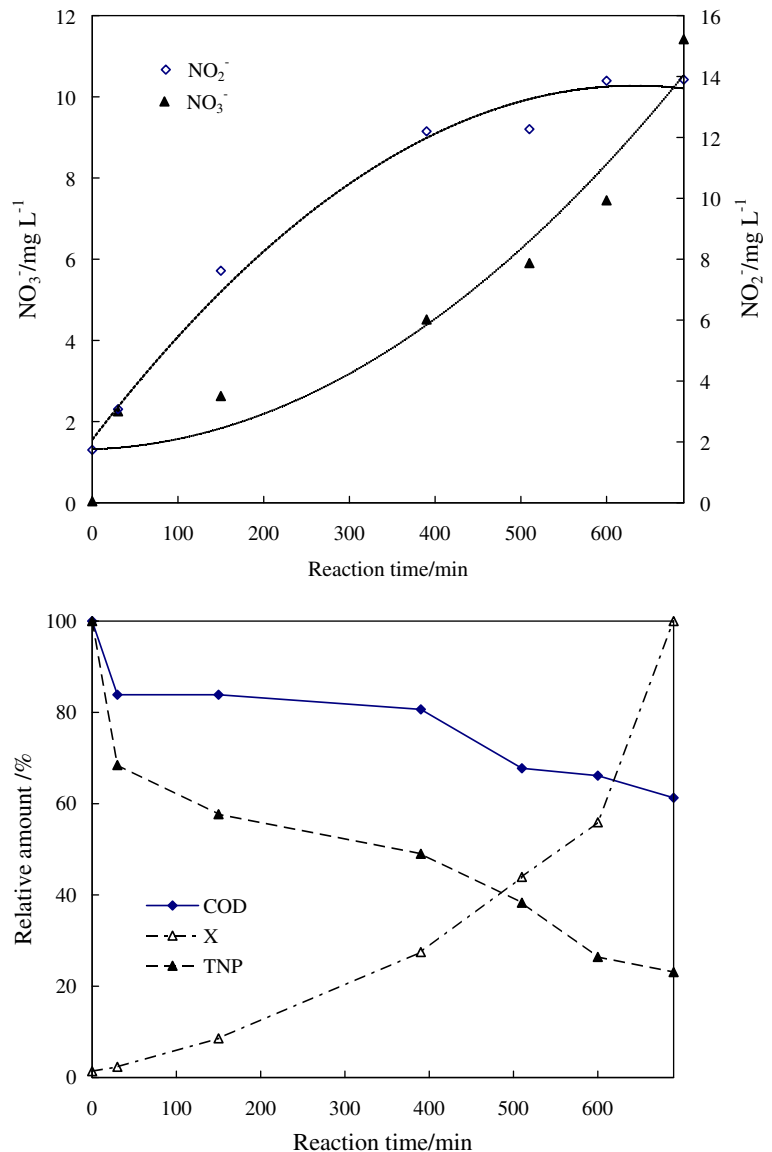


Fig. 4 Trend of NO_2^- , NO_3^- , TNP, X , and COD during the aerobic photodegradation reaction

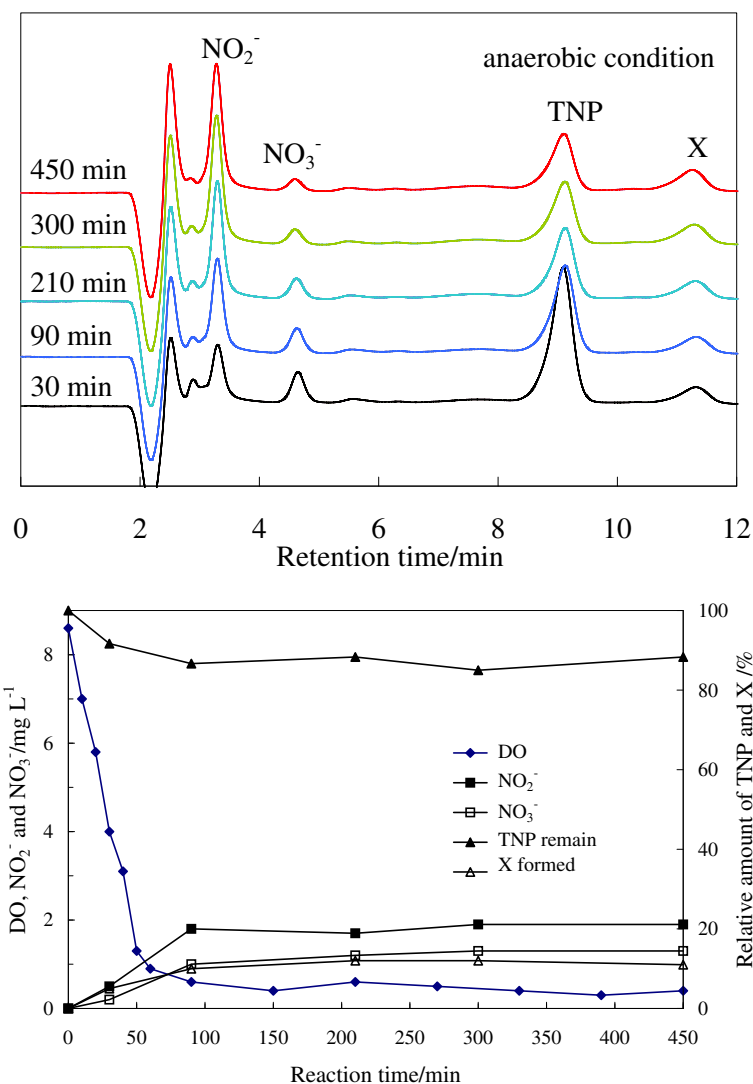


probably converted gradually to inorganic products at a slow rate.

The profile of photodegradation reaction under anaerobic condition is shown in Fig. 5. The top graph illustrates the chromatograms of samples collected at different time. The bottom graph shows the trend of concentrations of the components involved. The TNP concentration decreased before 90 min of reaction and became constant then. Accordingly, the concentrations of nitrite ion, nitrate ion, and component X all increased before 90 min and then leveled off. At the same time, Fig. 5 shows that dissolved oxygen diminished quickly

at first and leveled off from around 90 min. The trend of these concentrations suggests that dissolved oxygen played an indispensable role in this photodegradation reaction. With nitrogen being bubbled into the solution, dissolved oxygen decreased gradually. The TNP photodegradation occurred upon the remaining oxygen over the first period of about 90 min. As soon as dissolved oxygen was depleted the photodegradation of TNP terminated. The evolutions of nitrite ion, nitrate ion, and component X were accordingly stopped too. In addition, under the anaerobic condition, the produced nitrite ions could not turn to nitrate ions either. The

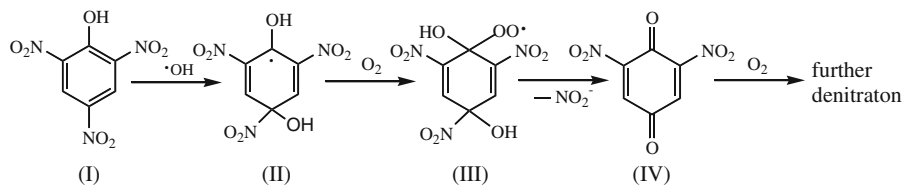
Fig. 5 Profile of the anaerobic photodegradation reaction. *Top* the change of chromatograms of test solution. *Bottom* trend of the concentrations of the components involved in this reaction



dependency of photodegradation upon dissolved oxygen was also observed by Wang et al. who achieved no appreciable photodegradation of TNT under anaerobic condition and a complete mineralization of TNT under aerobic condition (Wang et al. 1995).

Generally, degradation of nitrophenolics through advanced oxidation processes involves sequential additions of hydroxyl radicals upon the aromatic ring and consequently denitration (Kavitha et al. 2005; Liu et al. 2009; Imtiaz et al. 2013; Zhai et al. 2013). As a result, nitrite and nitrate species are released during the degradation process. Under aerobic condition, all nitrite species turn to nitrate species in the end. Meanwhile, the parent compound nitrophenolics are converted stepwise to a range of aromatic intermediates through processes

such as hydroxylation and polymerization. The intermediates are subsequently transformed to a serial of carboxylic acids, e.g., succinic acid, acetic acid, and oxalic acid, which can be finally mineralized (Liu et al. 2009). Regarding the role of dissolved oxygen in this research, we proposed the following scheme (Scheme I) to illustrate how it is involved in the pathway of TNP degradation. First, the photogenerated hydroxyl radical attacks the *para*-carbon atom which holds the highest electron density over the benzene ring (Kavitha et al. 2005). Then, dissolved oxygen went to the phenol $-\text{OH}$ group, giving rise to peroxide intermediate (III) (Zhai et al. 2013). This intermediate releases NO_2^- and leaves behind dinitro *p*-benzoquinone (IV) (Kavitha et al. 2005), which may undergo further denitration in the presence



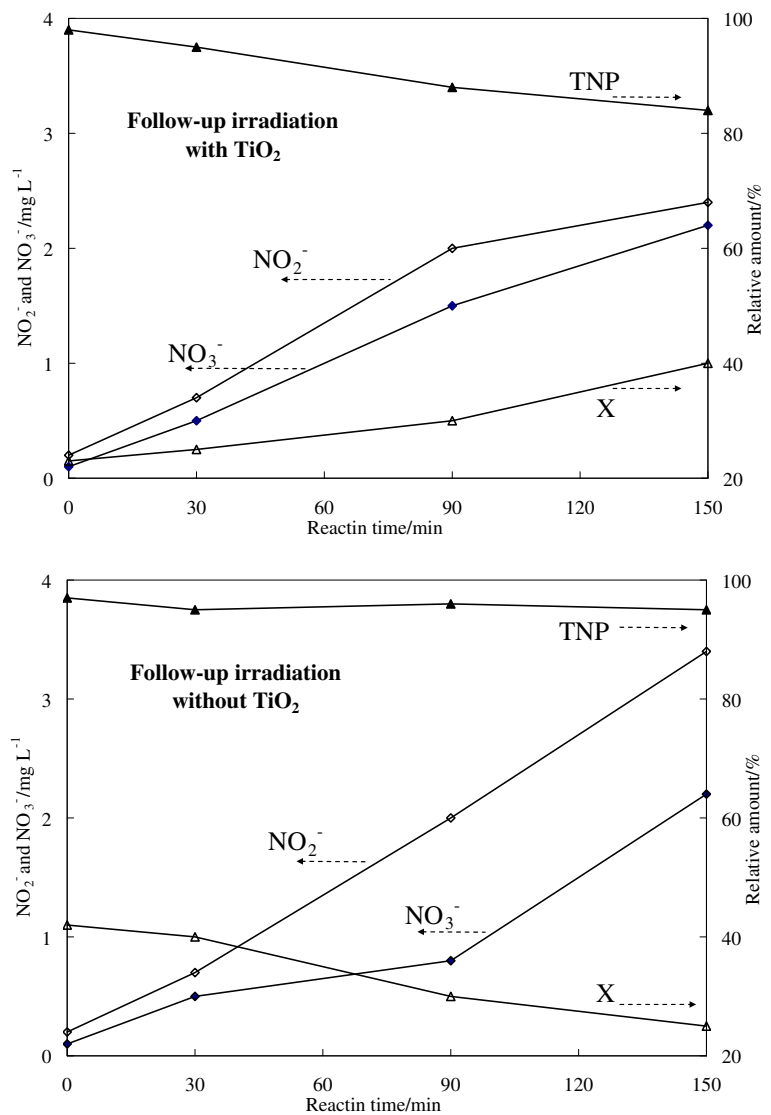
Scheme I The involvement of dissolved oxygen in the pathway of TNP photodegradation

of dissolved oxygen. Given the intensive involvement of oxygen in the above-mentioned pathways, the deficiency of dissolved oxygen probably prevents TNP from denitration process. Anaerobic condition therefore impedes the photodegradation of TNP, as was observed in this research.

3.2 Follow-Up Irradiation With or Without TiO₂

Figure 6 showed the profile of follow-up irradiation experiments with (top) and without TiO₂ (bottom). In the presence of TiO₂, the trends of TNP, NO₂⁻, NO₃⁻, and X look like those of using fresh TNP solution

Fig. 6 Trend of NO₂⁻, NO₃⁻, TNP, and X during follow-up photodegradation reaction with and without TiO₂ photocatalysts



(Fig. 3). This implies that the same mechanism governed from the photodegradation reaction with fresh TNP solution to the follow-up irradiation period. Furthermore, it was observed that a prolonged irradiation period up to 20 h could completely decolorize the remaining solution. This verifies that the photodegradation of TNP was a slow and stepwise denitration process where the chromophoric nitrous/nitric groups were gradually displaced by OH (Ishag et al. 1977). In the absence of TiO_2 , the concentration of TNP appeared constant whereas component X diminished. Additionally, the concentrations of both nitrite and nitrate anions increase. These observations suggest that the irradiation alone could not transform TNP but degrade component X . The increases of both nitrogen species presumably arose from the degradation of component X . In the experiments using fresh TNP solution in Section 3.1, we didn't check if direct photolysis (i.e., in the absence of TiO_2 photocatalyst) could have happened with fresh TNP solution. The observations here pronounce that the abatement of TNP should be attributed exclusively to TiO_2 -mediated photodegradation instead of direct photolysis. Similar results were reported elsewhere (Nipper et al. 2004; Priya et al. 2005).

Although direct photolysis was found to be ineffective for TNP in this research, a comparable compound TNT was reported to be directly photolyzed forming a colorful and stable complex (Wang et al. 1995), which resisted further mineralization (Hoffmann et al. 1995; Wang et al. 1995; Chun et al. 2000). TiO_2 -mediated photocatalytic processes, on the contrary, reportedly form hydroxylated intermediates which were more mineralizable (Chun et al. 2000). This is proved here by component X that could be diminished by direct photolysis. The identification of intermediates occurring in TNP photodegradation of this research will be carried out in further study.

4 Conclusions

In conclusion, this research reported the TiO_2 -mediated photodegradation of TNP in aqueous solution irradiated by an artificial light source. About 28.4 % TNP degradation was attained over a reaction period of 450 min from an initial TNP concentration of $1,000 \text{ mg L}^{-1}$. The photodegradation process gives rise to the evolution of nitrite, nitrate, and an unknown intermediate X . Nitrite anions turn to nitrate

anion under aerobic condition. The presences of both oxygen and TiO_2 photocatalysts are essential for the photodegradation of TNP. The deficiency of dissolved oxygen under anaerobic condition presumably prevents TNP from denitration, which disables the photodegradation reaction. Direct photolysis cannot degrade TNP but diminish the intermediate X .

As far as the industrial practice is concerned, this research suggests that photodegradation treatment is more applicable for TNP-contained effluent of low concentration (e.g., less than 100 mg L^{-1}) than for one of high concentration; this favors a complete conversion of the subject pollutant within a limited period of time. Furthermore, aerobic condition (e.g., via air bubbling) should be adopted to facilitate the photoreaction.

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