

# Photocatalytic Degradation of 2,4,6-Trinitrotoluene in Wastewater Using a Thin-Film TiO<sub>2</sub> Reactor

Gi-Bum Shin and Yeong-Kwan Kim<sup>†</sup>

Department of Environmental Engineering, Kangwon National University, Chuncheon, Kangwondo, 200-701, Korea

Received August 2007, accepted January 2008

---

## Abstract

The photocatalytic treatment of water contaminated with 2,4,6-trinitrotoluene (TNT) was explored in bench-scale experiments in batch mode using a Pyrex tube coated with a thin film of TiO<sub>2</sub> located inside a photoreactor. The reactor was aerated by purging it with compressed air before initiating the photocatalytic reaction. The rate of TNT degradation approximated first-order kinetics. The reaction rate constant decreased as the TNT concentration increased from 25 to 100 mg/L, while the first-order kinetics could be modeled using a Langmuir adsorption isotherm. The addition of the organic reductants methanol and EDTA significantly enhanced the rate of TNT degradation, with optimum results in the presence of 20% methanol by volume. EDTA increased the rate of TNT removal by enhancing the role of the reductants.

**Keywords:** TNT, TiO<sub>2</sub> thin-film, Photoreactor, Degradation, Adsorption, Kinetics

---

## 1. Introduction

Wastewater from the loading, assembling, and packing (LAP) operations involved in producing military explosives contains large amounts of 2,4,6-trinitrotoluene (TNT). This wastewater, referred to as pink water, is considered hazardous because of the toxicity of both the original explosive compounds and the by-products of the production process, such as dinitrotoluene and trinitrobenzene.<sup>1)</sup> Although Won *et al.*<sup>2)</sup> studied the toxicity and mutagenicity of TNT and its microbial metabolites, few studies in Korea have examined environmental contamination resulting from TNT. It is likely that TNT and other nitroaromatic compounds in various munitions have contaminated soil and groundwater since the Korean War, particularly near military camps.

Wastewater containing TNT can be treated by adsorption on activated carbon.<sup>3)</sup> However, this process suffers from problems associated with the regeneration and ultimate disposal of the contaminated carbon. Further, this process is inadequate for treating pink water while satisfying stringent future standards.<sup>1)</sup> Several studies have investigated the biological treatment of TNT-containing soil and wastewater with white rot fungus *Phanerochaete chrysosporium*.<sup>4-6)</sup> However, the failures to achieve

mineralization of TNT and the formation of by-products have led to a search for a new technology using an advanced oxidation process.

Attempts have been made to treat toxic compounds in wastewater by direct photochemical decomposition using ultraviolet (UV) irradiation. Other workers have used photocatalytic degradation in the presence of microheterogeneous media. For example, Carey *et al.*<sup>7)</sup> described the photocatalytic degradation of biphenyl and chlorobiphenyls in the presence of titanium dioxide (TiO<sub>2</sub>). Since this study, numerous investigations have examined the applicability of the TiO<sub>2</sub>/UV process, including treating water contaminated with metals.<sup>8)</sup> Schmelling and Gray<sup>9)</sup> and Wang and Kutal<sup>10)</sup> conducted titanium dioxide-mediated photocatalytic transformations of aqueous TNT solutions, while Hess *et al.*<sup>11)</sup> demonstrated the viability of a combined process using both fungal and photochemical methods with TiO<sub>2</sub> to treat aqueous TNT waste.

According to Matthews<sup>12)</sup> and Turchi and Ollis,<sup>13)</sup> the primary degradation step in the photo-oxidation of aromatic compounds by TiO<sub>2</sub> is a hydroxyl radical attack on the aromatic ring facilitated by the lability of the parent compound. They demonstrated that a wide range of organics could be photo-mineralized when irradiated in an aerated suspension of TiO<sub>2</sub>. Unlike less-substituted nitroaromatic compounds, the significant role of TiO<sub>2</sub> photocatalysts in the reduction of TNT in contaminated wastewater may be due to conduction band electrons. Schmelling and

---

<sup>†</sup> Corresponding author

E-mail: yeong@kangwon.ac.kr

Tel: +82-33-250-6353, Fax: +82-33-254-6357

Gray<sup>9)</sup> found that reductive transformations were involved in more than 90% of the TNT oxidized to CO<sub>2</sub> and approximately 35% of the TNT nitrogen recovered as ammonium ions. Prairie *et al.*<sup>8)</sup> obtained a similar result, and concluded that both oxidation and reduction processes need to be considered when designing photocatalytic systems for removing metals and organics.

Most previous studies of UV photocatalysis have used suspensions of TiO<sub>2</sub> particles. Photocatalysts may also be attached to or immobilized on various substrates, including glass tubing,<sup>14,15)</sup> sand,<sup>16)</sup> tin oxide covered glass,<sup>17)</sup> and stainless steel plate.<sup>18)</sup> By comparison with suspended catalysts, supported catalysts have less surface area and may suffer from mass transfer limitations during the photocatalytic reactions. Consequently, immobilized catalysts are more likely to be used in practical applications, since they eliminate the need for filtration or replenishment. However, one of the disadvantages of a reactor using supported catalysts is its low reaction rate. Part of the porous structure of a catalyst may be lost during the sintering process involved in its manufacture and only a portion of the catalyst makes contact with the solution. Consequently, the configuration of catalysts is of particular importance in any reactor that uses supported catalysts.

This paper presents the experimental results of an investigation of the photocatalytic treatment of TNT-contaminated water using a TiO<sub>2</sub> catalyst supported on a Pyrex tube in an aerated system. These results provide data on the degradation kinetics of TNT and on the synergistic effects that occur on adding organic reductants, such as methanol and EDTA.

## 2. Materials and Methods

A quasi-wastewater sample was prepared by dissolving 99.9% pure TNT, obtained from the Institute of Chemical Research, Korea, in distilled water with stirring for 24 hr. The stock solution was stored in an amber glass bottle in the dark until required. Additional samples that were used to explore the effect of methanol were prepared in the same manner, but some or all of the distilled water was replaced with a predetermined amount of methanol.

Fig. 1 shows a schematic representation of the photocatalytic reactor assembly consisting of a photoreactor, an air pump, and a support stand. The reactor (6 cm ID, 46 cm long) was constructed from a stainless steel column to prevent the adsorption of reactants and the loss of ultraviolet. Stainless steel was used because it is readily available, relatively inexpensive, and corrosion resistant. It contained a Pyrex tube, 3 cm in diameter and 50 cm long, coated with a thin TiO<sub>2</sub> film. With the outer reactor diameter of 6 cm and the inner tube diameter of 3 cm, the effective volume was 975 mL. A UV lamp (Sankyo Denki, 15 W, 45 cm long) was located inside this tube and its direct light intensity was measured as 1,300 μW/cm<sup>2</sup> (J-221 Black-Ray Ultraviolet Intensity Meter). After passing through the TiO<sub>2</sub> coating, the intensity fell to 400 μW/cm<sup>2</sup>. Air was supplied for mixing from the bottom of the reactor at a rate of 190 mL/min, and it flowed upward in the area between the Pyrex tube and the stainless steel reactor. The system was operated in a batch mode.

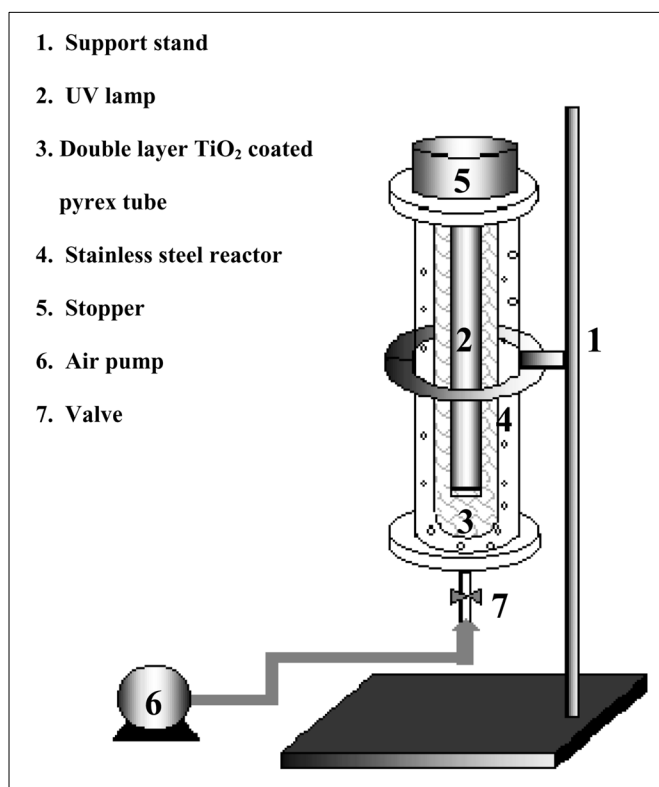


Fig. 1. Schematic diagram of the UV / TiO<sub>2</sub> thin film reactor (taken from Shin and Kim, 2002).

The TiO<sub>2</sub> sol was synthesized using titanium tetraisopropoxide, Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, (Aldrich, USA) using the sol-gel method.<sup>19)</sup> A solution containing 150 mL of H<sub>2</sub>O, 15 mL of titanium isopropoxide, and 1 mL of HNO<sub>3</sub> was refluxed at 80°C for 3 days. The subsequent sol was subjected to ultrasonic treatment for a few minutes in order to rupture large aggregates, and the resulting colloid was concentrated using a vacuum rotary evaporator. The TiO<sub>2</sub> sol was coated on the outside of the Pyrex tube by spinning it between supports. The coated gel was then dried at room temperature for 24 hr before being fired in an oven in which the temperature was ramped at a rate of 3 °C/min to 400°C, at which temperature the gel was sintered for 2 hr. It was then cooled to ambient temperature at a rate of 3 °C/min. This coating procedure was repeated twice in order to build up successive film layers. A scanning electron microscope (SEM) picture of the thin film showed that it was about 1.5 μm thick, with an interface between the two film layers.<sup>20)</sup> A typical run took 2 hr, with 5-mL samples collected every 30 min. The concentrations of TNT and organic byproducts were analyzed using a high-performance liquid chromatograph (Hitachi, Model L-7100) equipped with a Cosmosil RP-C<sub>18</sub> column (0.46 cm ID by 15 cm long; Nacalai Tesque, Inc., Japan). A UV-visible spectrophotometer (Hitachi, Model L-4200H) operating at 235 nm and connected to a Chromato-integrator (Hitachi, Model D-2500) was used for detection. The mobile phases were 100% acetonitrile (A) and H<sub>2</sub>O (B). The column was eluted at a flow rate of 1 mL/min with an initial 0- to 5-min isocratic elution (20% A-80% B) that changed to a linear gradient of 90% A-10% B over 60 min. Before analysis, all the samples were filtered

through a 0.2- $\mu\text{m}$  pore syringe filter (Millipore) and stored in amber glass vials.

### 3. Results and Discussion

#### 3.1. TNT Degradation Kinetics

In Fig. 2,  $\ln(C_0/C)$  is plotted against time for various initial TNT concentrations. The approximately linear decrease in the logarithm of the TNT concentration with irradiation time is consistent with the first-order kinetic expression:

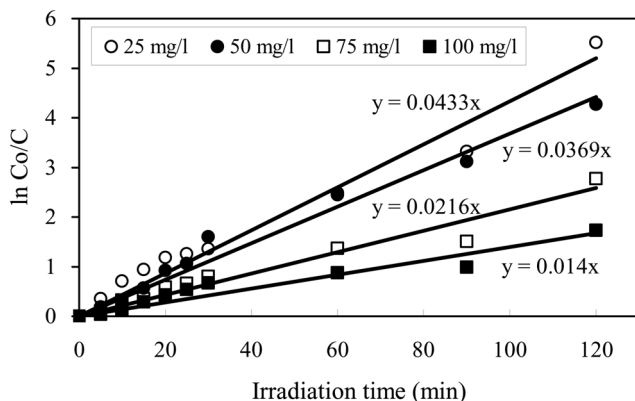


Fig. 2. The effect of initial concentration on the photocatalytic degradation of TNT.

$$\ln(C_0/C) = -k_a t \quad (1)$$

The apparent first-order rate constants ( $k_a$ ) obtained from least squares analyses are given in Table 1. They decrease with increasing TNT concentration. Table 1 also shows the experimental and calculated  $t_{0.5}$  values obtained when  $C/C_0 = 0.5$ . The deviation between the experimental and calculated  $t_{0.5}$  is greatest at higher TNT concentrations, which Matthews<sup>12)</sup> ascribed to the induction period necessary to obtain equilibrium. Excluding 3 data points after 30 min of reaction, the rates constants were 0.0455, 0.0509, 0.027, and 0.0237 in ascending concentration order, respectively. Data points toward the end of reaction appeared to have higher weights than other data in the regression, suggesting the necessity to eliminate those data in calculation.

Many researchers have modeled the rate of destruction of organics in UV-illuminated  $\text{TiO}_2$  systems in terms of the Langmuir isotherm equation

$$r_{\text{TNT}} = (k_1 k_2 C) / (1 + k_1 C) \quad (2)$$

where  $C$  is the solute concentration and  $k_1$  and  $k_2$  are constants related to the adsorption and reaction properties of the solute, respectively. In Equation (2), the  $k_1$  reflects solute molecules that adhere to the surface, while  $k_2$  reflects the reaction rate under the experimental conditions.

Matthews<sup>15)</sup> pointed out that the integral of Equation (2) at  $C=0.5C_0$  yields:

$$t_{0.5} = (0.5C_0)/k_2 + (0.693)/k_1 k_2 \quad (3)$$

If the Langmuir isotherm equation model approximates the rate of TNT destruction, Equation (3) should yield a straight line with slope  $1/k_2$  and intercept  $0.693/k_1 k_2$ . This plot is shown in Fig. 3. The plot is linear, indicating that the reaction occurs on the film surface, and the values of  $k_1$  and  $k_2$  are  $1.342 \text{ mg/L}^{-1}$  and  $1.033 \text{ mg/L min}^{-1}$ , respectively. The rate of destruction ( $r_{\text{TNT}}$ ) can be calculated by fitting the appropriate Langmuir isotherm for each initial TNT concentration and is given in Table 1.

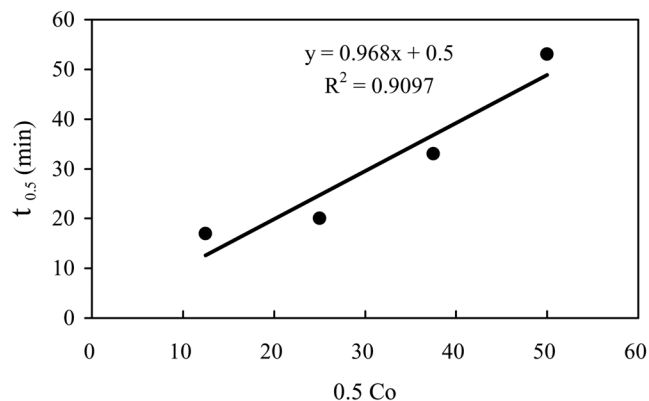


Fig. 3. A plot of  $t_{0.5}$  vs.  $0.5C_0$  values for different initial conditions.

To demonstrate the enhanced degradation rate on adding organics, an initial TNT concentration of 100 mg/L, which had the smallest value of  $k_a$ , was chosen for further experiments.

#### 3.2. Effects of Methanol Addition

In a photocatalytic process, TNT is transformed via both oxidation and reduction. In aerated systems, photo-excited electrons react primarily with adsorbed molecular oxygen. This scavenging of conduction band electrons during the photocatalytic degradation of TNT is crucial to prevent charge recombination and a loss of reaction efficiency.

Reductive transformation of TNT resulting in the production

Table 1. First-order rate constants and  $t_{0.5}$  values

| Conc. (mg/L) | $k_a$ ( $\text{min}^{-1}$ ) | Expt. <sup>a</sup> $t_{0.5}$ (min) | Cal <sup>b</sup> . $t_{0.5}$ (min) | Rate ( $\text{mg/L min}^{-1}$ ) |
|--------------|-----------------------------|------------------------------------|------------------------------------|---------------------------------|
| 25           | 0.0433                      | 10                                 | 16                                 | 1.003                           |
| 50           | 0.0369                      | 17                                 | 19                                 | 1.018                           |
| 75           | 0.0216                      | 26                                 | 32                                 | 1.023                           |
| 100          | 0.0142                      | 32                                 | 50                                 | 1.025                           |

<sup>a</sup> Experimental value determined from curves

<sup>b</sup> Value calculated using equation (1)

of ammonia has been proposed. According to Nahen *et al.*,<sup>5)</sup> reductive pathways are facilitated by the presence of methanol, which reacts with hydroxyl radicals, generated from electron holes, to produce  $\alpha$ -hydroxymethyl radicals that subsequently become involved in the photocatalytic degradation of organic compounds.

The effect of methanol on the photocatalysis of TNT in an aerated system was investigated by adding from 10 to 50% methanol by volume to the TNT-contaminated water. The initial TNT concentration was 100 mg/L and aeration was undertaken for 30 min.

The results of methanol addition on the degradation of TNT in the UV/TiO<sub>2</sub> process are presented in Fig. 4; they demonstrate that methanol addition significantly increased the amount of TNT removed. This suggests that the addition of the reductant supplants electron scavenging by oxygen. It concurs with the published results of Nahen *et al.*<sup>5)</sup> and points to a reductive degradation pathway as being the dominant process. A maximum degradation of 97.3% occurred within 120 min of irradiation in the presence of an optimum methanol content of 20%. Any further increase in methanol content (30% and 50%) inhibited the reaction rate, so a methanol content of 20% was used in further experiments.

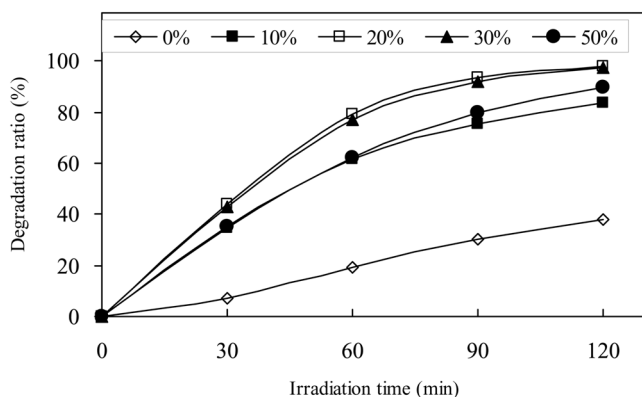


Fig. 4. The effects of methanol addition on the degradation of TNT. The initial TNT concentration was 100 mg/L.

### 3.3. Effects of EDTA Addition

Blake *et al.*<sup>1)</sup> showed that the addition of organic reductants, such as EDTA, citrate, formate, and sulfite, dramatically increases the rate of photocatalytic removal of TNT. These agents may facilitate the reduction of TNT by occupying holes and hence releasing electrons to react with TNT.

The effect of EDTA on TNT removal is shown in Fig. 5. EDTA was added to a 100 mg/L solution of TNT that had been primed with 20% methanol. The first-order reaction rate constants determined from Equation (1) increased with the amount of EDTA added, as shown in Table 2. Compared with the value of 0.0142 min<sup>-1</sup> in Table 1,  $k_a$  increased over two-fold (0.0327) when 1 g of EDTA was added to a solution containing 20% methanol. Over a range from 1 to 3 g of EDTA, however, the rate of TNT removal over a 2-hour reaction was nearly the same, at about 99%.

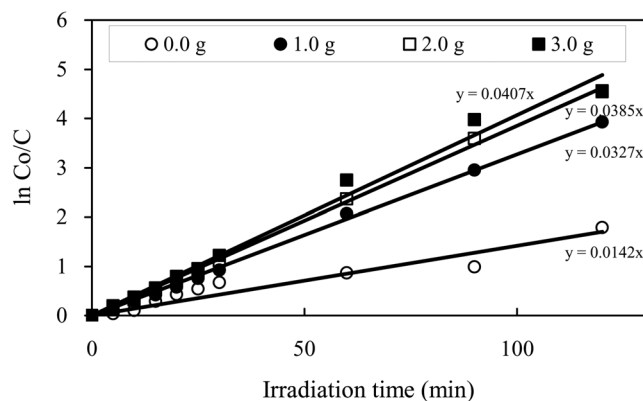


Fig. 5. The effect of EDTA addition on the removal of TNT in a solution primed with 20% methanol. The initial TNT concentration was 100 mg/L.

Table 2. Reaction rates ( $k_2$ ) and  $t_{0.5}$  values when EDTA was added to the solution of 100 mg/L TNT concentration

| EDTA added (g) | $k_a$ (min <sup>-1</sup> ) | Cal <sup>a</sup> . $t_{0.5}$ (min) | $k_2$ (mg/L min <sup>-1</sup> ) |
|----------------|----------------------------|------------------------------------|---------------------------------|
| 1              | 0.0327                     | 21                                 | 2.406                           |
| 2              | 0.0385                     | 18                                 | 2.806                           |
| 3              | 0.0407                     | 17                                 | 2.972                           |

<sup>a</sup> Value calculated using Equation (1)

In estimating the effect of EDTA on the degradation rate of TNT, it was assumed that  $k_1$  remained constant and was unaffected by the addition of EDTA. The  $k_1$  value of 1.342 mg/L<sup>-1</sup> obtained in the kinetic study was used to calculate the values of  $k_2$  shown in Table 2. These values increase with the amount of EDTA, and this was similar to the increase in  $k_a$ . Compared with the value of 1.033 mg/L min<sup>-1</sup> obtained in a reductant-free system, the addition of EDTA significantly increased the reaction rate,  $k_2$ .

## 4. Conclusions

The rate of photocatalytic degradation of TNT in aqueous solutions over a UV-illuminated TiO<sub>2</sub> thin film reactor approximated first-order kinetics. The reaction rate constant decreased as the TNT concentration increased from 25 to 100 mg/L, while the first-order kinetics could be modeled using a Langmuir adsorption isotherm. The addition of the organic reductants methanol and EDTA significantly enhanced the rate of TNT degradation. EDTA increased the rate of TNT removal by enhancing the role of the reductants.

## References

- Blake, D. M., Wolfrum, E., Boulter, J., Prairie, M., Showalter, S., Rodacy, P., Leslie, P., and Stange, B., "Photocatalytic oxidation and reduction chemistry and a new process for treatment of pink water and related contaminated water," NREL/TP-430-21580, National Renewable Energy Laboratory, Golden, CO (1996).
- Won, W. D., DiSalvo, L. H., and Ng, J., "Toxicity and mutagenicity of 2,4,6-trinitrotoluene and its microbial metabo-

- lites," *Appl. Environ. Microbiol.*, **31**, 576-580 (1976).
- Wujcik, W. J., Lowe, W. L., and Marks, P. J., "Granular activated carbon pilot treatment studies for explosives removal from contaminated groundwater," *Environ. Prog.*, **11**, 178-189 (1992).
  - Michels, J., and Gottschalk, G., "Inhibition of the lignin peroxidase of *Phanerochaete chrysosporium* by hydroxyl-amino-dinitrotoluene, an early intermediate in the oxidation of 2,4,6-trinitrotoluene," *Appl. Environ. Microbiol.*, **60**, 187-194 (1994).
  - Nahen, M., Bahnemann, D., Dillert, R., and Fels, G., "Photocatalytic degradation of trinitrotoluene: reductive and oxidative pathways," *J. Photochem. Photobiol. A: Chemistry*, **110**, 191-199 (1997).
  - Spiker, J. K., Crawford, D. L., and Crawford, R. L., "Influence of 2,4,6-trinitrotoluene(TNT) concentration on the degradation of TNT in explosive-contaminated soils by the white rot fungus *Phanerochaete chrysosporium*," *Appl. Environ. Microbiol.*, **58**, 3199-3202 (1992).
  - Carey, J. H., Lawrence, J., and Tosine, H. M., "Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions," *Bull. Environ. Contam. Toxicol.*, **16** (6), 697-701 (1976).
  - Prairie, M. R., Evans, L. R., Stange, B. M., and Martinez, S. L., "An investigation of TiO<sub>2</sub> photocatalysis for the treatment of water contaminated with metals and organic compounds," *Environ. Sci. Technol.*, **27**, 1776-1782 (1993).
  - Schmelling, D. C., and Gray, K. A., "Photocatalytic transformation and mineralization of 2,4,6-trinitrotoluene(TNT) in TiO<sub>2</sub> slurries," *Wat. Res.*, **29**(12), 2651-2662 (1995).
  - Wang, Z., and Kutal, C., "Photocatalytic mineralization of 2,4,6-trinitrotoluene in aqueous suspensions of titanium dioxide," *Chemosphere*, **30**, 1125-1136 (1995).
  - Hess, T. F., Lewis, T. A., Crawford, R. L., Katamneni, S., Wells, J. H., and Watts, R. J., "Combined photocatalytic and fungal treatment for the destruction of 2,4,6-trinitrotoluene (TNT)," *Wat. Res.*, **32**(5), 1481-1491 (1998).
  - Matthews, R. W., "Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide," *J. Catalyst*, **111**, 264-272 (1988).
  - Turchi, C. S., and Ollis, D. F., "Photochemical degradation of organic water contaminants: mechanisms involving hydroxyl radical attack," *J. Catalyst*, **12**, 178-192 (1990).
  - Low, G. K. C., McEvoy, S. R., and Matthews, R. W., "Formation of nitrate and ammonium ions in titanium dioxide mediated photocatalytic degradation of organic compounds containing nitrogen atoms," *Environ. Sci. Technol.*, **25**(3), 460-467 (1991).
  - Matthews, R. W., "Photooxidation of organic impurities in water using thin films of titanium dioxide," *J. Phys. Chem.*, **91**, 3328-3333 (1987).
  - Matthews, R. W., and McEvoy, S. R., "Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide," *J. Photochem. Photobiol. A: Chemistry*, **64**(2), 231-246 (1992).
  - Kim, D. H., Anderson, M. A., and Zeltner, W. A., "Effects of firing temperature on photocatalytic and photoelectrocatalytic properties of TiO<sub>2</sub>," *J. Environ. Eng.*, **121**(8), 590-594 (1995).
  - Ha, H. Y., and Anderson, M. A., "Photocatalytic degradation of formic acid via metal-supported titania," *J. Environ. Eng.*, **122**(3), 217-221 (1996).
  - Kim, D. H., and Anderson, M. A., "Photoelectrocatalytic degradation of formic acid using a porous TiO<sub>2</sub> thin-film electrode," *Environ. Sci. Technol.*, **28**, 479-483 (1994).
  - Shin, G., and Kim, Y., "Photocatalytic degradation of 2,4,6-trinitrotoluene(TNT) in a TiO<sub>2</sub> thin film reactor," *J. Kor. Soc. Water and Wastewater*, **16**(2), 145-152(2002).