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Effects of additives on 2,4,6-trinitrotoluene (TNT) removal and its mineralization in aqueous solution by gamma irradiation

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ABSTRACT

The effects of additives (i.e., methanol, EDTA, mannitol, thiourea, nitrous oxide, oxygen and ozone) on gamma irradiation of 2,4,6-trinitrotoluene (TNT) were investigated to elucidate the initial reaction mechanism of TNT degradation and suggest an practical method for complete by-product removal. All additives, except thiourea, significantly increased the TNT removal efficiency by gamma irradiation. The overall results of the additive experiments implied that the TNT decomposition would be initiated by •OH, e_{aq}^{-} , and HO₂•/O₂•⁻, and also implied that •H did not have any direct effect on the TNT decomposition. Additions of methanol and nitrous oxide were more effective in TNT removal than the other additives, achieving complete removal of TNT at doses below 20 kGy. Total organic carbon (TOC) of the irradiated solution was analyzed to evaluate the degree of TNT mineralization under the additive conditions. TOC under the nitrous oxide addition was very effective in the TNT removal, but it was not effective in reduction in TOC. Trinitrobenzene (TNB), oxalic acid and glyoxalic acid were detected as radiolytic organic by-products, while ammonia and nitrate were detected as radiolytic inorganic by-products. The most efficient TNT removal and its mineralization by gamma irradiation would be achieved by supersaturating the solution with nitrous oxide before irradiation.

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1. Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most stable and recalcitrant of high explosives and does not occur naturally in the environment. TNT has contaminated groundwater and soil at numerous sites which are located in explosive manufacturing plants, packing, storage and military-related facilities [1,2]. TNT is toxic, mutagenic and a suspected carcinogen, with an EPA lifetime health advisory of 2 μ g/L [3–6]. In addition to the toxicity of TNT, it has been known that metabolites are equally or more toxic than the parent compound [7]. Therefore, TNT degradation has attracted the attention of many scientists in the last decade.

Commonly used methods for treating soil and water contaminated by TNT are incineration, biological treatment and granular activated carbon (GAC) adsorption [8–11]. Although incineration of TNT is widely used, this is typically known as the most expensive way to degrade TNT in various media. Recently, advanced oxidation processes (AOP) using Fenton, $UV-H_2O_2$, $O_3-H_2O_2$, TiO₂-photocatalysis and gamma irradiation have been proposed for the decomposition of explosives [12–17]. These processes utilize hydroxyl radical that has a redox potential of 2.8 V. Hydroxyl radical is an extremely strong oxidant capable of oxidizing any molecule it encounter, representing high reaction rate constants for organic compounds, 10^8 to 10^{10} M⁻¹ s⁻¹ [18]. Among the AOP, gamma irradiation utilizes hydrogen atom and hydrated electrons as well as hydroxyl radicals for decomposition of target compound either directly or indirectly [19].

Gamma irradiation improves decomposition of target organic compounds by adding additives to the aqueous phase. The addition may induce either oxidative or reductive reaction conditions for improved decomposition of organic compounds. Gamma irradiation to water generates primary species (e_{aq}^{-} , •OH, and •H) and molecular products (H_2 , H_2O_2). Although the primary species produced from the water radiolysis initiate the decomposition of contaminants in solution, most of the species are quickly depleted by radical-radical reactions. The decomposition of contaminant present in water can be improved if scavengers of radical-radical reactions (i.e., gas and liquid additives) prohibit a series of reactions depleting the primary species.

The first gamma irradiation study for TNT degradation was recently conducted in the liquid phase under specific conditions [15]. The focus of the study was to evaluate the feasibility of oxidizing TNT by gamma irradiation. The most effective pH for TNT removal was 2 and the degradation reaction followed pseudo-first-

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Table 1
Reaction rate constants for primary species and various additives in aqueous solution.

Ion species	Rate constants (Lmol ⁻¹ s ⁻¹)							
	Thiourea	D-Mannitol	Methanol	EDTA	Nitrous oxide	Oxygen		
•H	$0.01{-}6.0\times10^{9a}$	-	$2.43.0\times10^6$	$6 imes 10^7$	$2.1 imes 10^6$	2.1×10^{10}		
•OH	$3.9-5.3 \times 10^{9}$	$1.5-2.1 \times 10^{9}$	$0.8 - 1.0 imes 10^9$	$0.25 - 2.0 \times 10^9$	-	-		
e _{aq} -	$2.94.3\times10^9$	$7 imes 10^6$	$< 1 \times 10^4$	$< 3 \times 10^{5}$	$8.09.1\times10^9$	$1.82.2\times10^{10}$		

^a pH 1–4.7.

order kinetics. However, the complete decomposition of TNT and its radiolytic by-products would be obtained at an acidic condition and under higher gamma irradiation doses. A gamma irradiation dose of 200 kGy would be required for 90% removal of the initial TOC present in the TNT solution. Providing the high gamma irradiation dose and low pH conditions may not be practical in an actual treatment system of wastewater and groundwater contaminated with TNT. Further studies are warranted to develop more practical gamma irradiation methods to degrade TNT and its radiolytic by-products.

The primary goal of the study was to investigate the effects of various liquid and gas additives on gamma irradiation of TNT. This study evaluated various additives such as methanol, EDTA, mannitol, thiourea, nitrous oxide, oxygen, and ozone. The secondary goal of the study was to elucidate the initial reaction mechanism of TNT degradation by evaluating the additives results. The final goal of the study was to suggest a practical gamma irradiation method for TNT removal and its mineralization.

2. Background

The additives used in the TNT solution as scavenger were thiourea, D-mannitol, methanol, EDTA (sodium salt), nitrous oxide and oxygen. The reaction rate constants between the primary species (*OH, $e_{aq}{}^-\!\!,$ and *H) and the additives are summarized in Table 1 [20,21]; the reaction rate constant between thiourea and •H was the largest, 6.0×10^9 at pH 1, and it was decreased as pH increase. It is expected that the reaction rate constant between thiourea and •H at around pH 7 which applied in this study would be smaller than that mentioned in Table 1, and thiourea scavenges mainly •OH and e_{aq}⁻ among primary species. Additives such as mannitol, methanol, and EDTA normally scavenge •OH from the primary species. Decomposition of contaminant can be initiated by \cdot H and e_{ag} if \cdot OH is scavenged by the additives described. In the case of nitrous oxide addition, e_{aq}^{-} is scavenged by nitrous oxide and thus generating •OH (reaction (1)); hence, much more OH radicals may be available for pollutant removal. For oxygen present in water, it converts \cdot H and e_{aq}^{-} to oxidizing species such as perhydroxyl radicals (HO $_2^{\bullet}$) and superoxide radical anions $(O_2^{\bullet-})$ (reactions (2)–(4)) [22]. The oxidizing species formed are also able to initiate the degradation of pollutants in water. However, •OH becomes the major oxidizing transient if the oxidizing species formed would have low reactivity with pollutants (reactions (5)–(7)) [20,23]. Therefore, we would elucidate the initial reaction mechanism of TNT removal by gamma irradiation if the results of each different additive experiment were available:

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow N_2 + OH^{-} + OH, \quad k = 9.1 \times 10^9 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$$
(1)

•H + O₂
$$\rightarrow$$
 HO₂•, $k = 2.1 \times 10^{10} \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ (2)

 $e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet -}, \quad k = 2.0 \times 10^{10} \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1}$ (3)

$$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet-}, \quad pK = 4.8$$
 (4)

 $\text{HO}_2^{\bullet} + \text{O}_2^{\bullet-} \rightarrow \text{HO}_2^- + \text{O}_2, \quad k = 1.02 \times 10^8 \,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$ (5)

 $O_2^{\bullet-} + {}^{\bullet}OH \rightarrow OH^- + O_2, \quad k = 7 \times 10^9 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ (6)

$$\text{HO}_2^{\bullet} + {}^{\bullet}\text{OH} \to \text{H}_2\text{O} + \text{O}_2, \quad k = 7 \times 10^9 \,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$$
 (7)

Reactive species of OH radicals as well as the other radical forms (e.g. peroxyl transients, $HO_2^{\bullet}/O_2^{\bullet-}$, ROO^{\bullet} , etc.) attack double bonds of aromatic target compounds. The OH radicals attack can occur on o-, m-, p- and ipso-positions, thus forming adducts (hydroxycyclohexadienyl radicals) that scavenge oxygen. The formed peroxyl transients are rather unstable and can undergo hydrolysis forming various final products [24–27].

3. Materials and method

3.1. Preparation of samples and gamma irradiation

Technical grade TNT was obtained from the Defense Development Agency, Daeion, Korea, TNT solutions of 100 mg/L were prepared with distilled and de-ionized water. For gas additives, the TNT solutions were purged with pure oxygen or medical grade nitrous oxide gas for 15 min. Liquid additives thiourea, methanol, D-mannitol, EDTA (Na-salts) were added into the TNT solutions. For ozone additive experiment, highly concentrated ozone water was used because the direct purging TNT solution with ozone gas could degrade TNT before gamma irradiation. The ozone water was prepared by using gas washing bottle and ozone generator (Ozonia, OZAT[®] CFS-3). The TNT solutions containing gas or chemical were prepared in 125-mL glass bottles without headspace. Gamma irradiations were performed using a high-level ⁶⁰Co source (AECL IR-79, Canada) at room temperature (around 20 °C). The radioactivity of the source was around 7.4×10^{15} Bq. The irradiation time was fixed to 16 h.

3.2. Analysis

Aqueous phase irradiated samples were mixed with acetonitrile (1:1), filtered through sterile Acrodisk-13 0.2-µm syringe microfilters (Gelman Sciences, Ann Arbor, MI), and then analyzed by high pressure liquid chromatography (HPLC) with a variable wavelength UV-detector (Hewlett Packard 1050 Series) set to 254 nm. The mobile phase was 50% methanol at a flow-rate of 0.3 mL/min. The injection volume was set to 20 µL using an autosampler and a C18, 5-µm reversed-phase column (ZORBAX SB-C18, Agilent, Santa Clarita, CA) was used. The TNT peak appeared at a retention time of 17.4-17.8 min under analytical method conditions. The radiolytic by-products such as trinitrobenzene (TNB) and low molecular weight organic acids were also analyzed using HPLC. Analysis conditions for TNB were same to the TNT analysis. The TNB peak was detected at a retention time of 10.5-10.9 min. Organic acids were measured using HPLC that UV wavelengths were set to 205, 210 and 214 nm. Here, the mobile phase was 0.1% phosphoric acid at a flow-rate of 0.5 mL/min. For measurement of organic acids, a carbohydrate column (C-610H, Supelcogel, Bellefonte, PA) was used and the injection volume was set to 20 µL using an autosampler.

Total organic carbon (TOC) was measured using a Shimadzu model TOC-VSCN analyzer. Chemical oxygen demand (COD), ammonia (NH_4^+ -N) and nitrate (NO_3^- -N) in the samples were measured by a closed reflux spectrophotometric method, a phenate method and a cadmium reduction method, respectively, according to Standard Methods [28].

4. Results and discussion

4.1. Effects of additives on TNT removal

A series of batch experiments were conducted to find the ion species which initiated the decomposition of TNT by gamma irradiation, and the additives which improved efficiency of TNT removal. The additives such as thiourea, methanol, EDTA and mannitol, were present in the TNT solution for the concentration range of 100–2000 mg/L. The gas additives, oxygen and nitrous oxide were supersaturated in the TNT solution by purging with oxygen and nitrous oxide gases. Then all samples were irradiated at 10 kGy (one gray is equal to an energy absorption of one joule per kilogram, 1 Gy = 1 J/kg = 100 rad).

Fig. 1 shows the TNT removal by gamma irradiation with increasing dosage of thiourea, methanol, EDTA, mannitol. Fig. 2 shows the TNT removal by gamma irradiation under supersaturated with oxygen and nitrous oxide. The additives significantly increased the TNT removal efficiency by gamma irradiation, except in the



Fig. 1. TNT removal by increasing of additives dosage at 10 kGy (initial condition: TNT = 100 mg/L, neutral pH).



Fig. 2. TNT removal by purging of O_2 or N_2O gas at 10 kGy (initial condition: TNT = 100 mg/L, neutral pH).

case of thiourea. The gamma irradiation only was more efficient in TNT removal than the thiourea addition. The thiourea addition run removed only 10% of the initial TNT due to its scavenging the primary species such as \cdot OH and e_{aq}^{-} ; it seems that an addition of 100 mg/L thiourea was sufficient to scavenge \cdot OH and e_{aq} . The results indicated that the decomposition of TNT would be initiated by •OH or e_{aq}^{-} , and •H remained by the scavenging of thiourea would not give effective TNT removal. In the additions of methanol, EDTA, and mannitol, enhanced removal efficiencies were found when comparing with the control (no addition). The methanol addition was most effective in enhancing TNT removal. As shown in the gas additives of Fig. 2, the nitrous oxide addition was more effective in TNT removal than the oxygen addition. Nitrous oxide would convert produced e_{aq}^{-} to OH radicals which are strong oxidative to target compounds. The oxygen addition also showed more efficient TNT removal when comparing to the control. This implied that oxidizing species such as perhydroxyl radicals (HO_2^{\bullet}) and superoxide radical anions $(O_2^{\bullet-})$ would also initiate the TNT decomposition. Therefore, the overall results of Figs. 1 and 2 implied that the TNT decomposition would be initiated by $\bullet OH$, e_{aq}^{-} , and $HO_2^{\bullet}/O_2^{\bullet-}$ which was produced under the oxygen existing condition, and also implied that •H did not give any direct effect on the TNT decomposition.

The combined effects of gamma ray and additive on TNT removal were evaluated as shown in Fig. 3. Seven different combination conditions were evaluated by changing irradiation dose: (1) no addition (NA); (2) oxygen saturation at neutral pH (OX); (3) nitrous oxide saturation (NO); (4) methanol (ME, 200 mg/L); (5) acidic condition (AC, pH 2); (6) oxygen saturation at pH 2 (OA); (7) ozone addition (OZ, 5.42 mg/L). The results show that the TNT removal ratio increases as the irradiation dose increases under all additive conditions. Additions of methanol and nitrous oxide were more effective in TNT removal than the other additions. In these conditions, the complete removal of TNT was achieved at doses less than 20 kGy. The ozone addition was also effective in removing TNT compared to the no addition case. The effectiveness of the ozone addition was attributed to the synergistic effect caused from ozone decomposition by gamma irradiation [29–31]. However, the enhanced TNT removal by ozone addition was minor compared to those by other addition.

The dose constants were calculated using the data of Fig. 3 and then shown in Table 2. All TNT removal reactions by gamma irradiation were found to follow pseudo-first-order kinetics. The methanol addition had the largest dose constant, 0.4074 kGy⁻¹.



Fig. 3. TNT removal by increasing irradiation dose under additive conditions: (\blacklozenge) NA (no addition), (\blacksquare) NO (supersaturation of nitrous oxide), (\blacktriangle) ME (methanol addition, 200 mg/L), (\blacklozenge) AC (pH 2), (\lor) OX (supersaturation of oxygen), (\diamondsuit) OA (supersaturation of oxygen at pH 2) and (\Box) OZ (ozone addition).

4	з	8

Table 2	
Change in dose constant under additive conditions.	

Conditions	Dose constant, d (kGy ⁻¹)	<i>R</i> ²	Remarks
Without additive	0.0580	0.9976	Without additive
N ₂ O	0.2941	0.9731	Supersaturation
CH₃OH	0.4074	0.9035	200 mg CH₃OH/L
pH 2	0.0939	1.0000	H ₂ SO ₄ used
O ₂	0.1086	0.9996	37.9 mg O ₂ /L
pH 2 + O ₂	0.1225	0.9984	37.9 mg O ₂ /L, H ₂ SO ₄ used
O ₃	0.0650	0.9980	$5.42 \text{ mg O}_3/L$

4.2. TNT mineralization and change of oxidation state

TOC of irradiated solution was analyzed to evaluate the degree of TNT mineralization under various additive conditions (Fig. 4). The initial TOC of the TNT solution was 38.8 mg/L, and the TOC decreased as irradiation dose increased. The TOC under the nitrous oxide addition was removed rapidly, and complete TNT mineralization was thus achieved at 50 kGy. As described earlier, nitrous oxide scavenges e_{aq}^{-} , leading the overall reaction to •OH formation (reaction (1)). Thus, nitrous oxide in the solution would act to increase the overall yield of •OH, which was very effective in TNT mineralization.

Effectiveness of TOC reduction under the additive conditions of oxygen can be explained as follows: (1) oxygen in the solution converted $^{\text{H}}$ and e_{aq}^{-} into the oxidizing species such as HO₂ and O₂⁻, leading to strong oxidative conditions [22]; (2) $^{\circ}$ OH adducts, which are produced by the reaction between $^{\circ}$ OH and TNT, adsorbed oxygen and then formed peroxyl transients which were rather unstable and could readily undergo hydrolysis [24–27].

There was no significant difference in TOC reduction between two oxygen addition results (OX and OA). In the methanol addition, the initial TOC became 115.7 mg/L because methanol addition contributed the TOC increase. TOC reduction in the methanol addition occurred only 28% of the initial TOC even at 200 kGy (data not shown).

The oxidation extent of TNT with irradiation dose increase was represented by the oxidation state. Stumm [32] suggested an oxidation state equation (Eq. (a)), which could represent an oxidation extent of the sample indirectly:





Fig. 4. TOC removal by increasing irradiation dose under additive conditions: (\blacklozenge) NA (no addition), (\blacksquare) NO (supersaturation of nitrous oxide), (\blacktriangle) AC (pH 2), (\blacklozenge) OX (supersaturation of oxygen), (\blacktriangledown) OA (supersaturation of oxygen at pH 2) and (\diamondsuit) OZ (ozone addition).



Fig. 5. Change in oxidation state by increasing irradiation dose under additive conditions: (\blacklozenge) NA (no addition), (\blacksquare) NO (supersaturation of nitrous oxide), (\blacktriangle) AC (pH 2), (\blacklozenge) OX (supersaturation of oxygen), (\blacktriangledown) OA (supersaturation of oxygen at pH 2) and (\diamond) OZ (ozone addition).

Fig. 5 shows changes in oxidation state under various additive conditions. The initial oxidation state of TNT solution was 1.47. The oxidation state was decreased and then gradually increased in the irradiation dose range of 0-40 kGy, and it was increased beyond this range. The highest oxidation state was 3.52 at 40 kGy under the nitrous oxide addition. The values of the oxidation state at 200 kGy were in the order from high to low; saturation of oxygen at pH 2 (OA)(3.34), pH 2 (AC)(3.31), saturation of oxygen (OX)(3.28), ozone (OZ) (2.77), and no addition (NA) (2.53).

4.3. Changes in organic by-products

Radiolytic organic by-products were analyzed for TNB, oxalic acid and glyoxalic acid. Fig. 6 shows changes in TNB concentration in the gamma irradiated solutions. Formation and removal of TNB were rapidly progressed under the condition of nitrous oxide addition. The TNB became sharply increased in the dose range of 10–20 kGy under conditions of OX and OA, and completely removed in the 60–80 kGy dose.

Figs. 7 and 8 show changes in oxalic acid and glyoxalic acid, respectively. The formation and removal of two by-products were progressed most rapidly under the condition of NO and oxalic acid



Fig. 6. Change in trinitrobenzene concentration by increasing irradiation dose under additive conditions: (♦) NO (supersaturation of nitrous oxide), (▲) OX (supersaturation of oxygen) and (●) OA (supersaturation of oxygen at pH 2).



Fig. 7. Change in oxalic acid concentration by increasing irradiation dose under additive conditions: (\blacklozenge) NO (supersaturation of nitrous oxide), (\blacktriangle) OX (supersaturation of oxygen) and (\bullet) OA (supersaturation of oxygen at pH 2).



Fig. 8. Change in glyoxalic acid concentration by increasing irradiation dose under additive: (\blacklozenge) NO (supersaturation of nitrous oxide), (\blacktriangle) OX (supersaturation of oxygen) and (\blacklozenge) OA (supersaturation of oxygen at pH 2).

and glyoxalic acid were then completely removed at 30 and 40 kGy, respectively.

Under conditions of OX and OA, concentrations of oxalic acid were sharply increased in the dose range of 0-40 kGy and then decreased beyond the range. Complete removal of oxalic acid occurred at 150 kGy. The concentration of glyoxalic acid increased in the dose range of 0-80 kGy and then decreased beyond the range. Glyoxalic acid was removed completely at 200 kGy under OA condition, but remained 4.2 mg/L even at 200 kGy under the condition OX. TNB was formed by the decarboxylation of -COOH group of trinitrobenzoic acid after the conversion (this conversion is due to electron-releasing abilities of -CH₃ group, leading to an increase in TNT reactivity) of TNT into trinitrobenzoic acid by oxidation of -CH₃ group of TNT by •OH or $HO_2 • / O_2 • -$. Consequently, complex intermediates would be produced by subsequent release of -NO2 groups from TNB and ring breakage of TNB. The organic compounds among complex intermediates were converted into low molecular organic acids such as glyoxalic acid and oxalic acid, and then converted to CO_2 .

4.4. Formation of inorganic by-products

The radiolytic inorganic by-products of TNT under conditions of NO, OX and OA were analyzed for ammonia, nitrite and nitrate (Fig. 9). Nitrate concentrations were sharply increased in the dose



Fig. 9. Change in ammonia and nitrate concentration by increasing irradiation dose under additive conditions: (\blacklozenge) NO (supersaturation of nitrous oxide), (\blacktriangle) OX (supersaturation of oxygen) and (\blacklozenge) OA (supersaturation of oxygen at pH 2).

range of 0–40 kGy, and then decreased beyond the range for conditions OX and OA. Complete removal of nitrate occurred at 100 kGy. Ammonia concentrations were gradually increased as irradiation dose was increased, and they were in the range of 11.0–14.8 mg/L at 200 kGy dose. Nitrate formation was due to the oxidation of nitrite, which was formed by release of $-NO_2$ group from TNT or TNB, by •OH. The rapid removal of nitrate was due to the conversion of nitrate into organic nitrogen through the polymerization with low molecular organic compounds formed in the TNT decomposition reaction [15,33]. Organic nitrogen would be converted into NH₄⁺. Under NO condition, nitrate did not undergo polymerization reaction and thus remained in the solution. Therefore, nitrate concentration was increased up to 16 mg/L.

5. Conclusions

This study used gamma irradiation for the treatment of TNT in aqueous solution. The effects of various additives on TNT removal and mineralization were investigated to discern the primary species initiating TNT destruction, and suggest a practical TNT removal condition in gamma irradiation. The study showed that TNT decomposition was initiated by •OH, e_{aq}^- , or HO₂•/O₂•⁻, and it was maximized by addition of nitrous oxide. Although methanol addition was very effective in the TNT removal, it was not effective in mineralization of TNT. TOC of irradiated solution was analyzed to evaluate the degree of TNT mineralization under various additive conditions. The TOC under the nitrous oxide addition was removed rapidly, and complete TNT mineralization was thus achieved at 50 kGy, implying that nitrous oxide scavenged e_{aq}^- , leading the overall reaction to •OH formation.

Trinitrobenzene, oxalic acid and glyoxalic acid were detected as radiolytic organic by-products, while ammonia and nitrate were detected as radiolytic inorganic by-products. Formation and removal of organic by-products were rapidly progressed under the condition of nitrous oxide addition, showing completely removal at a dose of 40 kGy. The most efficient TNT removal and its mineralization by gamma irradiation would be providing the TNT solution supersaturated with nitrous oxide before irradiation.

References

- J.D. Rodgers, N.J. Bunce, Treatment methods for the remediation of nitroaromatic explosives, Water Res. 35 (2001) 2101–2111.
- [2] S.Y. Oh, P.C. Chiu, B.J. Kim, D.K. Cha, Enhancing Fenton oxidation of TNT and RDX through pretreatment with zero-valent iron, Water Res. 37 (2003) 4275–4283.

- [3] W.D. Won, L.H. DiSalvo, J. Ng, Toxicity and mutagenecity of TNT and its microbial metabolites, Appl. Environ. Microbiol. 31 (1976) 576–580.
- [4] D.L. Kaplan, A.M. Kaplan, 2,4,6-Trinitrotoluene surfactant complexes: decomposition, mutagenicity, and soil leaching studies, Environ. Sci. Technol. 16 (1982) 566–571.
- [5] D.R. Wellington, N.R. Mitchell, In-vitro cytotoxicity of certain munitions nitroaromatic compounds, Chemosphere 23 (1991) 363–373.
- [6] US E.P.A., 2006 Edition of the Drinking Water Standards and Health Advisories, Washington, DC, 2006.
- [7] P.G. Rieger, H.J. Knackmuss, Basic knowledge and perspectives on biodegradation of 2,4,6-trinitrotoluene and related compounds in contaminated soil, in: J.C. Spain (Ed.), Biodegradation of Nitroaromatic Compounds, Plenum Press, New York, 1995, pp. 1–18.
- [8] R. Boopathy, C.F. Kulpa, TNT as a sole nitrogen source for a sulfate reducing bacterium *Desulfovibrio* sp. (B strain) isolated from an anaerobic digester, Curr. Microbiol. 25 (1992) 235–241.
- [9] R. Boopathy, J.F. Manning, C. Montemagno, C.F. Kulpa, Metabolism of 2,4,6trinitrotoluene by a *Pseudomonas consortium* under aerobic conditions, Curr. Microbiol. 28 (1994) 131–137.
- [10] L.S. Hundal, J. Singh, E.L. Bier, P.J. Shea, S.D. Comfort, W.L. Power, Removal of TNT and RDX from water and soil using iron metal, Environ. Pollut. 97 (1997) 55–64.
- [11] S. Hwang, T.J. Ruff, E.J. Bouwer, S.L. Larson, J.L. Davis, Applicability of a alkaline hydrolysis for remediation of TNT-contaminated water, Water Res. 39 (2005) 4503–4511.
- [12] M.J. Liou, M.C. Lu, J.N. Chen, Oxidation of explosives by Fenton and photo-Fenton processes, Water Res. 37 (2003) 3172–3179.
- [13] H.S. Son, S.J. Lee, I.H. Cho, K.D. Zoh, Kinetics and mechanism of TNT degradation in TiO₂ photocatalysis, Chemosphere 57 (2004) 309–317.
- [14] S. Hwang, E.J. Bouwer, S.L. Larson, J.L. Davis, Decolorization of alkaline TNT hydrolysis effluents using UV/H₂O₂, J. Hazard. Mater. 108 (2004) 61–67.
- [15] B. Lee, M. Lee, Decomposition of 2,4,6-trinitrotoluene (TNT) by gamma irradiation. Environ. Sci. Technol. 39 (2005) 9278–9285.
- [16] G. Yardin, S. Chiron, Photo-Fenton treatment of TNT contaminated soil extract solutions obtained by soil flushing with cyclodextrin, Chemosphere 62 (2006) 1395–1402.
- [17] Y. Wu, C. Zhao, Q. Wang, K. Ding, Integrated effects of selected ions on 2,4,6trinitrotoluene-removal by O₃/H₂O₂, J. Hazard. Mater. 132 (2006) 232–236.

- [18] P. Kakarla, R.J. Watts, Depth of Fenton-like oxidation in remediation of surface soil, J. Environ. Eng. 23 (1997) 11–17.
- [19] J.W. Spinks, J.R. Wood, An Introduction to Radiation Chemistry, Willey-Interscience, New York, 1990.
- [20] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (*OH/*O⁻) in aqueous solution, J. Phys. Chem. Ref. Data 17 (1983) 533–886.
- [21] S.P. Ramnani, S. Dhanya, P.K. Bhattacharyya, Pulse radiolysis of thiourea in aqueous solution, in: Proceedings of the International Symposium on Radiochemistry and Radiationchemistry, Department of Atomic Energy, Bombay, India, 1991, pp. 685–686.
- [22] N. Getoff, Radiation-induced degradation of water pollutants-state of the art, Radiat. Phys. Chem. 47 (1996) 581–593.
- [23] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, Reactivity of HO₂•/O₂•- radicals in aqueous solution, J. Phys. Chem. Ref. Data 14 (1985) 1041–1100.
- [24] N. Getoff, Peroxyl radicals in the treatment of waste solutions, in: Z.B. Alfassi (Ed.), Peroxyl Radicals, Wiley, Chichester, UK, 1997, pp. 483–506.
- [25] H.P. Schuchmann, C. von Sonntag, Heteroatom peroxyl radicals, in: Z.B. Alfassi (Ed.), Peroxyl Radicals, Wiley, Chichester, UK, 1997, pp. 439–456.
- [26] C. von Sonntag, H.P. Schuchmann, Peroxyl radicals in aqueous solution, in: Z.B. Alfassi (Ed.), Peroxyl Radicals, Wiley, Chichester, UK, 1997, pp. 173–234.
- [27] M. Sánchez, H. Wolfger, N. Getoff, Radiation-induced degradation of 4chloroaniline in aqueous solution, Radiat. Phys. Chem. 65 (2002) 611–620.
- [28] American Public Health Association, American Water Works Association, Water Environmental Federation, Standard Methods for the Examination of Water and Wastewater, 20th ed. Washington, DC, 1998.
- [29] E.K. Winarno, N. Getoff, Comparative studies on the degradation of aqueous 2chloroaniline by O_3 as well as by UV-light and γ -rays in the presence of ozone, Radiat. Phys. Chem. 65 (2002) 387–395.
- [30] J. Jung, J.H. Yoon, H.H. Chung, M.J. Lee, Comparative study of H₂O₂ and O₃ effects on radiation treatment of TCE and PCE, Chemosphere 51 (2003) 881–885.
- [31] P. Popov, N. Getoff, Ozonolysis and combination of ozonolysis and radiolysis of aqueous fluorene, Radiat. Phys. Chem. 69 (2004) 311–315.
- [32] W. Stumm, J.J. Morgan, Aquatic Chemistry, 2nd ed., Wiley-Interscience, New York, 1981.
- [33] R.J. Woods, A.K. Pikaev, Applied Radiation Chemistry: Radiation Processing, Wiley-Interscience, New York, 1944.