Comparison of simple ozonation and direct hydrogen peroxide processes in TNT removal from aqueous solution

Mohammad Mehdi Amin and Fahimeh Teimouri

ABSTRACT

Oxidation of 2,4,6-trinitrotoluene (TNT) using simple ozonation and direct hydrogen peroxide was studied. An analytical method based on the HPLC (high performance liquid chromatography) system was used for TNT detection. The influence of parameters such as pH of the solution (3–10), initial TNT concentration (10–100 mg/L), dosage of ozone (0.2–1 g/hr), H_2O_2/TNT molar ratio (250–1,000), and reaction time (15–60 min) on TNT degradation ratio were investigated. Maximum TNT degradation efficiency occurred at pH = 10, initial TNT concentration = 20 mg/L, dosage of ozone = 1 g/hr in simple ozonation (90%), while this amount was obtained in H_2O_2 oxidation process with pH = 3, initial TNT concentration of 10 mg/L and H_2O_2/TNT molar ratio = 1,000/L. The results of kinetic experiments were shown to follow pseudo-second reaction. It can be recommended that simple ozonation seems to be the best at TNT degradation from aqueous solution. However, low TNT concentration could be reduced by performance of the hydrogen peroxide process, in which case, a longer reaction time is also required.

Key words | 2,4,6-trinitrotoluene, advanced oxidation process, H_2O_2 oxidation, simple ozonation

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INTRODUCTION

The most widely used explosive is 2,4,6-trinitrotoluene (TNT), also known as trinitrotoluol, trotyl, and tilite (Čėnas *et al.* 2001; Ayoub *et al.* 2010; Singh 2013). Several methods are available for TNT production. The most frequently used method for TNT production is nitration of toluene that leads to the production of a benzene ring with nitro groups on positions 2,4,6 and a methyl group. It has been estimated that during the First World War, the Germans produced 2,500 tons of TNT a week. TNT enters the environment through wastewater and solid waste from manufacture of the processing of compounds and destruction of bombs (King 2012). Inhalation of TNT in micro-levels can cause liver disease, anemia, and cataracts. TNT has potential impacts on the environment because of the adsorption to soil (Liu *et al.* 2008).

TNT moves from surface water and soil to groundwater. When TNT enters the human body, it spreads to the liver, breaks down and changes to several substances. Exposure to TNT in high concentrations has many effects, including such blood disorders as anemia and abnormal liver function. The United States Environmental Protection Agency (US EPA) has classified TNT under group C, a possible human carcinogen (Richter-Torres *et al.* 1995). TNT is a known mutagen and can cause pancytopenia as a result of bone marrow failure. Oral LD_{50} in rats is near 1 g/kg.day. The US EPA has regulated TNT contamination in soil to 17.2 ppm and in water to 2 ppb (King 2012). TNT has been discharged into the aqueous effluents of explosive manufacturing facilities assembling, packing, etc. Studies have reported TNT concentrations between 20 and 120 mg/L in manufacturing plant effluents (Richter-Torres *et al.* 1995). The Department of Defense (DoD) and Department

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of Energy (DoE) have many sites where the groundwater is contaminated with explosive compounds.

In the past, granular activated carbon (GAC) adsorption and incineration processes were used for the treatment of high explosives in water and soil, respectively (Alnaizy & Akgerman 1999). Recently, studies have shown that natural organic substances act as an absorbent for TNT degradation (Zhang *et al.* 2012). Also, some studies have reported the degradation of nitroaromatics using nanoparticles such as nZVI (Fu *et al.* 2014). However, advanced oxidation process is a new method employing reactive oxidizing agents such as hydrogen peroxide or ozone which generate highly reactive free radicals (Mokrini *et al.* 1997; Quiroz *et al.* 2011). This method has gained interest in the treatment of contaminated water to remove organic and inorganic contaminants, with or without the addition of catalysts or photolysis (Mokrini *et al.* 1997). Studies have shown that photo-Fenton process is a useful method for treatment of explosives and explosive removal efficiencies increase with an increase in Fe(II) and UV light (Liou *et al.* 2003). Son *et al.* (2004) reported that in the presence of a photocatalyst process TNT was more effectively degraded than with either UV or catalyst (TiO_2) alone. Depending on the treatment method, different pathways are available for nitroaromatic degradation. For example, Sviatenko *et al.* (2014) reported that in alkaline hydrolysis, direct substitution of a nitro group by a hydroxide may be the most favorable pathway for all mentioned compounds (Sviatenko *et al.* 2014).

Nowadays, ozonation is considered as a process for oxidation of all organic contaminants in water (Hoigne & Bader 1976).

The main objective of this study was the investigation and comparison of TNT reduction by simple ozonation and direct H_2O_2 oxidation in different experimental conditions such as pH, contaminant initial concentration, dosage of ozone, various molar ratio of H_2O_2 to TNT, and reaction time.

MATERIAL AND METHODS

Analytical methods

TNT was analyzed using a high performance liquid chromatography (HPLC) system, a Model 486 UV detector, and a Nova pak C_{18} guard column. The analytical column was an ODS_2 optimal column (25 cm × 4.6 mm id, 5 μm) from Capital HPLC Ltd. The sample was injected into the HPLC system with the following condition: acetonitrile–water mixture (75:25 v/v) as the mobile phase at a flow rate of 1.0 mL/min (EPA 2007). Injection volume for all samples was 20 μl and a wavelength for the UV detector was 230 nm. Chemical oxygen demand (COD) was measured with HACH COD by the colorimetric method (APHA 1998). The sample was heated for about 2 hours in 150°C with potassium dichromate in the presence of silver sulfate and mercury sulfate. The absorbance was read at 620 nm by the spectrophotometric method. pH of the solution was adjusted by H_2SO_4 and NaOH (0.1 N) solutions. Initial pH solution was measured using a pH meter.

Experimental

Ozonation and hydrogen peroxide alone oxidation were performed on water contaminated with TNT. The experiments were carried out in a glass reactor with a working volume of 300 mL and 5 cm in diameter. Ozone was produced by a OWA-1000 generator (Figure 1).

Chemicals

TNT crystalline form with purity more than 95% was obtained from a local industry producing explosive materials and was used without further purification. All the chemicals were purchased from Merck Company. TNT

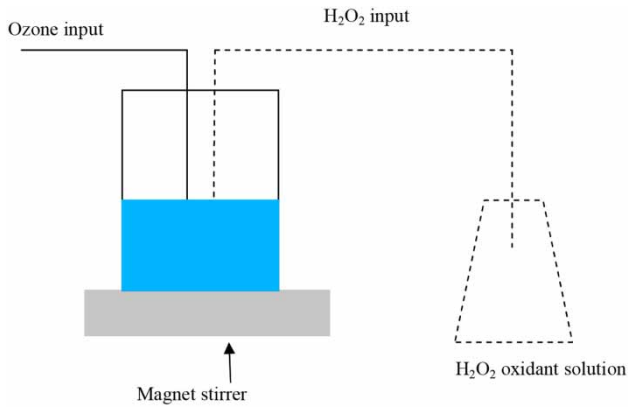

Figure 1 | Experimental set-up of the batch oxidation reactor.

stock solution was prepared by dissolving an appropriate amount of TNT in 1 L deionized water (El Diwani *et al.* 2009). All solvents of HPLC grade were filtered through a 0.45 μm PTFE filter. Hydrogen peroxide solution was prepared from a solution grade 35wt%.

RESULTS AND DISCUSSION

Effect of pH solution on TNT degradation

The effect of pH on TNT degradation was performed over the ranges 3, 5, 7, and 10. Indirect oxidation of contaminants is the key to their oxidation. It is easy for ozone to form hydroxyl free radicals, especially in alkaline aqueous solution. With increasing pH value, TNT degradation rate increased significantly (Figure 2). When the pH value increased from 7 to 10, TNT removal rate increased from 52 to 77% corresponding to TNT effluent concentration of 4.5 mg/L.

The degradation rate for decomposition of TNT was found to increase with an increase in pH from 3 to 10, as shown in Figure 2, while the degradation rate for decomposition of TNT was found to decrease with increasing of pH from 3 to 10 (Figure 3). TNT removal rate rapidly decreased from 65 to 15%, corresponding to TNT effluent concentration of 7 mg/L. Similar results have also been reported by Alnaizy *et al.* (1999), who found that hydrogen peroxide alone had no effect on the high concentration of nitroaromatic compounds' degradation from wastewater treatment (Alnaizy & Akgerman 1999). Biń *et al.* (2001) found that the reaction

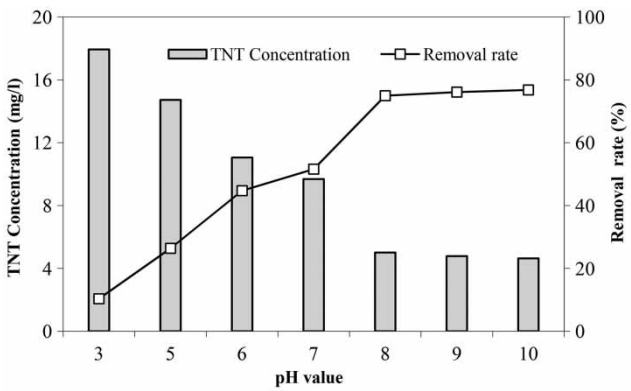

Figure 2 | Effect of pH solution on TNT decomposition (simple ozonation): TNT initial concentration = 20 mg/L, dosage of ozone = 0.5 g/hr, reaction time = 30 min.

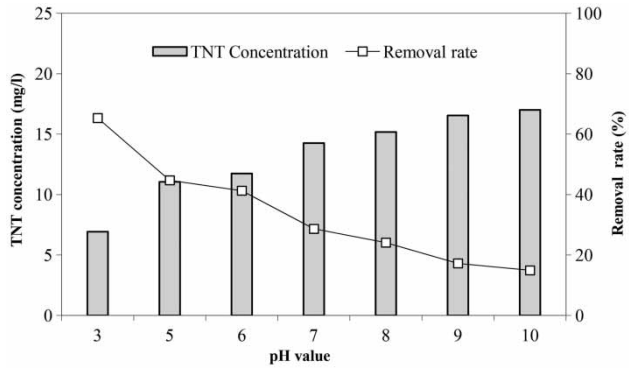

Figure 3 | Effect of pH solution on TNT decomposition (H_2O_2 oxidation): TNT initial concentration = 20 mg/L, H_2O_2/TNT molar ratio = 500:1, reaction time = 30 min.

rate is greater at the higher pH values due to the production of more hydroxyl free radicals by simple ozonation. Results of this experiment show that basic pH has a strong influence on the rate of TNT ozonation. At this pH, ozone decomposition starts to be important. It could be observed that at neutral and basic pH there is a minor contribution of free radical pathway in the H_2O_2 process, while in the ozonation process, the addition of H_2O_2 could basically increase the major contribution of the free radical pathway at neutral or basic pH.

Effect of initial concentration on TNT degradation

The effect of initial TNT concentration on ozonation and H_2O_2 alone oxidation processes was separately studied in a concentration range of 10 to 100 mg/L. pH of the solution was the optimum amounts obtained in the previous stage (pH = 10 for simple ozonation and pH = 3 for H_2O_2 oxidation) and 30 minutes as reaction time. Figures 4 and 5 are plotted between the initial concentration and removal rate of TNT concentration.

According to Figure 4, it can be observed that TNT degradation rate gradually decreases with an increase in TNT concentration (83% to 65%, respectively, corresponding to initial concentration of 10 to 100 mg/L) in simple ozonation and also rapidly decreases with an increase in TNT concentration (90% to 10%, respectively, corresponding to 10 to 100 mg/L) in the hydrogen peroxide process (Figure 5). A reason for this may be related to the generation of hydroxyl free radicals. The overall decomposition rate of TNT depends on the number of hydroxyl radicals in the solution. It is

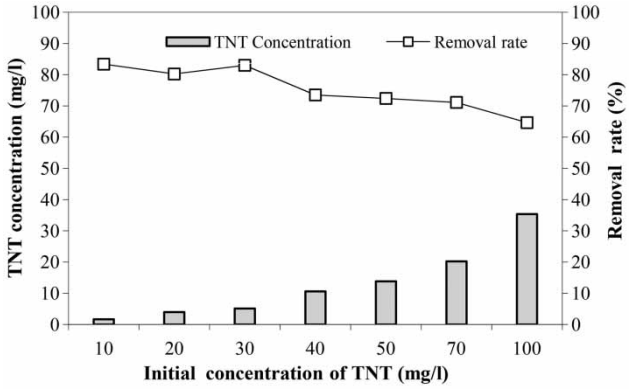

Figure 4 | Effect of initial concentration on TNT degradation rate (simple ozonation): pH of solution = 10, dosage of ozone = 0.5 g/hr, reaction time = 30 min.

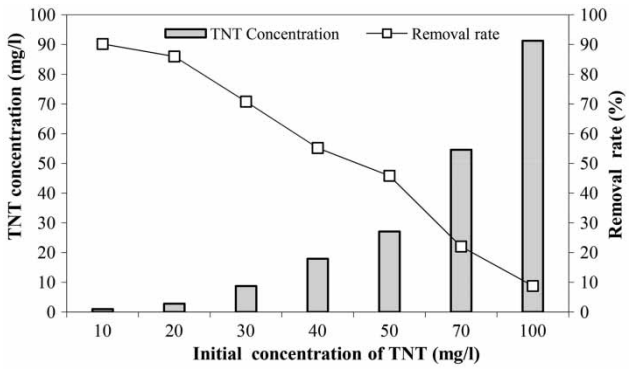

Figure 5 | Effect of initial concentration on TNT degradation rate (H_2O_2 alone oxidation): pH of solution = 3, H_2O_2/TNT molar ratio = 500:1, reaction time = 30 min.

obviously found from Figures 4 and 5 that in high explosive concentrations, hydroxyl free radicals could act as a scavenger, especially OH generation by the H_2O_2 alone process, while in the simple ozonation process, OH generation and distribution are more efficient and also scavenger forming is considerably less than that in the hydrogen peroxide process. Thus, in comparison with the H_2O_2 process, the distribution of hydroxyl free radicals was better and the removal rate variation in O_3 process was more significant. El Diwani *et al.* (2009) reported that higher initial concentration of TNT led to a slower degradation by the ozonation process.

Effect of dosage of ozone and hydrogen peroxide on TNT degradation

Operation conditions were similar to those of the previous stage, but TNT concentration was 20 mg/L. This experiment was separately achieved with the following parameters, including dosage of ozone and H_2O_2/TNT molar ratio (Figures 6 and 7).

Ozone doses were changed between 0.25 and 1 g/hr each at a contact time of 30 min, respectively, performed at pH = 10 and pH = 3 for O_3 and H_2O_2 experiments. The results showed an increase in ozone dose and H_2O_2/TNT molar ratio (250:1–1,000:1) had positive effects on TNT decomposition. This was related to increasing oxidant concentration, which resulted in an increase in formation of free radicals, causing an increase in TNT degradation rate. TNT removal up to 90% was observed by simple ozonation (ozone dosage = 1 g/hr) corresponding to TNT residual concentration of 2 mg/L

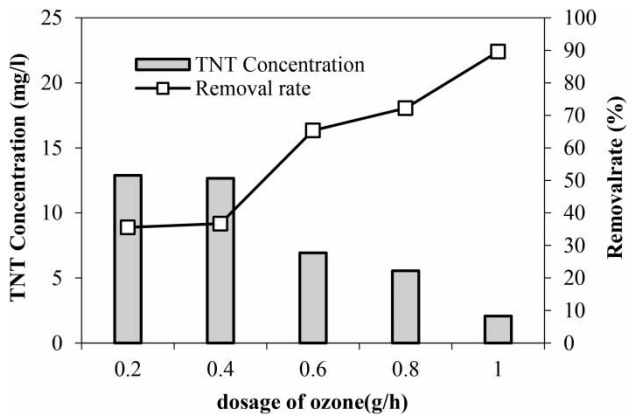

Figure 6 | Effect of dosage of ozone on TNT degradation (simple ozonation): TNT concentration = 20 mg/L, pH of solution = 10, reaction time = 30 min.

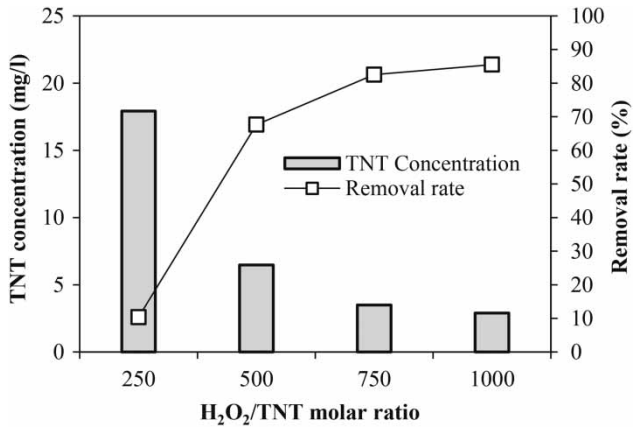

Figure 7 | Effect of H_2O_2/TNT molar ratio on TNT degradation (H_2O_2 oxidation): TNT concentration = 20 mg/L, pH of solution = 3, reaction time = 30 min.

and maximum removal around 85% by H_2O_2 alone oxidation (H_2O_2/TNT molar ratio = 1,000:1) corresponding to TNT residual concentration of 3 mg/L. El Diwani *et al.* (2009) reported that ozone dose parameter had a positive effect on TNT degradation by ozonation and multistage ozonation biological treatment. They reported that ozone dosage less than 0.177 g/L had a negative effect on TNT degradation.

Effect of reaction time on TNT removal rate

In this stage, TNT degradation rate was studied using numerous reaction times (15, 30, 45, 60 min) (Figures 8 and 9).

Figure 8 shows TNT degradation with simple ozonation. These runs were studied at optimum pH = 10 with initial TNT concentration of 40 mg/L. Due to the many TNT treatment studies that were achieved at high concentration (40 mg/L as initial concentration), the final stage of this experiment was performed with 40 mg/L as the initial concentration. It is apparent that more than 80% of TNT was oxidized in a reaction time of 60 min (TNT residual concentration = 8 mg/L). There is a linear relation between an increase of run time and TNT degradation rate in simple ozonation. We also studied TNT degradation rate with H_2O_2 alone at different reaction times at optimum pH of 3 and the same TNT concentration. It is learned from Figure 9 that although an increase in reaction time has a positive effect on TNT degradation rate, it is rather stable around 60% (TNT residual concentration = 17 mg/L) in reaction time of 45–60 min. It can be described that the destruction efficiency of TNT seems to be independent of the solubility of ozone (Chen *et al.* 2007). Therefore, in simple ozonation, TNT degradation rate increases as reaction time increases (Figure 8). In H_2O_2 alone oxidation, this phenomenon could be reversed; meanwhile, the TNT degradation rate depends on H_2O_2 solubility and distribution in solution. With the passage of time, hydroxyl free radicals, due to reaction with TNT contaminant, decrease and the degradation rate becomes constant (Figure 9).

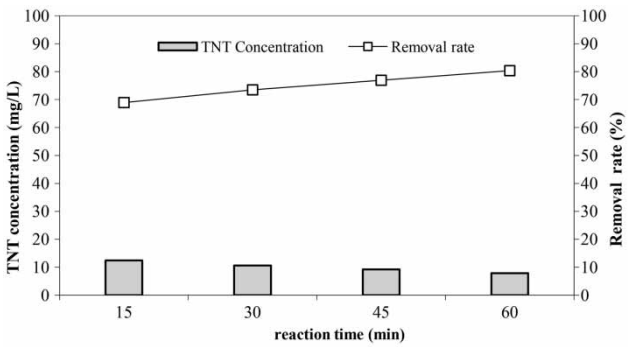

Figure 8 | Effect of reaction time on TNT degradation (simple ozonation): TNT initial concentration = 40 mg/L, pH of solution = 10, dosage of ozone = 1 g/hr.

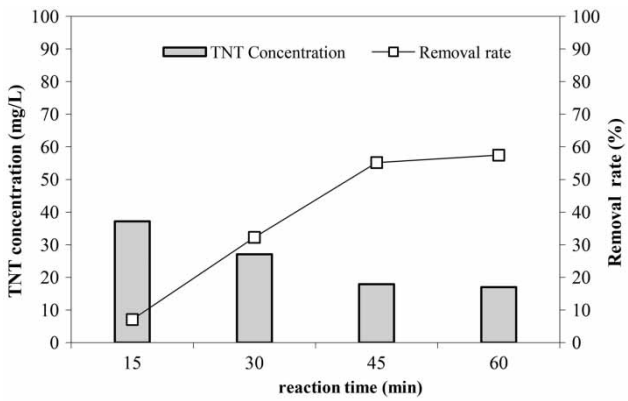

Figure 9 | Effect of reaction time on TNT degradation (H_2O_2 alone oxidation): TNT initial concentration = 40 mg/L, pH of solution = 10, H_2O_2/TNT molar ratio = 1,000:1.

Kinetic analysis

Table 1 shows the kinetic results of this study. Table 1 makes it evident that TNT degradation by simple ozonation and direct hydroxide oxygen follows the pseudo-second reaction with $R^2 > 0.85$ and 0.9, respectively.

Direct H_2O_2 and simple ozonation processes indicate the second-order behavior with rate constants of 0.019 and 0.033.

Table 1 | Reaction rate constants for TNT advanced oxidation processes

	H_2O_2 oxidation		Simple oxidation	
	R^2	K	R^2	K
Zero-order	0.6	25	0.65	29
First-order	0.71	0.3	0.82	0.36
Second-order	0.86	0.019	0.93	0.033

CONCLUSION

TNT degradation by direct H_2O_2 oxidation and ozonation was separately investigated. The conclusions are as follows:

- H_2O_2 oxidation alone is not applicable for high TNT concentrations and could only be effective for low TNT concentrations.
- Maximum TNT removal rate (90%) was obtained by the H_2O_2 oxidation process in the following conditions: pH = 3, initial TNT concentration 10 mg/L, H_2O_2/TNT molar ratio = 1,000:1; while in simple ozonation it was the same with the following conditions: pH = 10, initial TNT concentration 20 mg/L, ozone dosage of 1 g/hr with reaction time of 30 min.
- The kinetic of two processes was studied through fitting data on TNT degradation. The comparison of reaction orders showed that TNT degradation was in accordance with the pseudo-second reaction.
- Simple ozonation seems to be the best method for TNT degradation from aqueous solution.
- Generally, using hydrogen peroxide in combination with ozonation may be efficient and there is no need to use hydrogen peroxide at a high dose.

REFERENCES

Alnaizy, R. & Akgerman, A. 1999 Oxidative treatment of high explosives contaminated wastewater. *Water Research* **33** (9), 2021–2030.

APHA, WEF & AWWA 1998 *Standard Methods for the Examination of Water and Wastewater,* 20th edn. American Public Health Association, Washington, DC.

Ayoub, K., van Hullebusch, E. D., Cassir, M. & Bermond, A. 2010 Application of advanced oxidation processes for TNT removal: a review. *Journal of Hazardous Materials* **178** (1), 10–28.

Biń, A. K., Machniewski, P., Sakowicz, R., Ostrowska, J. & Zieliński, J. 2001 Degradation of nitroaromatics (MNT, DNT and TNT) by AOPs. *Ozone Science and Engineering* **23** (5), 343–349.

Čėnas, N., Nemeikaitė-Čėnienė, A., Marozienė, A., Šarlauskas, J., Vilutienė, V. & Baublys, J. 2001 *Explosives as Toxic Environmental Pollutants: the Level of Contamination, Toxicity and its Mechanisms. EUExcert (Certifying Expertise in European Explosives Sector)*. Institute of Biochemistry, Mokslininkų 12, LT-08662 Vilnius, Lithuania, pp. 1–8.

Chen, W.-S., Juan, C.-N. & Wei, K.-M. 2007 Decomposition of dinitrotoluene isomers and 2,4,6-trinitrotoluene in spent acid from toluene nitration process by ozonation and photo-ozonation. *Journal of Hazardous Materials* **147** (1), 97–104.

El Diwani, G., El Rafie, S. & Hawash, S. 2009 Degradation of 2, 4, 6-trinitrotoluene in aqueous solution by ozonation and multi-stage ozonation biological treatment. *International Journal of Environmental Science & Technology* **6** (4), 619–628.

EPA 2007 *Method 8330A Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)*. Available from: https://www.epa.gov/hw-sw846/sw-846-test-method-8330a-nitroaromatics-and-nitramines-high-performance-liquid.

Fu, F., Dionysiou, D. D. & Liu, H. 2014 The use of zero valent iron for groundwater remediation and wastewater treatment: a review. *Journal of Hazardous Materials* **267**, 194–205.

Hoigne, J. & Bader, H. 1976 The role of hydroxyl radical reactions in ozonation processes in aqueous solutions. *Water Research* **10** (5), 377–386.

King, S. M. 2012 *Enhancement in Degradation of Environmental Pollutants: Fenton Degradation of 2,4,6-Trinitrotoluene and Photodegradation of Deepwater Horizon Crude Oil*. PhD Thesis, University of New Orleans, New Orleans, LA, USA.

Liou, M. J., Lu, M. C. & Chen, J. N. 2003 Oxidation of explosives by Fenton and Photo-Fenton processes. *Water Research* **37**, 3172–3179.

Liu, X., Fu, Y., Wang, H., Zhong, Z. & Xu, Y. 2008 Photocatalytic degradation of 2,4,6-trinitrotoluene. *Science in China Series B: Chemistry* **51** (10), 1009–1013.

Mokrini, A., Ousse, D. & Esplugas, S. 1997 Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Science and Technology* **35** (4), 95–102.

Quiroz, M. A., Martínez-Huitle, C. A. & Bandala, E. R. 2011 *Advanced Oxidation Processes (AOPs) for Removal of Pesticides from Aqueous Media: INTECH Open Access Publisher*.

Richter-Torres, P., Dorsey, A. & Hodes, C. 1995 *Toxicological Profile for 2,4,6-Trinitrotoluene: U.S. Department of Health and Human Services*, Agency for Toxic Substances and Disease Registry, Atlanta, GA, USA.

Singh, S. N. 2013 *Biological Remediation of Explosive Residues.* Springer, Heidelberg, Germany.

Son, H.-S., Lee, S.-J., Cho, I.-H. & Zoh, K.-D. 2004 Kinetics and mechanism of TNT degradation in TiO_2 photocatalysis. *Chemosphere* **57** (4), 309–317.

Sviatenko, K. C., Gorb, F., Hill, F. C., Bednar, A. J., Okovytyy, S. & Leszczynski, J. 2014 Comprehensive investigations of kinetics of alkaline hydrolysis of TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), and DNAN (2,4-dinitroanisole). *Journal of Environmental Science and Technology* **48** (17), 10465–10474.

Zhang, Y., Wei, F., Xing, J., Lv, F., Meng, X. & Chu, P. K. 2012 Adsorption behaviour and removal of organic materials from TNT red water by lignite activated carbon. *Journal of Residual Science and Technology* **9** (3), 121–129.

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