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REVIEW

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Application of photo degradation for remediation of cyclic nitramine and nitroaromatic explosives

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The advantages of photo degradation for remediation of potentially hazardous and widely used explosives deposited in ground and surface water reserves has received continuous attention from researchers over the past 20 years, particularly due to energy efficiency, rapidness and the environmental safety associated with photo degradation processes. Hence, this review has introduced an up-to-date collation of knowledge regarding the radiation sources for effective photo degradation of cyclic nitramine and nitroaromatic explosives, irradiation time, photocatalysts as well as important physical–chemical parameters such as pH and substrate concentrations. Most importantly, this review has highlighted the fact that recent advances in continuous-flow photo chemistry, micro photo-reactor technology, energy efficient light sources at low wavelengths as well as advances in synthesizing photosensitive nanostructures have opened up new possibilities in regards to the application of advanced oxidation technology using photon energy for rapid, safe and energy efficient remediation of hazardous organic contaminants in the environment.

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Introduction

Contamination of surface and ground water reserves resulting from the release of energetic materials (EM) contained in pink water (generated during the demilitarisation of munitions in

the factories by sinking the munitions in hot water basins) as well as in red water (generated during the production of munitions in ammunition plants) is a serious problem worldwide.^{1–3} In 2010, more than 12 million pounds of EMs were released into waterways by the US Army's Radford Ammunition Plant.⁴ Additionally, EMs contained in unexploded ordnances in warfare zones and live firing ranges were reported to infiltrate into the near-surface and ground water reserves *via* leaching through soil.^{5,6} Certini *et al.*⁷ attributed the modern era

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chemical contamination of soils by warfare activities and the resultant negative impact on ground water quality largely to EMs such as, cyclic nitramine and nitroaromatic explosives. Both cyclic nitramine and nitroaromatic explosives were classified as high explosives (HE) in the United Nations listing due to their mass explosion hazards through secondary detonation.⁸ Hence, the environmental remediation of cyclic nitramine and nitroaromatic explosives through degradation is an important task as it aims to abating the detrimental impacts of such substances on human health and ecosystem. Depending on the chemical and physical characteristics of the EM in the target explosives to be degraded, four types of degradation techniques namely, acid degradation, photo degradation, thermal degradation and bio degradation were employed by the remediation practitioners and chemists.^{9,10} Fig. 1 illustrates the chemical structures of the cyclic nitramine and nitroaromatic explosives currently being used worldwide.

The fate and transport of cyclic nitramine and nitroaromatic explosives were extensively studied by researchers with a view to understand the far reaching impact of such EMs on human health and environment through potential transport pathways.

Sorption and transport studies of various nitramine and nitroaromatic explosives established the fact that nitramine explosives such as RDX and CL-20 as well as photo degraded products of nitroaromatic explosives such as 2-amino-4,6-dinitrobenzoic acid can reach groundwater through sorption of these HE molecules/degradation products to the colloidal fractions of soil.^{11–13} To the contrary, undegraded nitroaromatic explosives such as 2,4,6-TNT was reported to be increasingly partitioned to soil-immobile phase which inhibited its transport to groundwater.¹⁴ The relatively high aqueous solubility of TNT (130 mg L⁻¹ at 20 °C;¹⁵) compared to that of RDX (38.9 mg L⁻¹ at 20 °C;¹⁶) and CL-20 (3.11 mg L⁻¹ at 20 °C;¹⁷) may contribute towards faster dissolution and transport of TNT into the surface water reserves *via* surface runoff rather than groundwater reserves *via* sorption and leaching. Brannon and Myers¹⁸ described the dissolution of cyclic nitramine and nitroaromatic explosives into the aqueous phase as one of the primary processes determining their fate, once released into the environment. Both Kalderis *et al.*⁹ and Pichtel¹⁰ reported photolysis of cyclic nitramine and nitroaromatic explosives in aqueous phase as the major transformation process in waste streams and surface

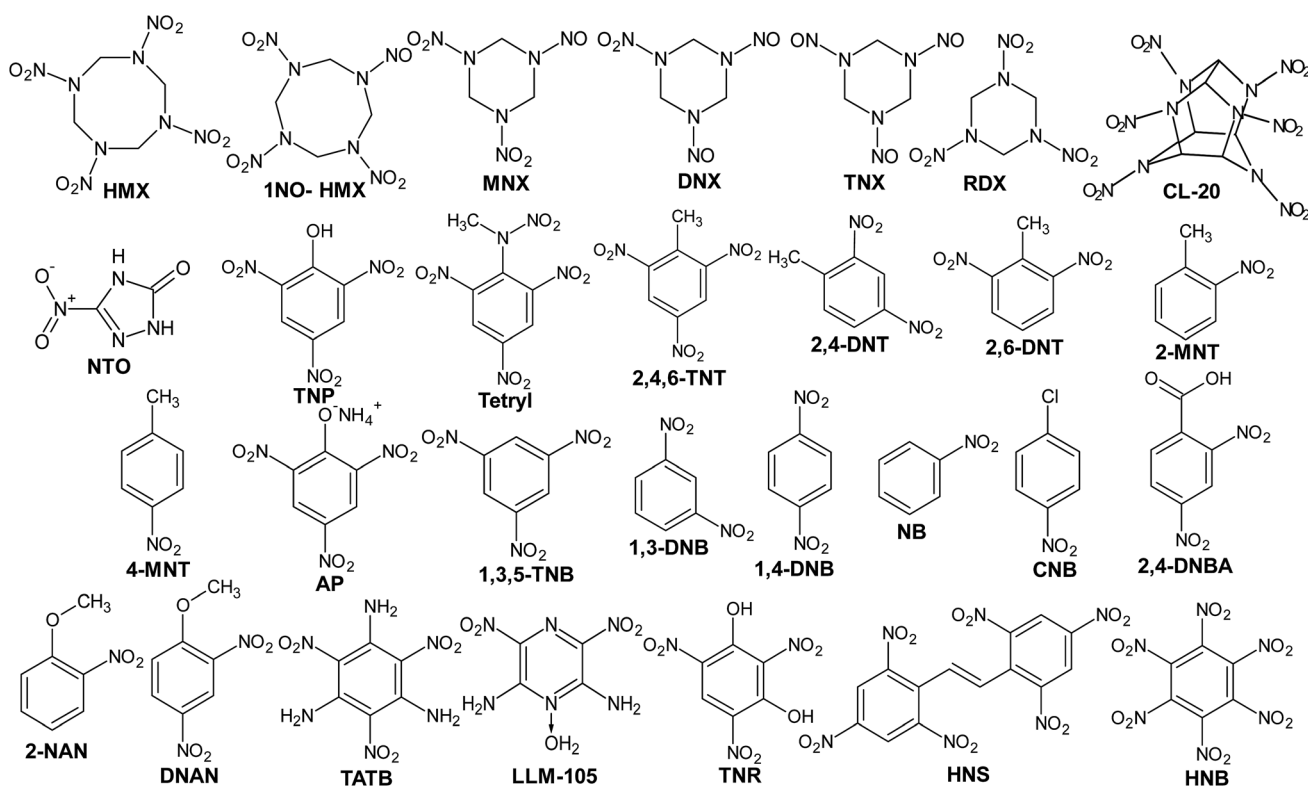


Fig. 1 Structures of cyclic nitramine and nitroaromatic explosives: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (1NO-HMX), hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), 5-nitro-2,4-dihydro-(1,2,4)triazol-3-one also known as nitrotriazolone (NTO), 2,4,6-trinitrophenol also known as picric acid (TNP), 2,4,6-trinitrophenylmethyl nitramine also known as *N*-methyl-*N*,2,4,6-tetranitroaniline (tetryl), 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), mononitrotoluenes or MNT (2-MNT, 4-MNT), ammonium picronitrate (AP), 2,4-dinitrobenzoic acid (2,4-DNBA), 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB), 1,4-dinitrobenzene (1,4-DNB), nitrobenzene (NB), 4-chloronitrobenzene (CNB), *ortho*-nitroanisole (2-NAN), 2,4-dinitroanisole (DNAN), triaminotrinitrobenzene (TATB), 2,6-diamino-3,5-dinitropyrazine-1-oxide also known as LLM-105 (LLM-105), trinitroresorcinol also known as styphnic acid (TNR), hexanitrostilbene (HNS), hexanitrobenzene (HNB).

water bodies in terms of degree of mineralisation and rapidness compared to other transformation processes such as hydrolysis, thermolysis and bio degradation. Additionally, Bordeleau *et al.*¹⁹ ascribed photolysis as a major attenuation mechanism while investigating photo degradation of RDX in infiltrated water and surface water bodies after the release of this HE from a military training range nearby.

A number of cyclic nitramine and nitroaromatic HEs such as RDX and 1,3,5-TNB (a degradation product of TNT) were identified as potential water contaminants by the USEPA.²⁰ The detrimental effects of cyclic nitramine and nitroaromatic explosives and their residues on human health and ecosystem were well documented in literatures.^{16,21–24} Detailed accounts of bitter taste, burning eyes and discolouration of skin and hair of workers in TNT and DNT disposal facilities were presented by Letzel *et al.*²⁵

In 2002, a total of 6.2 metric tons of nitroaromatic explosives such as, NB and DNT were released in soil in the United States with 70 sites contaminated with nitroarene and their chemical precursors.²¹ In 2006, 3130 metric tons of cyclic nitramine explosives such as RDX was produced in the USA.²⁶ The 2015 Australian explosive manufacturing market research report stated 5.2% annual growth of explosive production from 2011 to 2016.²⁷ In the 2013–2014 financial year, Australia had a 3.5 billion dollar explosive industry which mainly produced cyclic nitramines, nitroaromatics and ammonium nitrate based commercial explosives.²⁸ A site specific policy by the Department of Defence (DOD) in Australia stipulated the use of the chemical oxidation/reduction technologies for the remediation of cyclic nitramine and nitroaromatic explosives in groundwater mainly due to the shorter clean-up time compared to bio degradation technologies.²⁹ Additionally, Sheremata *et al.*³⁰ reported that only traces of RDX were mineralised to CO₂ and N₂O by the indigenous microorganisms in nonsterile topsoil with production of toxic nitroso metabolites such as MNX, DNX and TNX in aqueous phase and 55–99% recovery of RDX from sterile topsoil after 5 weeks. Although the chemotaxis-mediated biodegradation of 20 μM cyclic nitramine explosives such as RDX, HMX and CL-20 resulted relatively faster mineralisation within 50 hours³¹ and photo assisted biological transformation of 30 μM RDX required 40 hours,³² the influence of initial concentrations of HEs and pH in aqueous solutions on such degradation were unknown. The nitroaromatic explosives contain at least one nitro (–NO₂) group attached to the aromatic ring which contributes to formation of stable complexes as well as recalcitrance to oxidative degradation in the environment.²¹ Additionally, cyclic nitramine explosives contain at least one nitro (–NO₂) group along with amine (–NH₂) or nitroso (–NO) group, with at least three nitrogen atoms forming the cyclic structure.³³ The denitration of RDX in aqueous solutions by photolysis was reported to be more rapid than the enzymatic denitration of RDX.³⁴ Hence, during the past 20 years, researchers utilised the high absorption of photon energy by the nitro (–NO₂) groups present in the cyclic nitramine and nitroaromatic explosives at various wavelengths with a view to initiate photo degradation and complete mineralisation of these HEs rapidly. The two earliest works on photo degradation of nitroaromatic explosives in aqueous solutions were undertaken by Mabey *et al.*³⁵ and

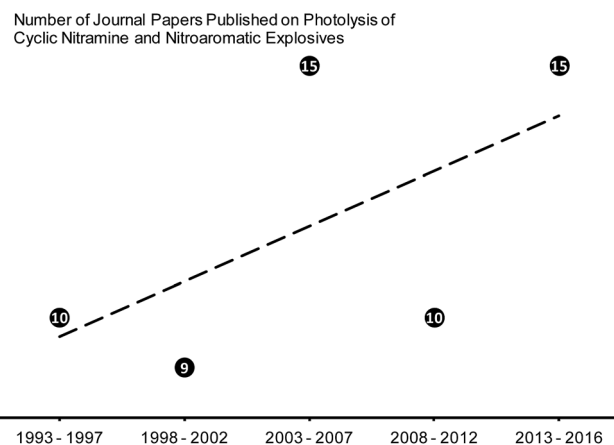


Fig. 2 The number of journal papers published in every 5 year on the photolysis of cyclic nitramine and nitroaromatic explosives since 1993 to present are shown in black circles while the dotted line illustrating the upward trend; a total of 59 papers on the topic was published up to July 2016.

Simmons and Zepp.³⁶ Since then a steady growth of interest in photolysis of both nitroaromatic and cyclic nitramine explosives was observed as illustrated in Fig. 2.

Despite the fact that photo degradation is a very cost effective, safe and rapid remediation technique for cyclic nitramine and nitroaromatic explosives, only one review paper regarding remediation of trinitrotoluene in water partially addressed photo degradation along with other processes.¹⁵ Hence, there is a need to collate the detailed knowledge regarding the absorption wavelength, characteristics of the light sources, photo degradation products, pH of the aqueous solutions, influence of photo catalysts and photo sensitizers as well as initial concentrations of these explosives for better implementation of photo degradation based remediation technology of these HEs. The aim of this review is, therefore, to collate the knowledge from the photo degradation studies of cyclic nitramine and nitroaromatic explosives from the past 20 years with a view to inform remediation practitioners with up-to-date scientific knowledge regarding the applicability of photo degradation of these HEs as a rapid, safe and energy efficient technology.

Methods of photo degradation

The photo degradation process starts with the initial selection of the phases of the reactants and the catalysts in the solution. Depending on the reactants and catalysts in the same or different phases, the photo degradation methods can be either homogeneous or heterogeneous, respectively. Interestingly, both the homogeneous and heterogeneous photo degradation can only incorporate two different modes of operating conditions inside the physical reactors where the degradation takes place. Depending on costs of reagents, degradation time required to mineralising the target hazardous substances as well as fate and toxicity of the degradation products, the photo degradation process may employ reactors which incorporate either batch mode or continuous-flow mode. The photo

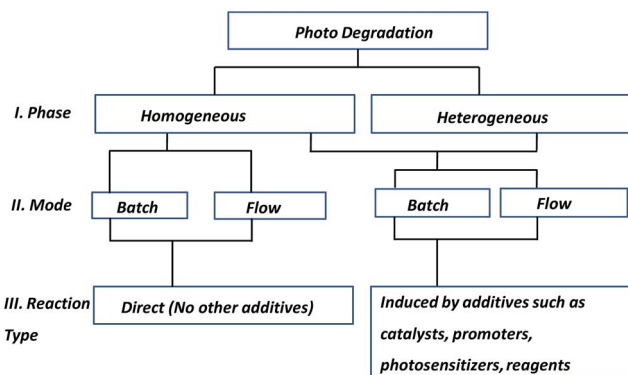


Fig. 3 Photo degradation methods are classified in terms of solution phase, operating mode and reaction type.

degradation of the target analytes in homogeneous phase may take place without any additives such as catalysts, promoters, photosensitizers or reagents. Hence, we termed the photo degradation reaction in the absence of any additives in the homogeneous phase as direct photo degradation. However, in many instances, the photo degradation reactions employ different additives to enhance the reaction rates in both homogeneous and heterogeneous phases. Fig. 3 illustrated the different methods of photo degradation.

Photo degradation of explosives

Photo degradation of explosives in soil and water is an effective technique that employed the energy of photons from various light sources to cause dissociation of bonds within the explosive molecule to create simpler molecules. The high absorption of photon energy by the nitro ($-\text{NO}_2$) groups present in cyclic nitramine and nitroaromatic explosive molecules from ultraviolet and visible light sources is the main driving force behind the photo degradation of these HEs. The cyclic nitramine and nitroaromatic

explosives include 2,4,6-TNT, 1,3,5-TNB, 2,4-DNT, 2,6-DNT, 1,3-DNB, 1,4-DNB, tetryl, TNP, RDX, HMX, HNS, HNB, NAN, DNAN, NTO, TATB and TNR.^{21,37} Since 2011, the TNT based explosives in artillery shells of US Army were gradually being replaced by IMX-101 which is a mixture of DNAN, NTO and nitroguanidine (NQ).³⁸ Recently, Mahbub *et al.*³⁹ reported another type of explosive known as organic peroxide explosives (OPEs) that manifested efficient photo degradation phenomenon despite having very low molar absorptivity coefficients. As opposed to cyclic nitramines and nitroaromatic explosives, the OPEs are extremely unstable and very sensitive to temperature, shock and friction. Hence, OPEs are not suitable for mass production as military/commercial explosives. Additionally, the hazardous effects of OPEs on human health and ecosystem are not yet established. Hence, this review will not discuss the photo degradation of OPEs.

The photo degradability of these HEs will depend on the photon absorption characteristics of the explosive molecules at a particular wavelength. Dubroca *et al.*⁴⁰ investigated the absorption spectra of TNT, RDX, HMX and tetryl in UV and visible region and reported that the intermolecular hydrogen bonding of these molecules was the key parameter that controlled the photon absorption. In an earlier kinetic study of fulvic acid initiated photolysis of 19 nitroaromatic compounds in aqueous solution with explosive potential, Simmons and Zepp³⁶ demonstrated that the largest enhancement in the rate of photolysis, ranging from 2 to 26 fold, occurred for nitroaromatics that were methylated *ortho* to the nitro group.

Table 1 compiled the molar absorptivity coefficients at maximum absorption wavelengths of various cyclic nitramine and nitroaromatic explosives.

Photo degradation methods applied to the cyclic nitramine and nitroaromatic explosives

There were many examples when researchers simply utilised different light sources without employing any additives in terms of catalysts, promoters, photosensitizers or reagents in the

Table 1 Photo degradable explosives with corresponding groups are listed with their maximum absorption wavelengths, λ_{max} and molar absorptivity coefficients, ϵ_{max} . Places were left blank where data were unavailable

Explosives	Solvent	λ_{max} , nm	ϵ_{max} , $\text{M}^{-1} \text{cm}^{-1} \times 10^3$	Ref.	
Cyclic nitramines	HMX	Ethanol	228–229	21	41
	RDX	Ethanol	213	11	41
	CL-20	Methanol	228	23	42
Nitroaromatics	TNP	Dimethylsulfoxide (DMSO)	378	19	41
	Tetryl	Ethanol	225	25	41
	2,4,6-TNT	Water	233	16	43
	2,4-DNT	5% ethanol in water	240	29	41
	2,6-DNT	Water	245	—	44
	1,3,5-TNB	Water	220	25	45
	1,3-DNB	Water	231	17	45
	1,4-DNB	Water	262	13	45
			200	18	45
	NB	Water	260	7.5	45
	2-NAN	—	267	5.4	45
	DNAN	Water	300	11	46
TNR	DMSO	352	10	41	

photochemical reaction. Therefore, the subsequent discussions of photo degradation of cyclic nitramine and nitroaromatic explosives will cover photo degradation methods applied for degrading these HEs with and without additives. The discussions also focussed on key information needed for remediation practice such as energy requirement by the light source, yield and products of degradation as well as irradiation time.

Direct photo degradation

Just and Schnoor⁴⁷ employed direct photo degradation of RDX using simulated sunlight (170–2200 nm) generated from a 1000 W metal halide lamp. Direct photo degradation of nitrobenzene was reported by Li *et al.*⁴⁸ at a wavelength of 172 nm. However, they found that UV photocatalytic degradation of nitrobenzene in presence of H₂O₂ was 3 times more efficient than UV only in terms of irradiation time. A comparison between direct photo degradations of CL-20 and RDX was carried out by Hawari *et al.*^{34,49} The initial photo degradation of the monocyclic nitramine (RDX) lead to ring cleavage and decomposition yielding HCHO, HCOOH, NH₂CHO, N₂O, NO₂⁻ and NO₃⁺ after 16 hour at 350 nm and at pH 5.5.³⁴ The direct photolysis of the rigid molecule CL-20 at 254–350 nm produced NO₂⁻, NO₃⁻, NH₃, HCOOH, N₂ and N₂O.⁴⁹ The natural photo degradation of RDX and nitroglycerin in aqueous and solid samples collected from military training camps were undertaken by Bordeleau *et al.*¹⁹ They reported UV degradation of both compounds when dissolved in water, with half-lives between 1 and 120 days. Much slower rates of photo degradation (half lives 2–4 months) were reported for RDX and nitroglycerin bearing solid particles by Bordeleau *et al.*¹⁹ Recently, Čapka *et al.*⁵⁰ employed 125 W high-pressure mercury lamp to convert -NO₂ and -ONO groups, typical for cyclic nitramine and nitroaromatic explosives such as HMX, RDX, tetryl, TNT, 2,4-DNT, 2,6-DNT, TNB, 1,3-DNB and NB, to peroxyxynitrite by absorption of UV light and peroxyxynitrite was detected by the chemiluminescence reaction with the alkaline solution of luminol. The chemical and physical fates of trace amount of TNT and RDX in environment were reported by Kunz *et al.*⁵¹ through direct UV photo degradation using 150 W

halogen source and formation of 2-aminodinitrotoluene and 4-aminodinitrotoluene were reported along with net loss of mass of TNT through sublimation within 30 min irradiation. Interestingly, no degradation product of RDX was reported by Kunz *et al.*,⁵¹ which suggested that the initial concentration of RDX may play a crucial role on the yield of direct photo degradation of RDX. The direct photo degradation as well as humic acid and salt (NaCl) sensitised homogeneous photo degradation of 2,4-DNT in aqueous solution resulted in 50% degradation in 4 hour, 2 hour and 1 hour, respectively.⁵²

Homogeneous photo degradation

The homogeneous photo degradation of nitroaromatics employed UV oxidation with ozone,^{53–55} or with hydrogen peroxide,^{53,56} or with the Fenton's reagent (H₂O₂ + Fe²⁺).^{57,58} Rodgers and Bunce²² termed these UV oxidation processes as homogeneous photolysis where UVC (290–200 nm) radiation produced OH[•] radicals by breaking down H₂O₂ or O₃. There are currently no research studies on homogeneous UV oxidation with peroxyxone (H₂O₂ + O₃) systems in regards to the degradation of nitroaromatics or cyclic nitramines.

Beltran *et al.*⁵⁴ and Mcphee *et al.*⁵⁹ suggested that UV oxidation with O₃ was superior to the UV oxidation with H₂O₂, possibly due to higher molar extinction coefficient of O₃ than H₂O₂. However, Mcphee *et al.*⁵⁹ criticised that despite removing 2,4,6-TNT from solution, 1,3,5-TNB was one of degradation products of TNT resulting from UV oxidation with O₃. Hence, the toxicity of the solution was retained even after the UV oxidation with O₃.

Liou *et al.*⁶⁰ reported oxidative destruction of TNP, AP, 2,4-DNT, tetryl and 2,4,6-TNT, RDX and HMX using Fenton and photo-Fenton processes. For all explosives, Liou *et al.*⁶⁰ found that the oxidation rates significantly increased with increasing the concentration of Fe²⁺ in the Fenton system, as well as through illumination with UV light in the photo-Fenton system. The added UV efficiency of photo-Fenton compared to Fenton system was reported within a range of 1–3 by Liou *et al.*⁶⁰ and is reproduced in Table 2.

Table 2 Pseudo-first-order constants for Fenton/photo-Fenton oxidation of explosives (adapted from Liou *et al.*⁶⁰)

Explosives	Reagent [Fe(II)] (mM)	Reaction rate constant in Fenton, k_F (min ⁻¹)	Reaction rate constant in photo-Fenton (40 W UV), k_P (min ⁻¹)	Added UV efficiency, k_P/k_F
TNP	0.144	0.0935	0.1087	1.16
	0.288	0.1691	0.1741	1.03
AP	0.144	0.0947	0.1260	1.33
	0.288	0.2000	0.2190	1.10
DNT	0.090	0.0049	0.0089	1.80
	0.180	0.0108	0.0158	1.46
TNT	0.360	0.0135	0.0359	2.57
	1.440	0.0588	0.0918	1.26
Tetryl	0.360	0.0083	0.0140	1.69
	0.720	0.0264	0.0437	1.66
RDX	0.720	0.0242	0.0274	1.13
	1.440	0.0407	0.0411	1.01
HMX	0.720	0.0015	0.0031	2.10
	1.440	0.0017	0.0032	1.90

Interestingly, Li *et al.*⁵⁷ reported the increased oxidation rate of mononitrotoluenes (MNT) at 254 nm UV light using Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) at pH 6 whilst adjusted aqueous solutions of pH 3.0 in UV-Fenton systems were required for the degradations of higher nitro-substituted toluenes. The low molar absorptivity coefficient of H_2O_2 at 254 nm was unsuitable for employing UV with H_2O_2 for the degradation of nitrotoluenes, according to the Li *et al.*⁵⁷ study. Under simulated solar light, Carlos *et al.*⁶¹ demonstrated an autocatalytic behaviour during the reaction between nitrobenzene and Fe^{3+} and concluded that simulated solar light with cut-off wavelength from 300 nm had negligible impact on $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ initiated degradation of NB. Therefore, conventional UV oxidation with H_2O_2 at 254 nm as well as solar light ($\lambda > 300$ nm) induced photo degradation may not be very effective for the photo degradation of either cyclic nitramine or nitroaromatic explosives. In this regard, Li *et al.*⁴⁸ illustrated nearly 90% degradation of NB in combination of UV and H_2O_2 (7 : 1 molar ratio of H_2O_2 : NB) with 172 nm excimer (Xe_2^* 7.21 eV) UV light where, 4.07 mM NB solution drastically decreased to 0.41 mM NB after treatment of only 20 min. Although the excimer and exciplex UV sources have illustrated characteristic features such as, incoherence, near monochromaticity, more than 22 wavelengths, high UV and vacuum UV intensities, large absorption cross section, low temperature and mercury-free operation as well as long life,⁶² these innovative UV sources have been under-utilised in the degradation of nitroaromatics and cyclic nitramine explosives. Other methods such as flushing with cyclodextrin solution in photo-Fenton treatment of TNT for its removal from contaminated soil was employed by Yardin and Chiron⁶³ and they reported 1.3 times increase in the TNT degradation rate which was ascribed to the formation of a ternary complex (TNT-cyclodextrin-iron) that directed hydroxyl radical reaction toward the oxidation of TNT.

Heterogeneous photo degradation

Rodgers and Bunce²² termed heterogeneous photolysis as the processes where OH^{\cdot} radicals were generated at the surface of a semiconductor (such as TiO_2) in presence of UVA light (400–320 nm). Due to competition between electron-hole recombination and water oxidation in aqueous solution, the semiconductor assisted photolysis was deemed to be an inefficient technique for the degradation of organic pollutants.²² Anatase TiO_2 suspension with UV radiation was employed by Lee *et al.*⁶⁴ to photodegrade aqueous form of TNT, RDX and HMX without sufficient information regarding the support mechanism for immobilisation of TiO_2 in suspension. Recently, Alam *et al.*⁶⁵ demonstrated graphene oxide (GO) supported Ag- TiO_2 nanofilms for effective photo degradation of 4-nitrobenzenethiol (4-NBT) upon UV irradiation. Different support mechanisms for TiO_2 catalyst such as, TiO_2 film on borosilicate glass,⁶⁶ nano- TiO_2 on activated carbon fibre or ACF,⁶⁷ surface modification of nanosize TiO_2 by chemical adsorption⁶⁸ were employed by researchers to develop efficient UV- TiO_2 photocatalytic processes for degradation of nitroaromatic explosives. Schmelling and Gray⁶⁹ reported that coloured sensitizers

did not play any detectable role in photo degradation of 2,4,6-TNT in a TiO_2 slurry reactor in near UV radiation ($\lambda > 340$ nm) with 90% degradation of TNT achieved in 120 min. The anticipation of considerable economic savings in large scale operations prompted researchers to utilise sunlight or near visible UV light (400–320 nm) in semiconductor assisted heterogeneous photo degradation of nitroaromatic contaminants in different waste matrices.¹⁵ Rajamanickam and Shanthi⁷⁰ utilised ZnO supported heterogeneous photo degradation of 4-nitrophenol (4-NP) under solar light irradiation. However, they reported that the degradation was strongly enhanced in the presence of electron acceptors such as H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 . This was attributed to the fact that the conduction band electron hole recombination in ZnO was reduced effectively with addition of electron acceptors such as H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 . Fe-doped TiO_2 dispersions along with H_2O_2 was employed by Zhao *et al.*,⁷¹ who reported 67.53% removal of total organic carbon of a solution containing 20 mg L^{-1} 4-NP at pH 6.17. In this regard, new narrow-band-gap semiconductor photocatalyst with high negative value of the conduction band was investigated by Qusti *et al.*⁷² Silver reduced graphene oxide supported nanocomposites (Ag-RGO with conduction band gap 2.4 eV) were utilised by Qusti *et al.*⁷² to reduce nitrobenzene to aniline under visible light. Approximately 100% decomposition of aqueous 0.8 mM nitrobenzene to aniline under 4 hour irradiation under visible light source from xenon (Xe) lamp with maximum emission at 470 nm was reported in this study.

The weak reactivity of RDX and HMX and their poor degradation yield in TiO_2 -UV photo degradation scheme was reported by Perchet *et al.*⁷³ While they attributed the weak reactivity of RDX and HMX to their incapacity to approach the TiO_2 catalyst surface, the effect of experimental pH condition of such reactivity was not discussed by Perchet *et al.*⁷³ To the contrary, wavelengths >320 nm from a xenon source at pH ranging 3 to 11 were employed by Dillert *et al.*⁷⁴ for homogeneous and heterogeneous photo degradation of TNT and TNB. At pH 7, Dillert *et al.*⁷⁴ found that TiO_2 -UV photo degradation reaction rate of TNT was similar to the photo degradation reaction rate of TNT in H_2O_2 -UV. However, photo degradation reaction rate of degradation product of TNT (*i.e.*, TNB) was reduced by 16 fold in H_2O_2 -UV homogeneous system at pH 7. There was a general increase in the photo degradation reaction rate of TNT in TiO_2 -UV suspension than in H_2O_2 -UV solution for an increase of pH from 3 to 11. However, this effect was not observed for the TNB solutions. Although it was ascribed by Dillert *et al.*⁷⁴ that the bathochromic and hypsochromic shifts of UV-vis absorption of TNT with increased pH were more pronounced in homogeneous solutions than TiO_2 -UV, the slower rate of TNB photo degradation in homogeneous solutions prompted them to recommend in favour of TiO_2 -UV system for TNT and TNB photo degradation. More recently, Khue *et al.*⁷⁵ reported 100% degradation of 2,4,6-trinitroresorcine (TNR) in 30 minutes in homogeneous H_2O_2 -UV system. Nevertheless, they found that the combined application of nano- TiO_2 (anatase)/UV/ H_2O_2 was the most efficient system for the 98% removal of the degradation product of TNR in 60 minutes.

Parameters affecting photo degradation of cyclic nitramine and nitroaromatic explosives

The radiation source and wavelength, radiation time and catalysts and photosensitizers used in photo degradation, initial concentrations of explosives as well as pH of the solution can affect the yields of photo degradation. Tables 3–5 and the subsequent discussions summarised the parameters affecting all three types of photo degradation discussed in this review.

Radiation source and wavelength

To apply the photo degradation techniques effectively, researchers utilised the ultraviolet absorption wavelength of the energetic molecules, where applicable. For example, the molar absorptivity coefficient of HMX was reported in the order of $21\,000\text{ M}^{-1}\text{ cm}^{-1}$ at a maximum absorption wavelength of 225 nm in Table 1. Hence, Wang *et al.*¹¹⁴ employed 229 nm laser UV irradiation for direct photo degradation of HMX in solid samples without reporting details of photo degradation yields and photo degradation products. Additionally, Tanjaroan *et al.*⁸⁶ reported photo dissociation rate of NB as $1.7 \times 10^7\text{ s}^{-1}$ at 266 nm using picosecond tunable laser where NB was excited to higher absorption band at 250 and 266 nm than at 280 nm from its ground state. This was in conformity with the maximum absorption wavelength of NB at 260 nm as illustrated in Table 1.

For both direct and homogeneous photo degradation of cyclic nitramine and nitroaromatic explosives, the radiation sources primarily employed were mercury vapour lamps ranging from low to medium pressure. For heterogeneous photo degradation of these explosives, high pressure xenon lamps and simulated sunlights were employed. This generally implied to the higher energy requirements in the heterogeneous process for the photo degradation of these explosives. To the contrary, the usual 254 nm wavelength of the mercury vapour lamps was not sufficient for complete mineralisation of these HEs in the direct photo degradation schemes. Near 100% photo degradation was reported in the homogeneous photo degradation schemes that employed the 254 nm wavelength. The heterogeneous photo degradation systems reported 67–100% photo degradation of HEs using wavelengths ranged from 300 to 800 nm.

Radiation time

The irradiation times varied 0.37 to 15 minutes for direct photo degradation of cyclic nitramine and nitroaromatic explosives where low pressure mercury sources were used. Hence, the direct photo degradation mechanisms are suitable for implementing ultra-fast continuous-flow micro-photoreactor technology. To the contrary, the homogeneous photo degradation mechanisms required 10 to 240 minutes irradiation while the heterogeneous photo degradation mechanisms required 90 to 1200 minutes irradiation times. Although the irradiation time will depend on initial concentrations of explosives, the usually longer irradiation times in homogeneous and heterogeneous photo degradation systems will require special design considerations for implementing fast and continuous-flow micro-

photoreactor technology for the degradation of nitroaromatics and cyclic nitramine explosives.

Catalysts and photosensitizers used

All of the homogeneous photo degradation mechanisms of nitroaromatics and cyclic nitramine explosives employed either Fenton's reagent ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) or ozone as catalysts while the heterogeneous photo degradation mechanisms of nitroaromatics and cyclic nitramine explosives employed metal oxides such as graphene oxide, ZnO, TiO₂ as well as sulphides such as CdS as catalysts. Yang *et al.*⁸⁴ and Cui *et al.*⁸⁵ employed riboflavin as a photosensitizer for photo degradation of 2,4,6-TNT under natural sunlight. The combined effect of photosensitizer such as humic acid and photocatalyst such as TiO₂ on the photo degradation of 2,4,6-TNT in near UV radiation ($\lambda > 340\text{ nm}$) was reported by Schmelling *et al.*¹¹⁰ The strong absorbance of humic acid in the visible region was attributed to the increased rate of sensitised degradation (both photolytic and photocatalytic) of TNT. Nevertheless, the scavenging of reactive species such as OH[•] by the photosensitizers may lower the rate of direct photocatalytic transformation of nitroaromatic and cyclic nitramine explosives. Recently, Vione *et al.*¹¹⁵ reported that 10–55% degradation of NB in deep water bodies (10 m depth with dissolved organic carbon concentration 10 mg L^{-1}) occurred due to homogeneous photo degradation in presence of chromophoric dissolved organic matters (CDOMs) where OH[•] radicals were scavenged by the dissolved organic matters (either chromophoric or not). Hence, the choice of catalysts or photosensitizers in photo degradation studies of cyclic nitramine and nitroaromatic explosives depends on the reactivity of the radicals towards these explosives during photo reaction.

Initial concentrations of explosives

Lee *et al.*⁶⁴ reported increased rates of heterogeneous photo degradation of HMX in anatase TiO₂ suspension at decreasing initial concentrations of HMX of 2, 1 and 0.5 mg L^{-1} . It should be noted that while the rate of photo degradation can increase with decreasing initial concentrations of explosives, the initial reaction rate actually increases with increasing initial concentrations of explosives. For example, Priya and Madras⁹⁷ reported the increased initial reaction rates with increasing initial concentrations (from 0–0.7 M) of various nitroaromatic explosives such as NB and 1,3-DNB in both combustion synthesized TiO₂ (CST) and Degussa P-25 TiO₂ suspensions. Priya and Madras⁹⁷ found faster initial reaction rates in the CST mainly due to the higher surface area, lower band gap and higher hydroxyl species content of CST compared to that of Degussa. The effects of initial concentrations of explosives on the degradation efficiency in both homogeneous and heterogeneous photo degradation systems were also studied by Herrera-Melián *et al.*¹¹⁶ who reported that solar-TiO₂ photocatalysis combined with adsorption in bench-scale constructed wetland (CW) efficiently degraded up to 200 mg L^{-1} 4-nitrophenol after 4 hour irradiation and 16 hour adsorption whilst higher concentration up to 500 mg L^{-1} 4-nitrophenol required Fenton plus photo Fenton treatment.

Table 3 Summary of direct photo degradation studies of cyclic nitramine and nitroaromatic explosives

Compounds	Radiation Source	Irradiation		Mode	Photo degradation products	Yield, %	Ref.
		t, min	λ , nm				
RDX	Natural sunlight	—	—	Batch	Nitrate (NO_3^-), nitrite (NO_2^-)	Half lives 1–120 days in aqueous solutions and 2–4 months in solid matrices	19
	Simulated sunlight from 1000 W metal halide lamp	8400	170–2200	Batch	Nitrous oxide (N_2O), NO_2^- and 4-nitro-2,4-diazabutanal	99% degradation of 8.45 μM RDX in aqueous solution was achieved	47
	150 W Xe short arc	90	254	Batch	1,3-Dinitro-1,3,5-triazacyclohex-5-ene, 1-nitro-1,3,5-triazacyclohex-3,5-ene	95% degradation of 170 μM pure RDX in aqueous solution was achieved	76 and 77
HMX, RDX, tetryl, TNT, 2,4-DNT, 2,6-DNT, TNB, DNB, NB	125 W high-pressure mercury	—	—	Continuous-flow	Peroxy nitrite	—	50
RDX, CL-20	1000 W Hg-Xe arc	5	—	—	$\cdot\text{NO}_2$ radical	In perdeutero-dimethylsulfoxide (DMSO-d_6) solution, free $\cdot\text{NO}_2$ production ratio was 1 : 1 for RDX and 4 : 1 from CL-20	78
2,4-DNT	125 W medium pressure mercury	60	—	Batch	—	In aqueous solution, 45% removal of DNT after 1 hour, 39% removal of total organic carbon (TOC) after 2 hour and 18% removal of total nitrogen (TN) after 2 hour was achieved	79
2-MNT, 2,4,6-TNT, 2,4-DNT, 2,4-DNBA	Simulated sunlight from 1500 W xenon lamp	240–480	290–800	Batch	Intermediate product of degradation of TNT was 5-amino-2,4-dicarboxy-3,3,5-trinitroazoxybenzene	100% degradation of MNT, TNT and DNT in aqueous solutions after 8 h irradiation at 700 W m^{-2} was achieved; 10% degradation of DNBA at that time	80
2,6-DNT, TNP	Simulated solar radiation (SSR)	4320	200–800	Batch	—	In sea water solution, 100% degradation for 2,6-DNT was achieved in 72 h; no photo degradation observed for TNP in sea water	81
2,4-DNT, 2,6-DNT	Solar simulator from 1.5 kW Xe lamp	300	<305	—	Dinitrobenzaldehydes and dinitrobenzoic acids	In sea water, 85% and 27% degradation of 55 μM 2,6-DNT and 2,4-DNT, respectively was achieved	82
	Solar simulator from 1.5 kW Xe lamp	360	>295	Batch	—	In sea water, 83% and 42% degradation of 0.06 mM 2,6-DNT and 2,4-DNT, respectively was achieved	83

Table 3 (Contd.)

Compounds	Radiation Source	Irradiation		Mode	Photo degradation products	Yield, %	Ref.
		<i>t</i> , min	λ , nm				
RDX, TNT	150 W halogen	30	—	—	2-Aminodinitrotoluene and 4-aminodinitrotoluene from 10 μg TNT; RDX degradation products were reported to be completely volatilized	—	51
2,4,6-TNT	Natural sunlight	—	>400	Batch	3,5-Dinitroaniline (3,5-DNA) and 1,3,5-TNB	In aqueous solution, half life of 50 μM TNT in the presence of 1 μM riboflavin photosensitizer was 21.87 min	84
	Natural sunlight	—	—	Batch	1,3,5-TNB in absence of riboflavin, 1,3,5-TNB and two unknown intermediates in presence of riboflavin	In surface fresh water solution, half life of 20 mg L^{-1} TNT in the presence of 1 μM riboflavin photosensitizer was 23.96 min	85
NB	Xe [*] excimer	60	172	Batch	<i>p</i> -Benzoquinone, phenol, <i>o</i> -nitrophenol, 1,2-benzenediol, <i>p</i> -nitrocatechol, <i>m</i> -nitrophenol, <i>p</i> -nitrophenol	57% of 2.44 mM aqueous solution of NB was degraded in 60 min	48
	20–25 ps tunable Laser	—	250, 266 and 280	—	10 ⁶ molecules per cm ³ NO per pulse	NB dissociation rate in gas phase was 1.7 $\times 10^7 \text{ s}^{-1}$ at 266 nm. NB was excited to higher absorption band at 250 and 266 nm than 280 nm from its ground state	86
DNAN	3 different set-up: UVA, UVB and a solar simulator 1700 W Xe	—	UVA (316–400 nm), UVB (280–315 nm), solar simulator (300–400 nm with cut-off filter <300 nm)	Batch	NO ₃ ⁻ , NO ₂ ⁻ and 2,4-dinitrophenol	In aqueous solution, half-lives of 0.7, 0.37 and 0.11 days were achieved for 1 mg L^{-1} DNAN in sunlight, UVA and UVB, respectively	46
	Solar simulator	1440	—	Batch	2-Hydroxy-4-nitroanisole and 2,4-dinitrophenol were intermediate products; at complete degradation, each mole of DNAN yielded 0.7 M NO ₃ ⁻ , 1 M NH ₄ ⁺ , total of 0.9 M HCHO and HCOOH	In aqueous solution, 100% degradation was achieved after 21 days of exposure	87
HNS	10 ns Nd-YAG laser	—	532	—	NO ₂ -ONO isomer of HNS	—	88

Table 4 Summary of homogeneous photo degradation studies of cyclic nitramine and nitroaromatic explosives

Compounds	Radiation Source	Irradiation		Mode	Oxidiser and/or sensitizer used	Photo degradation products	Yield, %	Ref.
		t, min	λ , nm					
TNP, AP, 2,4-DNT, tetryl, 2,4,6-TNT, RDX and HMX	40 W UV	25–90	254	Batch	H_2O_2 (0.29 μM) + Fe^{2+} (0.09–0.72 mM)	—	In aqueous solution, the residual TNP, AP, DNT, TNT, tetryl, RDX and HMX were 6.76%, 4.65%, 67.1%, 19.5%, 55.6%, 7.1% and 76.1%, respectively	60
CNB	Low pressure Hg (15 W and 90 W)	4–35	—	Batch and continuous-flow	$\text{H}_2\text{O}_2/\text{O}_3$	Cl^- , NO_3^- and CO_2	In aqueous solution, 95% degradation of 90 μM CNB was achieved in 35 min in batch mode (UV + 1 mM H_2O_2) and 92% degradation of 25 μM CNB was achieved in 4 min. In continuous-flow mode and in 20 μM aqueous O_3 solution of, 75% degradation of 2.2 μM CNB was achieved in 4 min	53
RDX	150 W Xe short arc	40	254	Batch	H_2O_2	PFBHA (<i>O</i> -pentafluorobenzyl-hydroxylamine) derivatised formamide and urea	98% degradation of 20 μM RDX in aqueous solution	76 and 77
TNT, RDX, HMX	Low pressure Hg UV	2.5	—	Continuous-flow	O_3	<i>N</i> -Hydroxyformamide, nitroformaldehyde	99% degradation of 6.7 μM RDX in aqueous solution	76 and 77
NB, 2,6-DNT	15 W Hg UV	25	254	Batch	H_2O_2 (0.38–65 mM)	—	In aqueous solution, near 100% degradation of 23–55 mg L^{-1} RDX, 4 mg L^{-1} HMX and 29–80 mg L^{-1} TNT	89
NB	Low pressure Hg	10–20	—	Batch	O_3	—	In aqueous solution, 6 $\times 10^{-5}$ M DNT completely degraded in 10 min at pH 7 and 1.2×10^{-4} M NB 93.3% degraded in 20 min at pH 8.5	54
NB	125 W medium pressure Hg	5	>190	Batch	H_2O_2	—	In aqueous solution, 100% degradation of 0.25 mM NB in presence of 10 mM H_2O_2 was achieved	90
1,3-DNB	125 W medium pressure Hg	90	—	Batch	H_2O_2	NO_3^- , NO_2^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$	In aqueous solution, 73.6% degradation of 1.9 mM NB in presence of 11 mM H_2O_2 was achieved	91
1,3-DNB	1 kW medium pressure UV	45	220–580	Batch	H_2O_2	Intermediates such as resorcinol (RS), catechol (CC), hydroquinone (HQ), benzoquinone, nitrohydroquinone (NHQ), 4-nitrocatechol (4-NC), 2,4-dinitrophenol, phenol, 3-nitrophenol as well as final mineralisation products such as NO_3^- , NO_2^- and CO_2	In aqueous solution, around 97% degradation of 0.11 mM 1,3-DNB in presence of 9.3 mM H_2O_2 was achieved in 30 min. Complete mineralisation was achieved in 45 min	92

Table 4 (Contd.)

Compounds	Radiation Source	Irradiation		Mode	Oxidiser and/or sensitizer used	Photo degradation products	Yield, %	Ref.
		t, min	λ , nm					
2-MNT, 2,4-DNT, 2,4,6-TNT	6 W low pressure Hg	—	254	—	$H_2O_2/O_3/H_2O_2 + Fe^{2+}$	—	40% decrease of initial DOC level for 2,4,6-TNT in aqueous solution in presence of 12–14 mM H_2O_2 . Evidences for other UV methods were inconclusive	56
2,4-DNT	125 W medium pressure Hg	60	—	Batch	$H_2O_2/H_2O_2 + Fe^{2+}$	—	In aqueous phase, 90% and 100% removal of 100 ppm DNT in photo-peroxide system and photo-Fenton system, respectively after 1 h 96% and 57% removal of TOC and TN in photo-Fenton system after 2 h irradiation	79
Low pressure Hg UV	—	4	254	Batch	Cationic surfactant cetyltrimethylammonium, bromide (CTAB) with the anionic nucleophile, borohydride (BH_4^-)	2-Methyl-5-nitroaniline, 4-nitrotoluene, 2-nitrotoluene, 4-methyl-3-nitroaniline, 2,4-diaminotoluene, <i>o</i> -toluidine, 1,3-dinitrobenzene, 3-nitroaniline, <i>p</i> -cresol, and 2,4-diaminophenol	In aqueous solutions, 70% degradation of 0.1 mM 2,4-DNT with overall half-life 2.1 min in 3 mM CTAB was achieved	93
MNT, DNT, TNT	—	15–60	254	Batch	$H_2O_2 + Fe^{2+}$	Oxalic acid, CO_2 , NO_3^- and H_2O	95% degradation of TNT in aqueous soil extract was achieved in 60 minutes at pH 3. For MNT and DNT, 15 and 30 minutes were required, respectively to achieve similar degradation at pH 3	57
2,4,6-TNT	Medium pressure mercury	240	254	Batch	Methylated- β -cyclodextrin (MCD), hydroxypropyl- β -cyclodextrin (HPCD), $H_2O_2 + Fe^{2+}$	Ternary complex (TNT-cyclodextrin-iron), oxalic acid and formic acid	In soil extract solution, 95% of the initial TOC value abatement was achieved	63
8×10 W low pressure mercury	—	120	—	Batch	$H_2O_2/H_2O_2 + Fe^{2+}$	1,3,5-Trinitrobenzene, 1-methyl-2,4-dinitrobenzene, 2,5-dinitrobenzoic acid and 1,3-dinitrobenzene	In aqueous solutions, TNT residual ratios were 43.4% and 5% in photo-peroxide and photo-Fenton systems, respectively for 2.4 mW cm^{-2} UV intensity	94
TNP	Natural sunlight as well as 150 W medium pressure Hg UV	120	254	Batch	$H_2O_2 + Fe^{2+}$	NO_3^-	In aqueous solution, >92% of 0.87 mM TNP was mineralised in solar Fenton as well as UV Fenton process at pH 3	95

Table 5 Summary of heterogeneous photocatalytic degradation studies of cyclic nitramine and nitroaromatic explosives

Compounds	Irradiation		λ , nm	Mode	Semi-conductor photocatalyst	Photo degradation products	Yield, %	Ref.
	Radiation Source	t, min						
NB	Xe lamp	240	470	Batch	Ag-Reduced graphene oxide (RGO)	Aniline	100% decomposition of 0.8 mM NB in ethanol solution to aniline in presence of 50 mg Ag-RGO powder	72
	3 W blue LED	Up to 1200	>420	Batch	CdS nanocomposite (Ag-RGO)	Aniline	19–97% decomposition of 10 mM NB in alcoholic solution to anilines in presence of 20 mg CdS nanopowder	96
	125 W high pressure Hg	240	365	Batch	Combustion synthesized nano-TiO ₂	—	87% degradation of 75 mg L ⁻¹ NB in aqueous solution with anatase TiO ₂ loading of 75 mg L ⁻¹ . Hydroxy and chloro substitution on NB accelerated the degradation rate while nitro substitution on NB decelerated the photo degradation rate	97
1,3-DNB	125 W high pressure Hg	150	<340	Batch	TiO ₂	Nitrohydroquinone, <i>p</i> -benzoquinone, nitrophenols (NPhOH), nitrosobenzene, dinitrobenzenes, CH ₃ COO ⁻ , HCOO ⁻ , NO ₃ ⁻	Around 100% degradation of 3 μ M NB in aqueous solution with anatase TiO ₂ loading of 2.5 g L ⁻¹ . Chemical yields of 2-, 3- and 4-NPhOH were 6.3%, 7.5% and 6%, respectively at irradiation times corresponding to 25 min, 35 min and 45 min	98
TNP	125 W low pressure UV	240	254	Batch and continuous-flow	TiO ₂	<i>o</i> -, <i>m</i> -, <i>p</i> -Nitrophenol, 2,4-dinitrophenol, CO ₂ , H ₂ O	65% degradation of 1,3-DNB in aqueous solution with 0.2% (w/v) anatase TiO ₂ loading was achieved	99
	500 W super-high pressure Hg	60–180	330–390	Batch	TiO ₂	NO ₃ ⁻ , formic acid and acetic acid	98% degradation of 0.2 mM aqueous solution of TNP in 60 min whilst 60% degradation of 1 mM aqueous solution of TNP in 180 min with anatase TiO ₂ loading of 75 mg in 25 mL sample (w/v); 33% TOC of 1 mM TNP reduced in 240 min whilst complete reduction of TOC of 0.2 mM TNP in 120 min	100
RDX	Simulated sunlight and medium pressure Hg	120	—	Batch	ZnO, TiO ₂	Formic acid, CO ₂	120 min UV irradiation resulted 100% degradation of 1 mM TNP and 15 min UV irradiation resulted 100% degradation of 0.1 mM TNP, both in 2 g L ⁻¹ ZnO suspension. In sunlight, 80 hour irradiation was required to achieve 90%, 80% and 55% degradation of 0.1 mM TNP through ZnO, TiO ₂ and direct photolysis, respectively	101
	Simulated sunlight	120	400–800	—			When ACF cloth loaded with nano-TiO ₂ immersed in simulated	67

Table 5 (Contd.)

Compounds	Radiation Source	Irradiation		Mode	Semi-conductor photocatalyst	Photo degradation products	Yield, %	Ref.
		t, min	λ , nm					
RDX, HMX	415 W/05 UV	480	300–450	Batch	Nano-TiO ₂ (anatase : rutile = 1 : 1) on activated carbon fibre (ACF) cloth TiO ₂	—	wastewater solution containing 40 mg L ⁻¹ RDX, 95% degradation of aqueous RDX was achieved at pH 7.4, 13.7% RDX and 0% HMX degradation in 1 : 100 diluted sludge solution was achieved with 1 g L ⁻¹ TiO ₂ loading	73
	100 W Hg and 500 W halogen	120	—	Batch	ZnS doped with Cu (Zn _{0.95} Cu _{0.05} S)	—	At pH 7, 91% and 93% degradation of 40 mg L ⁻¹ RDX and 4 mg L ⁻¹ HMX in aqueous solution, respectively was achieved with 150 mg L ⁻¹ photocatalyst loading	102
	15 W UV	150	254	—	TiO ₂	HCOO ⁻ , NO ₃ ⁻ , NO ₂ ⁻ and NH ₄ ⁺	At pH 7, 20% reduction in TOC for 20 mg L ⁻¹ RDX and 60% reduction in TOC for 5 mg L ⁻¹ HMX in aqueous solution was achieved with 0.7 g L ⁻¹ TiO ₂ loading	103
NTO	—	180	>290	Batch	TiO ₂ P25 (Degussa)	NO ₃ ⁻ and NO ₂ ⁻	100% degradation of 150 mg L ⁻¹ NTO in aqueous solution was achieved with 0.4 g L ⁻¹ TiO ₂ loading	104
2,4,6-TNT	8 W UV	210	254	Batch	TiO ₂ -SiO ₂ aerogel + H ₂ O ₂ (0.35 mM)	—	99% mineralisation of 100 mg L ⁻¹ TNT in aqueous solution with 0.3 g L ⁻¹ TiO ₂ -SiO ₂ (1 : 1) aerogel powder loading was reported	105
	15 W UV	150	254	Continuous-flow	TiO ₂	CH ₃ COO ⁻ , HCOO ⁻ , NO ₃ ⁻ , NO ₂ ⁻ and NH ₄ ⁺	At pH 7, 100% degradation of 30 mg L ⁻¹ TNT in aqueous solution with 1 g L ⁻¹ TiO ₂ loading	106
	500 W halogen + 9 W UV	35	254, 365, >400	Batch	TiO ₂ , WO ₃ /TiO ₂ , Au/TiO ₂ and Au/WO ₃ /TiO ₂ in presence of O ₃ or O ₂ -O ₃ mixture	—	At pH 7 and at 254 nm wavelength, 100% degradation of 0.53 mM TNT in aqueous solution in presence of O ₂ -O ₃ with 1 g L ⁻¹ loading of Au/WO ₃ /TiO ₂ photocatalyst	107
	200 W Hg UV	300	>290	Batch	TiO ₂	NO ₃ ⁻ and NH ₄ ⁺	50 mg L ⁻¹ TNT in aqueous solution was degraded 98% in 60 min but 100% mineralisation of degraded TNT products required 300 min irradiation in O ₂ bubbled TiO ₂ slurry with 0.1 g L ⁻¹ TiO ₂ loading	108
	400 W low pressure Hg UV	25–90	—	Batch	TiO ₂	Trinitrobenzene, 3,5-dinitroaniline, 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene	With 1 g L ⁻¹ TiO ₂ loading, 100% oxidative degradation of aqueous solution of 50 mg L ⁻¹ TNT in absence of 1% methanol was achieved in 30 minutes. However, 100% reductive	109

Table 5 (Contd.)

Compounds	Radiation Source	Irradiation		Mode	Semi-conductor photocatalyst	Photo degradation products	Yield, %	Ref.
		t, min	λ , nm					
Red water containing 2,4,6-TNT, 2-MNT, 4-MNT, 2,6-DNT, 2,4-DNT, 2,5-DNT, 1,3,5-TNB	450 W medium pressure Hg UV	60	>340	Batch	TiO ₂	1,3,5-TNB	degradation of TNT in presence of 1% methanol was achieved in 90 minutes With 0.25 g L ⁻¹ TiO ₂ loading, 100% degradation of aqueous solution of 50 mg L ⁻¹ TNT at both pH 5 and 8.5. To the contrary, 60% mineralisation of 50 mg L ⁻¹ TNT at pH 8.5 compared to 90% mineralisation of 50 mg L ⁻¹ TNT at pH 5	110
Red water containing 2,4,6-TNT, 2-MNT, 4-MNT, 2,6-DNT, 2,4-DNT, 2,5-DNT, 1,3,5-TNB	500 W Hg-W	300	—	Batch	ZnO : Cu ₂ O (4 : 2.5) on diatomite	1,3,5-TNB	With 5 g L ⁻¹ photocatalyst loading, 72.8% of red water degraded in 420 nm wavelength	1
DNT	300 W Xe	240	250–380	Batch	H ₃ PW ₁₂ O ₄₀ /TiO ₂ and H ₄ SiW ₁₂ O ₄₀ /TiO ₂	—	At pH 2 with 0.8 g L ⁻¹ H ₃ PW ₁₂ O ₄₀ /TiO ₂ catalyst loading, 95% degradation of aqueous solution of 40 mg L ⁻¹ DNT was reported	111
TNR	15 W UV	30	254	Continuous-flow	TiO ₂ + H ₂ O ₂	TNT, CO ₂ , NO ₃ ⁻	With 1 g L ⁻¹ TiO ₂ loading and in presence of 10 mM H ₂ O ₂ , 90% degradation of aqueous solution of 0.1 mM TNR was achieved but 40% TOC from the degradation products of TNR was removed	75
NB, 2,4,6-TNT, 1,3,5-TNB, DNT, DNB	150 W Xe	10–20	>320	Batch	TiO ₂	In neutral and alkaline pH, 1,3,5-TNB was the intermediate product of 2,4,6-TNT photodegradation and 1,3-DNB was the main product of 2,6-DNT photodegradation. In acidic pH, no such products were observed	With 1 g L ⁻¹ TiO ₂ loading, 16% and 4% degradation of aqueous solution of 100 μ M 2,4,6-TNT, 1,3-DNB and 1,3,5-TNB in 20 minutes, respectively at pH 3. 20% and 28% degradation of 100 μ M 2,6-DNT and NB in 10 minutes, respectively at pH 3	112
TNT and NB mixture	15 W high pressure Hg	60–300	>290	Continuous-flow	TiO ₂ + O ₂	—	With 0.6 g L ⁻¹ TiO ₂ loading and continuous bubbling of O ₂ , 90% degradation of aqueous solution of 50 mg L ⁻¹ TNT and 30 mg L ⁻¹ NB mixture was reported in 60 minutes at pH 6.5	113

Table 6 Effects of pH and incident light intensity on the initial reaction rates ($\mu\text{M L}^{-1} \text{min}^{-1}$) of nitroaromatic explosives (100 μM) with 1 g L^{-1} TiO_2 suspension (partially adapted from Dillert *et al.*¹¹²)

Compounds	Light intensity, $\mu\text{M photons per min}$	Initial reaction rates, $\mu\text{M L}^{-1} \text{min}^{-1}$						
		pH 3	pH 4	pH 5	pH 7	pH 9	pH 10	pH 11
2,4,6-TNT	3.5	1.13						1.6
	3.1	0.94	1.01	1.19	1.31	1.2	1.26	1.19
	2.6	1.13	1.19	1.19	1.13	1.1	1.22	1.3
2,4-DNT	3.5	3.24						2.06
2,6-DNT	3.1	2.37						1.66
1,3,5-TNB	3.9	0.38	0.39	0.38	0.32	0.3	0.3	0.22
	2.9	0.32	0.35	0.32	0.45	0.33	0.28	0.29
1,3-DNB	3.0	1.95	0.91	0.81	0.82	0.83	0.93	0.74
1,4-DNB	3.1	1.2						0.83
NB	3.0	3.96	3.5	4.19	4.01	3.79	4.2	3.31

pH

Dillert *et al.*¹¹² demonstrated the fact that whilst pH did not affect the initial reaction rate of a wide range of nitroaromatic explosives in TiO_2 suspensions, pH of the suspension had a pronounced effect on the degradation pathways of these nitroaromatic explosives. For example, at pH 9 and pH 11, about 18% of the reacted 2,4,6-TNT were identified as 1,3,5-TNB after 10 minutes of irradiation, in acidic media, to the contrary, no 1,3,5-TNB was found. Similar observations were made in the degradation of 2,6-DNT where 1,3-DNB was identified as an intermediate in alkaline but not in acidic suspensions. Recently, Sisco *et al.*¹¹⁷ also re-established the fact that salinity alone had a negligible impact on the degradation of TNT and RDX in aqueous solutions and RDX was more stable than TNT in aqueous solutions after 3 days of UV exposure. Table 6 is reproduced from Dillert *et al.*¹¹² to demonstrate the relatively unchanged initial reaction rate for a number of nitroaromatic compounds at acidic and alkaline pH.

Future direction of application of photo degradation in explosive remediation

The future direction of application of photo degradation in remediation of extremely hazardous organic substances such as explosives will rely on the integration of engineering advancements facilitating the pilot or industry scale application of following photo-oxidative processes with principles of photochemistry:¹¹⁸

- UV only.
- UV + Fe^{2+} + H_2O_2 .
- UV + H_2O_2 .
- UV + O_3 .
- UV/visible light + new generation semiconductors.

In this context, the recent advances of the continuous-flow photochemistry have been described as the next generation mean for 'rapid, safe and efficient' application of photon sciences in a number of industries such as, water treatment, polymer synthesis, nanoparticle and small molecule synthesis.¹¹⁹ It is important to note that all of the above listed photo-oxidative processes can be applied in both batch photo

reactors and continuous-flow photo reactors. At present the batch photo reactors overwhelmingly outnumber continuous-flow photo reactors in the context of large scale application of photo degradation. This could be attributed to lack of research studies regarding the effects of the irradiation time, radiation sources, radiation and mass transport constraints as well as solvent constraints on the quantum yields of various photochemical reactions to facilitate "scale-up" in continuous-flow photo reactors.¹²⁰ However, the recent evolution of micro-reactor technology and its impact on continuous-flow photochemistry have the potential to overcome the "scale-up" issues encountered in continuous-flow photo reactors.¹²¹ In this context, Su *et al.*¹²² demonstrated 2^n ($n = 0, 1, 2, 3$) parallel micro photo reactors to scale-up the photocatalytic aerobic oxidation of thiols to disulfides with excellent yield result. Various homogeneous and heterogeneous photocatalytic reactions in continuous-flow micro photo reactors with comparable yields at a much faster rate compared to batch photo reactors were reported by Oelgemöller.¹²¹ Additionally, recent advances in the development of light emitting diodes (LEDs) in vacuum UV range with high radiometric energy efficiency¹²³ as well as LED based accurate and facile techniques to measure the radiometric outputs of different light sources¹²⁴ will surely play a significant role in regards to the development of highly energy efficient light sources at low wavelength particularly in industrial applications of continuous-flow photochemistry in coming decades. Nonetheless, the remediation of cyclic nitramine and nitroaromatic explosives in liquid form using the micro photo reactor technology is not reported yet and it is envisaged that the requirement of fast, safe, green and cost effective remediation of these hazardous explosives in liquid form will surely draw researchers' attention into the integration of continuous-flow micro photo reactor technology with the aforementioned photo-oxidative processes.

Neither homogeneous nor heterogeneous photocatalytic systems currently have complete upper-hand for the degradation of nitroaromatic explosives. While the electron-hole recombination is a major and well-known disadvantage in large scale heterogeneous photocatalytic systems, sustainable methods to suppress electron-hole recombination process in

Table 7 A qualitative comparison of various degradation techniques of EMs in water in terms of existing or future potential (✓) as well as absence of existing or future potential (✗)

Remediation method	Portability	Rapidity	Low cost	Energy efficiency	Environment friendly	Green practice	Scalability
Photo degradation (continuous-flow mode)	✓	✓	✓	✓/✗	✓	✓/✗	✓
Photo degradation (batch mode)	✗	✗	✗	✓/✗	✓/✗	✗	✗
Thermal degradation	✗	✓	✗	✗	✗	✗	✓
Bio degradation	✗	✗	✓	✓	✓/✗	✓	✗
Acid degradation	✗	✓	✗	✓	✗	✗	✗

graphene modified TiO₂ photo catalytic systems using cheap industrial organic waste products such as, glycerols were investigated by Ibadurrohman and Hellgardt.¹²⁵ Recently, significant efforts have also been made to shift the light sensitivity of TiO₂ from UVA region to visible region through chemical additives (electron donors and suppression of backward reaction), noble metal loading, ion doping, sensitization and metal ion-implantation with a view to produce visible light responsive TiO₂ or VLR-TiO₂.^{126,127} However, efforts to increase the quantum efficiency of VLR-TiO₂ under solar light is still in its infancy¹²⁶ and hence, practical applications of these technologies for remediation of cyclic nitramine and nitroaromatic explosives in large scale are currently not viable. Balkus Jr¹²⁸ introduced nanoparticles in a variety of shapes including nanotubes, nanorods as well as quantum dots for heterogeneous photocatalysis in various applications including environmental remediation. In this context, Eskandari *et al.*⁹⁶ illustrated that CdS nanostructures under visible LED light sources degraded various aromatic nitro compounds to corresponding amines with maximum irradiation time up to 20 h and percentage yield ranged from 40% to 97%. The compromise between photoabsorption efficiency and quantum efficiencies of CdS nanostructures under visible LED light sources might have played a role in the prolonged irradiation time as reported by Eskandari *et al.*⁹⁶ Recently, a series of mesoporous materials such as, H₃PW₁₂O₄₀/TiO₂, Y-H₃PW₁₂O₄₀/TiO₂ and La-H₃PW₁₂O₄₀/TiO₂ were introduced by Liu *et al.*¹²⁹ for rapid and environmentally safe degradation of 2,4-DNT and 2,6-DNT. Hence, this review envisage that the future of application of photo degradation in remediation of hazardous photo degradable explosives relies on several research domains, namely, continuous-flow photochemistry, micro photo reactor technology incorporating energy efficient light sources at low wavelength as well as advances in photosensitive nanostructure development. Additionally, continuous-flow photo degradation has the potential to incorporate rapid, energy efficient, cost effective, portable and green remediation practices not only for effluents from military ranges and ammunition plants but also for the remediation of water in swimming pools, rain water tanks, surface water reserves, fish tanks and ponds used in fisheries industries as well as wastewater from agricultural, livestock and poultry industries. With the advent of energy efficient light sources, green reagents and environmentally safe photocatalysts, the principles of continuous-flow photochemistry will strengthen the futuristic views of cheap and portable

solution for 'scaling-up' the yield of photo degradation in minimal time through direct, homogeneous or heterogeneous photo degradation, where the resultant reactive species from photo degradation will be utilised for remediation of water. In light of the discussions based on future directions of remediation of EMs in water using photo degradation, Table 7 illustrates a qualitative guidance for chemists and remediation practitioners to compare photo degradation with the traditional techniques.

Conclusions

Three types of photo degradation techniques namely direct, homogeneous and heterogeneous photo degradation can be applied for remediation of cyclic nitramine and nitroaromatic explosives. The percentage yield of degradation and degree of mineralisation through photo degradation are influenced by radiation sources, irradiation time, photocatalysts as well as important physical-chemical parameters such as pH and initial substrate concentrations. While the photo degradation of these explosives in batch mode are widely practiced at present, the need for 'fast, safe, cost effective, and energy efficient' remediation of these hazardous explosives has resulted significant advances towards the next generation photo degradation technology. In this context, the recent advances in the synthesis of photosensitive nanostructures as well as highly energy efficient light sources at low wavelength (*e.g.*, deep UV LED) possess the potential to facilitate "scale-up" in continuous-flow micro photo reactors incorporating direct, homogeneous or heterogeneous photo degradation processes.

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