Photochemical oxidation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in aqueous phase

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Abstract

Degradation of RDX in aqueous phase was investigated using photo per oxidation and photo-Fenton oxidation. Destruction and mineralization of RDX were compared for both processes. The oxidation rate was influenced by the amount of H_2O_2 and iron salt. In photo per oxidation, H_2O_2 at 26.5mM concentration was found to give the best possible elimination (97.5% in 30 minutes). It was found that the photo-Fenton process was more efficient than the photo per oxidation process. In photo-Fenton oxidation, the addition of 3 ml of Fenton's reagent at 3:1 ratio (H_2O_2: Fe^{2+}) resulted in the destruction of RDX to below detectable level in 30 minutes of irradiation time. The time taken for complete mineralization of RDX in terms of TOC, TN and COD removal was 60 minutes. NO_3^- and NO_2^- were the major ionic species produced and trace amounts of NO_2 gases were produced. RDX degradation was found to follow first order reaction kinetics.
Keywords: RDX, photo-oxidation, direct photolysis, photo peroxidation, photo Fenton oxidation, mineralization.

1 Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine is a very important secondary explosive, known by various names such as RDX ('Research Development Explosive'/ 'Royal Demolition Explosive' in Anglo Saxon literature), cyclonite, hexogen and t_4. RDX has been widely used as an explosive since the early 1900s and achieved great importance during 'World War II' as a constituent of many explosive mixtures from which a high power was required. RDX is 1.3 times powerful in explosive properties as compared to tri nitro toluene (TNT) [1]. RDX dissolves

in water very slowly and also evaporates very slowly from water. Disposal of wastewater from military ammunition plants leads to contamination of water and more so if there are spills and leaks from improper disposal at these plants or at hazardous waste sites. The major toxicological effects observed on exposure to RDX are nausea, irritability, convulsions, unconsciousness and amnesia in humans. The United States Environmental Protection Agency (USEPA) has established the drinking water limit for RDX as 0.030 μg/L [2]. Therefore, it is vital to treat this contaminant before discharge into water bodies.

RDX present in wastewater can be removed by adsorption through granular activated carbon [3], alkaline hydrolysis [4], microbial degradation [5] etc. All these treatment methods do not result in complete destruction as the contaminant is merely transferred from one phase to the other. Treatment methods based on the photo-oxidation principle on the other hand result in complete destruction, as powerful hydroxyl radicals (E^o=2.8V) are produced during these processes, which oxidise the contaminant to simpler products such as CO_2, H_2O and non-toxic molecules [6]. Photo-degradation processes for treating a variety of refractory and toxic organic compounds have been successful; RDX was found to degrade by direct photolysis (Burrows et al. [3]) and photo-oxidation with H_2O_2 [7]. However, no information is available on the comparative efficiency of various photo degradation processes in degrading RDX. Hence the present study has been undertaken to carry out extensive observations on photo-degradation of RDX by direct photolysis, photo-peroxidation and photo-Fenton oxidation.

2 Experimental details

2.1 Irradiation experiments

Studies were conducted in an annular type photochemical reactor of 1 L capacity. The reactor details were discussed elsewhere [9]. RDX (99.95% pure) was obtained from the High Energy Materials Research laboratory (HEMRL), Pune. Synthetic solutions of 50 mg/L RDX were prepared in Milli-Q water and 1000 ml of the RDX solution was taken in the photo-reactor and subjected to UV irradiation emitted from a low and medium pressure Hg lamp of varying UV intensity viz. 8, 15 and 25 W and 125, 250 and 400 W respectively. The initial pH of the RDX solution was 6.8. Analytical grade H_2O_2 (30% W/V) and Fenton's reagent (mixture of H_2O_2 and $FeSO_4.7H_2O$) were used as oxidants. The effect of oxidant concentration on photo-degradation of RDX was studied by varying the oxidant dose. H_2O_2 concentration varied from 8.8 to 35.3 mM. The Fenton reagent, a mixture of 30% (W/V) H_2O_2 and 1mM $FeSO_4.7H_2O$ (W/V) was used in three different ratios viz., 1:1, 1:3 and 3:1 for optimising the volume ratio. Experiments were carried out thrice for each set of experimental conditions and mean values have been reported.

2.2 Analytical methods

Samples were taken at specific time intervals and concentrations of RDX, TOC and COD were determined. The RDX concentration was estimated by HPLC

(Perkin Elmer Model-1022) with a photo-diode array detector at 235 nm. Acetonitrile and water were used as the mobile phase (25 : 75) at a flow rate of 1 mL/min and a C8 column was used as the stationary phase. A TOC analyzer (Elementar High TOC-GmbH, Germany) was used for the determination of total organic carbon (TOC) and total nitrogen (TN) on photo-degradation. The COD content was estimated by oxidation with $K_2Cr_2O_7$. In addition to this, ionic species such as nitrite, nitrate evolved during photo-degradation, were monitored using a HACH spectrophotometer. Total gaseous nitrogen oxides evolved during the experiments were measured by the Indian Standard Procedure [10].

3 Results and discussion

3.1 Direct photolysis (UV) of RDX

The effect of UV irradiation on removal efficiency of RDX in aqueous phase was studied without oxidants in direct photolytic experiments. Low pressure (8, 15 and 25 W) and medium pressure (125, 250 and 400 W) UV intensities were evaluated for their performance. It was found that exposure to 8, 15, and 25 W UV lamps resulted in 50, 53 and 69% destruction of RDX after 30 minutes and exposure to 125, 250 and 400 W medium pressure UV intensities resulted in 73.4, 75, and 77% destruction of RDX after 30 minutes (Figure 1).
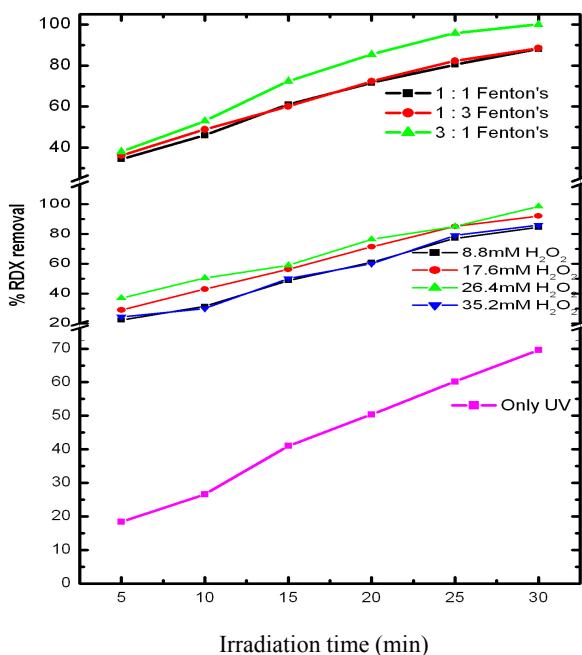

Figure 1: Comparative degradation of RDX by direct photolysis, photo peroxidation and photo-Fenton oxidation.

In direct photolysis, the organic molecule gets excited on absorption of UV photons. It has been reported that [6] a large number of electronically excited organic molecules could transfer an electron to an acceptor present in its complex environment and form free radical ions These radical ions with subsequent recombination or hydrolysis form radicals, which then react with oxygen to form peroxyl radicals, which on further photolysis get converted to partially oxidized intermediates. In the present study, direct photolysis resulted in a slower rate of oxidation of RDX indicating the capability of UV light in activating the organic molecule into more reactive radical species, which are responsible for the destruction process. In general, however, the direct photolytic experiments are of low efficiency and are less effective compared to procedures involving hydroxyl radical generation [6].

3.2 Photo peroxidation (UV/H_2O_2 process)

Experiments were carried out at different H_2O_2 doses in order to optimize the dose of oxidant needed for maximum RDX destruction. The results are graphically illustrated in Figure 1. It is seen from the graph that the rate of destruction of RDX increased with an increase in the initial concentration of H_2O_2. The molar ratio of H_2O_2 to RDX was increased with the increase in the H_2O_2 dose. More hydroxyl radicals were available to attack the organic compound and the rate of reaction was increased. The optimum dose was found to be 26.5 mM, as the maximum RDX degradation (97.5%) was attained at this dose in 30 minutes of irradiation time. However, after the optimum dose (26.5 mM), the rate of degradation declined. At a higher dose, H_2O_2 acts as a scavenger of highly reactive hydroxyl radicals to form hydro peroxyl radicals, which are much less reactive and do not contribute to oxidative degradation of substrate. Increasing the amount of H_2O_2 led to the following competing reaction.

$$OH^\circ + H_2O_2 \longrightarrow HO_2^\circ + H_2O \qquad ...(1)$$

Moreover, the effect of UV is lowered at higher concentrations of H_2O_2, due to competitive absorption of UV light among the molecules of oxidant and contaminant. Thus, by increasing the H_2O_2 concentration above a limiting value, undesirable parallel reactions of H_2O_2 were found to occur leading to a decrease in the rate of RDX destruction, in accordance with earlier observations [11,12].

3.3 Photo-oxidation with Fenton's reagent (UV/H_2O_2 + Fe^{++})

The UV/Fenton system is based on the capture of a photon by an iron salt with its subsequent conversion to ferric ion plus hydroxyl radical [13]. The rate of degradation increased in the presence of ferrous ions, as ferrous ions are catalytic activators in Fenton's reagent and rapid generation of Fe^{2+} from Fe^{3+} resulted in more production of OH radicals.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\circ \quad . \quad (2)$$
$$Fe^{2+} + OH^\circ \longrightarrow Fe^{3+} + OH^- \quad\qquad (3)$$
$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^\circ + H^+ \qquad (4)$$

$$Fe^{3+} + HO_2° \longrightarrow Fe^{2+} + H^+ + O_2 \qquad (5)$$

The percentage removal of RDX as a function of UV exposure is given in Figure 1. Complete removal of RDX was obtained when 3 ml of Fenton's reagent was used at 3:1 ratio along with 25 W UV intensity. Fenton oxidation provoked ring cleavage and subsequent elimination of carbon atoms of RDX as CO_2.

Photo-Fenton system was found to be superior in its performance compared to photo-peroxidation (Figure 1). In the present study, at higher ratios of H_2O_2/Fe^{2+} (3:1), all Fe^{2+} is rapidly converted to Fe^{3+} according to reaction in equation (2). For the Fenton reaction to continue, Fe^{2+} must be rapidly regenerated from Fe^{3+}. Two of the possible reaction sequences yielding Fe^{2+} from Fe^{3+} are given in equations (4) and (5). The reaction rate of these sequences would be lower if Fe^{3+} formed condensed species. It was also observed that, higher level of iron salt also result in brown turbidity that interferes in absorption of UV light in contaminant molecules and results in recombination of OH° radicals. Lower iron concentration gave best results (Figure 1). As Fe^{2+} ions form complexes with other waste effluent components, and downstream removal of iron being difficult, lower concentration of Fe^{2+} is highly desirable [11,14,15].

3.4 Mineralization of RDX

3.4.1 Reduction in TOC and TN values on photodegradation of RDX

The rate of TOC and TN removal from the aqueous RDX solutions was monitored. It was found that the total mineralization in terms of TOC removal under photo per oxidation and photo Fenton oxidation systems was 85.1 and 91.6% respectively and TN removal was 69.1 and 70.7% respectively. Photo-oxidation was extremely effective in accelerating the mineralization of RDX. It is most likely that during photo degradation process, the early oxidation reactions of RDX were governed by Fenton/H_2O_2 and its decomposition products, where as the destruction of the oxidation intermediates is achieved by the joint action of UV and oxidant. Among the two-photo oxidative systems evaluated, maximum TOC and TN reduction was achieved with UV/Fenton system (91.6 and 70.7% respectively in 1.00 hour). The actual mechanism that facilitates the removal of TOC and TN from RDX can be explained by the hydroxyl radical attack on the organic pollutant with the formation of carbon radical intermediates. Subsequently hydroxylated oxidation products are formed that are converted into aldehydes and carboxylic acids and finally via C=C bond fragmentation to CO_2. The rate of mineralization process is strongly influenced by the number of carbon atoms, structure of the individual compound and the rate of formation of lower molecular species [17, 18].

The maximum reduction in TOC level was achieved after 1.00 hour of UV irradiation, whereas the time needed for complete removal of RDX was 30 minutes, i.e., the time needed for the maximum conversion of RDX to CO_2, NO_2^- etc. was more than the time needed for complete destruction of RDX. This confirms that the degradation of RDX to final products occur through formation of lower molecular compounds which in turn are oxidised to CO_2. Similar observation was made on degradation of dimethyl-2,2,2-trichloro-1-hydroxy

ethyl phosphonate and asulam (sodium N-methoxy carbonyl sulfanilamide) wherein the time required for maximum conversion to CO_2 was higher [19]. Studies on different organic contaminants have also confirmed the above finding [20–22]. COD removal on Photo-oxidation of RDX was also monitored and it was found that 93% reduction in COD was obtained in the samples subjected to photo-Fenton oxidation.

3.5 Estimation of end products produced during photo-oxidation of RDX

Ionic species and gases formed during the photo-oxidation of RDX were monitored in the middle (15 minutes) and at the end of the photochemical reaction process (30 minutes and 1.0 hour). The results are given in Table.1. NO_3^- and NO_2^- were the major ionic species formed and trace amounts of NO_2 gas also evolved. It is important to note that the nitrite ion concentration was more at 30 minutes and at the end of the photochemical reaction, i.e. at 60 minutes, the concentration of nitrite ion reduced almost to zero. Whereas the nitrate ion concentration was very less at 30 minutes and at the end of the photo-oxidation it increased. This decrease in concentration of nitrite ion and increase in concentration of nitrate ion at the end of the process is due to the oxidation of nitrite to nitrate. The above observation was confirmed by measuring the pH of the treated solution. The pH of the reaction media decreased from neutral to acidic range. This is because the nitrogen contained in the RDX molecule could partially lead to nitric acid formation, which is proved by the presence of nitrate ions as discussed above. Similar study on TiO_2 photo catalytic degradation of TNT reported the oxidation of TNT to initially nitrite and finally to nitrate [23].

Table 1:   End-products formed on photo-oxidation of RDX.

Ionic Species	UV + H_2O_2	UV + Fenton
30 minutes		
NO_2^- - N (mg/L)	13.81	13.5
NO_3^- - N (mg/L)	3.92	4.80
60 minutes		
NO_2^- - N (mg/L)	3.30	2.80
NO_3^- - N (mg/L)	14.00	14.20
Gaseous NOx (mg/L)	1.0	1.2
Total Nitrogen (mg/L)	18.3	18.2

3.6 RDX destruction–reaction kinetics

Photo-oxidation of RDX may be represented as follows

$$RDX \xrightarrow{\text{UV + Oxidant}} \text{Products} \quad \dots \quad \text{(Eq.10)}$$
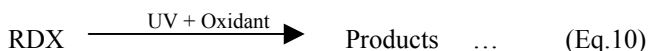
A linear plot of {-ln (C_t/C_0)} (Figure 2.) shows that the rate of degradation of RDX is a pseudo first order reaction assuming that the degradation is

independent of hydroxyl radical concentration. The average over all rate constants under the UV/H_2O_2 and UV/Fenton systems were found to be 0.12 and 0.15 min^{-1} respectively. Half-life values for both the systems were calculated to be 5.7 and 4.6 minutes respectively.
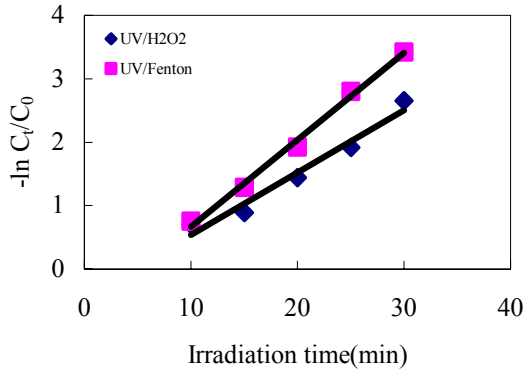

Figure 2:   First order reaction kinetics of RDX.

4   Conclusion

Photo-oxidation with H_2O_2 /Fenton's reagent is highly efficient for destruction and mineralization of RDX. The oxidation rates were influenced by the amount of H_2O_2 and iron salt. In photo peroxidation, H_2O_2 at 26.5mM concentration was found to give the best possible elimination. In photo-Fenton oxidation, addition of 3 mL of Fenton's reagent at 3:1 ratio (H_2O_2: Fe^{2+}) resulted in destruction of RDX to below detectable level. Direct photolysis resulted in slower rate of degradation. On comparison of two photo-oxidative processes, it was found that photo-Fenton process is more efficient than photo peroxidation. In 30 minutes of UV irradiation, complete destruction (below detectable level) of RDX occurred in the photo-Fenton process. In UV/H_2O_2 process, 97.5% destruction of RDX was found to occur. Prolonged exposure (60 minutes) to UV irradiation resulted in complete mineralization of RDX to simpler products. In the photo-Fenton process, reduction in TOC, TN and COD contents were found to be 91.6%, 70.7% and 93% respectively. In the photo peroxidation process, reduction in TOC, TN and COD contents were found to be 85.1%, 69.1% and 88.7% respectively. NO^{2-} and NO^{3-}were the major ionic species produced and trace amounts of NOx gases were also produced. RDX degradation was found to follow first order reaction kinetics.

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