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Radiolytic degradation of explosives in aqueous solutions and 'red' wastewater

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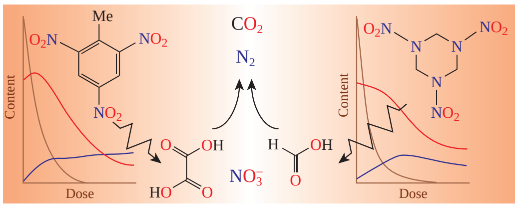
Electron beam treatment would cause conversion of trinitrotoluene and 1,3,5-trinitrohexahydro-1,3,5-triazine into biodegradable products and thus can be employed for the practical decontamination of 'red' wastewater in combination with bio-treatment.



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The production of explosives generates toxic red wastewater called 'red water', which contains nitro derivatives of toluene and/or 1,3,5-triazine, in particular 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX).[1,2] The components of red water are stable, they are easily accumulated by plants and living organisms, and are dangerous, including carcinogenic, even in trace amounts. Trinitrotoluene and its isomers can cause mutations in microorganisms as well as acute and chronic diseases of the liver, skin, eyes, blood and nervous systems of people.[3] As a rule, the removal of nitro derivatives from red water is carried out by evaporation and incineration methods. However, this treatment requires too much heat and generates toxic products in the form of ash and gases. Alternatively, various methods combined with biological treatment were developed.[1–4]

Radiolysis is also capable of degrading organic nitro-containing compounds, which has been demonstrated using pulsed radiolysis, gamma radiation, and X-rays.[4–7] Moreover, radiolysis is suitable for improving the post-radiation biological treatment of wastewater with nitrogen-containing compounds.[8] The main prerequisite for effective biochemical degradation of dissolved pollutants is the proximity of COD (chemical oxygen demand) and BOD (biochemical oxygen demand) indexes of wastewater. Radiolysis is just able to lead to the convergence of COD and BOD.[9] Due to the high beam power, electron accelerators are most suitable for continuous radiolysis of wastewater with a high flow rate on an industrial scale. This study for the first time imitates the practical electron-beam treatment (EBT) of aqueous explosive solutions as well as trinitrotoluene-containing red water in the jet mode of irradiation using an industrial type of electron accelerator and subsequent bio-treatment.[†]

Figures 1 and 2 show the radiation-induced change in the composition of aqueous solutions of TNT and RDX, respectively. The observed dose for the half-decay of TNT and RDX is about 10 and 1.8 kGy, respectively. This corresponds to 0.26 and 0.62 molecules per 100 eV (0.027 and 0.064 μmol J^{-1}) degradation yields. Such yield values are typical of a complex transformation mechanism, including competing and back reactions.[11,12]

Undoubtedly, differences in the structures of TNT and RDX determine the difference in their radiation resistance. Conjugated aromatic bonds provide TNT with greater resistance. However, there are similar patterns. Firstly, an increase in the absorbed dose leads to an increase in the biodegradability of the components in both solutions. A decrease in COD and TOC is accompanied by an increase in BOD. The initial ratios of BOD/TOC and BOD/COD in TNT and RDX solutions are less than 0.1, which characterizes these substances as resistant to biodegradation. In turn, at 20 kGy dose, the BOD/COD ratio becomes almost 8 times higher for TNT and 15 times for RDX. A rise in biodegradability may indicate an increase in the degree of the solute oxidation, as was previously observed for nitrogen-containing dyes.[8]

[†] Samples of red water, TNT and RDX were provided by the explosives manufacturer in the Republic of Korea. Solutions containing TNT and RDX (120 and 50 mg dm^{-3}, respectively, with the corresponding solubility being of 130 and 60 mg dm^{-3} at 20 °C) were investigated. The content of TNT, RDX and organic acids was monitored using HPLC (Hewlett Packard 1050 Series). Content of TNT and RDX was determined from the acetonitrile phase using an Acrodisk-13 0.2 μm syringe microfilter (Gelman Sciences, Ann Arbor, MI) and 5 μm reversed-phase column (ZORBAX SB-C18, Agilent Tech., Santa Clarita, CA). Organic acids were analyzed using Supelcogel Bellefonte COD PA column and auto-sampler. The composition of the samples was monitored using GC/MS (electron impact). The red water sample contained about 12 wt% of organic compounds and their sodium salts (including 2,4,5-TNT, 5.0%; 2,3,4-TNT, 2.1%; 2,3,6-TNT, 0.4%; 2,4,6-TNT, traces; hexanitrobenzene, 3.5%; trinitrobenzoic acid, 0.2%; and sodium nitroformate, 0.2%); Na_2SO_3, 4.1%; $NaNO_3$, 6.0%; and $NaNO_2$, 2.9%. Initial indicators:[10] COD = 1490 ± 30 mg dm^{-3}; BOD = = 170 ± 13 mg dm^{-3}; total nitrogen content (TN) = 690 ± 21 mg dm^{-3}; colour (Pt/Co scale) = 68,700 ± 100 degrees; suspended solids = 1350–25 mg dm^{-3}. Red water samples were irradiated after coagulation with $Al_2(SO_4)_3$ and neutralization with NaOH. All samples were irradiated in a jet mode[8] at a flow rate of 5 dm^3 min^{-1} with access of air. The initial dissolved oxygen content in TNT and RDX solutions at pH 7 was 6.0 and 4.5 mg dm^{-3}, respectively. An ELV electron accelerator (2.5 MeV, 40 mA, located at EB Tech, Republic of Korea) served as an irradiator. A copolymer film doped with the phenazine dye, CO PD (F) P-5/50 (GSO 7865-2000) was used for dosimetry.[11]

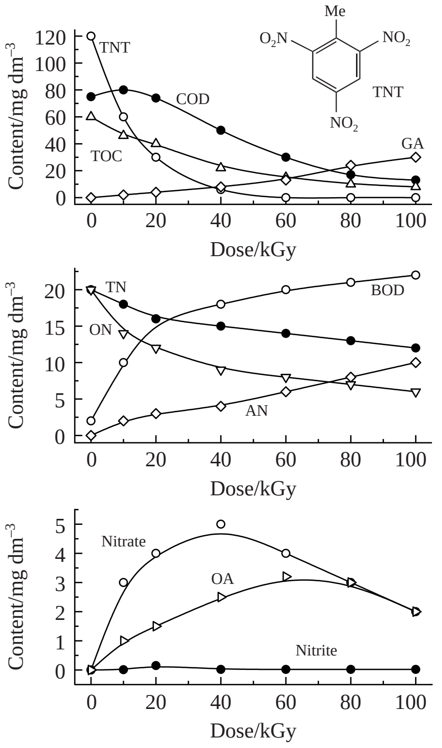


Figure 1 Dose dependence of TNT aqueous solution composition. TN is the total nitrogen content; TOC and ON are the total content of organic carbon and nitrogen, respectively; AN, GA and OA are the contents of ammonium, glyoxalic and oxalic acids, respectively.

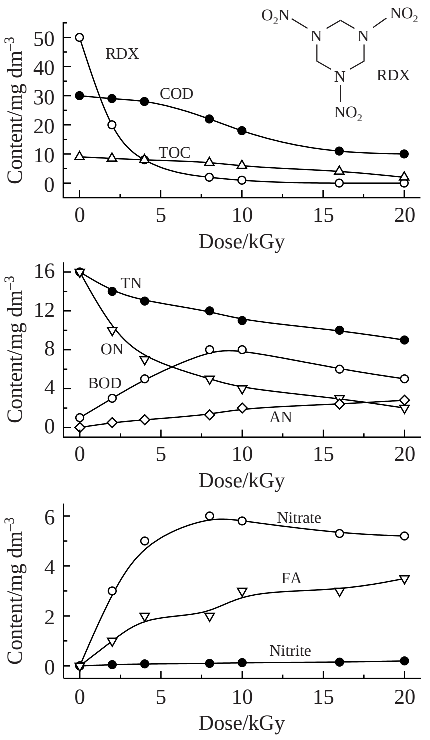


Figure 2 Dose dependence of RDX aqueous solution composition. TN is the total nitrogen content; TOC and ON are the total content of organic carbon and nitrogen, respectively; AN and FA are the contents of ammonium and formic acid, respectively.

Another important consequence of radiolysis is mineralization, *i.e.*, the conversion of TNT and RDX to inorganic products. This process is confirmed by a decrease in TOC and the simultaneous appearance of nitrate in solution. Moreover, the organic nitrogen (ON) content is more dose sensitive than the total nitrogen (TG) content. Thus, the elimination of nitro groups makes an important contribution to mineralization. In addition, a decrease in TOC and TN indicates that carbon and nitrogen compounds are partially removed in the form of volatile products.

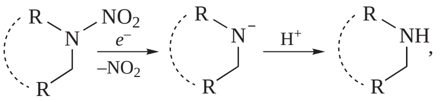
The appearance of glyoxalic and oxalic acids in the case of TNT and formic acid in the case of RDX indicates the cleavage of skeletal bonds (C–C for TNT and C–N for RDX). At the same time, the accumulation of nitrate with increasing dose is much easier than that of acids and ammonium. This means that nitrate is formed at earlier stages *via* a simpler mechanism. At low doses, nitrate accumulates almost linearly with increasing dose, while larger doses lead to a decrease in its content. Such an effect may indicate the involvement of secondary radiolytic products in nitrate degradation. It was previously shown that nitrate in individual solutions is resistant to radiolytic transformations due to back reactions initiated by reductive (hydrated electron e_{aq}^{-} and hydrogen atom $^{\cdot}$H) and oxidative ($^{\cdot}$OH radical) intermediates of water radiolysis:[13,14]

$$\mathrm{NO_3^-} \xrightarrow{e_{aq}^-,\ \mathrm{H}} \mathrm{NO_2^{\bullet}} \xrightarrow{e_{aq}^-,\ \mathrm{H}} \mathrm{NO_2^-} \xrightarrow{e_{aq}^-,\ \mathrm{H}} \mathrm{NO} \xrightarrow{e_{aq}^-,\ \mathrm{H}} \mathrm{N_2O} \xrightarrow{e_{aq}^-,\ \mathrm{H}} \mathrm{N_2}, \quad (1)$$

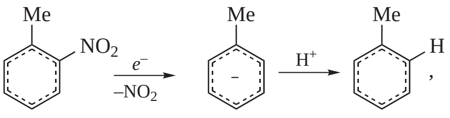
$$\mathrm{NO} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{NO_2^-} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{NO_2^{\bullet}} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{NO_3^-}. \quad (2)$$

However, the presence of formate, which is a selective scavenger of $^{\cdot}$OH, supports process (1) and, as a result, the conversion of nitrate to volatile compounds.[13] Obviously, the appearance of glyoxalic, oxalic and formic acids in irradiated solutions of explosives also weakens process (2). Moreover, like the decrease in TOC, the nonlinear dynamics of acid accumulation with increasing dose (see Figures 1 and 2) indicates their partial conversion to CO_2.[9] The structure of TNT and RDX molecules enables selective capture of intermediates, since e_{aq}^{-} and $^{\cdot}$H more readily react with nitro groups, and the predominant reactions of $^{\cdot}$OH radicals are the hydrogen abstraction from alkyl groups and/or addition to an aromatic ring.

The radiolytic degradation of TNT and RDX is multi-stage. Radiolytic damage leads to a redistribution of bond stability in radicals compared with molecules.[12] As the dose increases, a sequential appearance and disappearance of lighter products recorded chromatographically is observed. Eventually, at a dose of 100 kGy in TNT solution and 20 kGy in RDX solution, organic products are represented only by light acids. The elimination of the nitro group is mainly due to dissociative capture of e_{aq}^{-} or $^{\cdot}$H, as well as the decay of H- and OH-adducts in the case of TNT:



(3)



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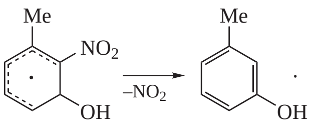


(5)

The main product is $^{\cdot}NO_2$, which is easily converted to nitrate *via* reactions with $^{\cdot}$OH, $^{\cdot}O_2H$, H_2O_2. The formation of nitrite plays a much smaller role (see Figures 1 and 2). Ring opening in TNT and RDX molecules can occur mainly due to the formation of a radical center on one of the ring atoms. In TNT, such radical centers arise mainly as a result of $^{\cdot}$H and $^{\cdot}$OH addition. In RDX, cyclic radicals are formed mainly as a result of hydrogen abstraction

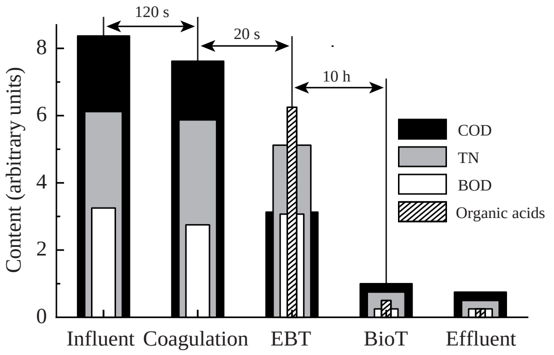
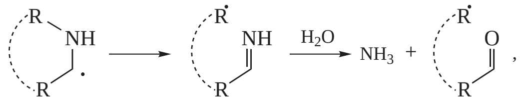
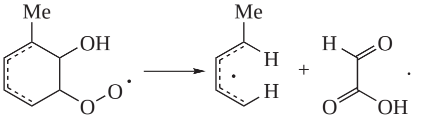


Figure 3 Contribution of coagulation, electron beam treatment (EBT) and bio-treatment (BioT) to the combined decontamination of red water.

by $^{\cdot}$OH or $^{\cdot}$H. As a rule, bond cleavage in the resulting radicals occurs in the β-position relative to the radical center:



(6)



(7)

Intermediates formed *via* reactions of type (3)–(7) participate in further radiolytic transformations, turning into light organic acids and ammonium. Undoubtedly, the formation of acids is facilitated by the complicity of dissolved oxygen.[14]

Figure 3 shows the effect of electron beam treatment in a combined process on a real sample of red water containing TNT isomers. In view of the high content of suspended solids, red water is first subjected to coagulation treatment, and then irradiated. The most significant changes occur at the stages of radiolysis (100 kGy) and post-radiation biological treatment. Electron beam treatment reduces COD by almost a factor of 2.4 and converts the stable nitrotoluenes into a biodegradable form. In particular, the effective conversion of nitrotoluenes (BOD/COD $\leqslant$ 0.1) to light acids (BOD/COD $\approx$ 1) takes place. Hence, the degradation of TNT and its isomers occurs in a similar way. The combined treatment provides a reliable and economical reduction of red water indicators to regulatory requirements (COD $\leqslant$130, BOD $\leqslant$ 120, SS $\leqslant$120, TN $\leqslant$ 60 mg dm^{-3}). Due to the initial presence of nitrates and nitrites, the effect of the dose on red water is slightly weaker than that on the TNT solution. Therefore, red water before practical exposure should be doped with selective, easily mineralizable, scavengers of $^{\cdot}$OH radicals, for example, formate or oxalate.

In conclusion, the present work demonstrates the upgrading of electron beam treatment from the level of fundamental laboratory research to the level of applied modeling of degradation of water-dissolved explosives using an industrial accelerator and flow mode of irradiation. The solutions considered are felicitous systems where there are simultaneously selective scavengers of e_{aq}^- (nitro group) and $^{\cdot}$OH (alkyl group). Denitration steadiness is ensured by maintaining the concentration of $^{\cdot}$OH scavengers, since a decrease in the content of dissolved explosives is accompanied by an increase in the content of small organic acids. Thus, a unique mechanism is realized in which radiolysis not only ensures the degradation of the explosive molecules themselves, but also generates secondary products that intensify this degradation. Radiolysis leads to the mineralization of nitro compounds such as TNT and RDX due to the sequence of denitration and decarboxylation processes. A powerful electron beam generates a high concentration of reactive radicals and, thus, ensures the rapid completion of the multi-stage transformations of dissolved explosives into light biodegradable acids and harmless volatile compounds. Accordingly, electron beam treatment can be a very useful step before biological treatment of explosive-containing solutions and red water. Practical electron beam pre-treatment of real red water is recommended in the presence of light organic acids, which accelerate the degradation of excess nitrates and nitrites.

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