

COMPARATIVE ASSESSMENT OF NUCLEOPHILIC ALKALINE HYDROLYSIS FOR REMEDIATION OF HIGH EXPLOSIVES-CONTAMINATED GROUNDWATER

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Abstract : This study was conducted to assess the feasibility of nucleophilic alkaline hydrolysis using a continuous flow stirred-tank reactor as an ex-situ remediation technology for groundwater contaminated with high explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The reactivity of TNT and RDX had a strong dependence on the reaction pH (11.0 to 11.9) and hydraulic retention time (HRT, 0.5 to 2 days). For the same influent concentration of 1 mg/L, the reaction pH of 11.9 and 2-day HRT, the best nucleophilic alkaline hydrolysis was achieved at 99 and 73% reduction for RDX and TNT, respectively, with the respective half-lives of 0.02 and 0.5 days. Greater and faster removal with less alkaline demand for RDX hydrolysis than TNT hydrolysis was attributed to the structural characteristics and simpler degradation pathway of RDX. Formate and oxalate were produced as the major hydrolysates in alkaline hydrolysis of RDX and TNT, respectively, indicating that alkaline hydrolysis of high explosives occurred through ring cleavage. Therefore, it is concluded that nucleophilic alkaline hydrolysis can be a promising ex-situ treatment technology for remediation of high explosives-, especially RDX-, contaminated groundwater.

Key Words : Alkaline hydrolysis, Continuous flow stirred-tank reactor, Formate, Oxalate, RDX, TNT

INTRODUCTION

Military activities such as the manufacturing, assembling, loading, and disposal of explosive compounds and range training have generated widespread contaminations with explosives and their derivatives.^{1,2)} Among those explosives, 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) have been the most extensively produced nitroaromatic and nitramine

high explosives, respectively, and therefore have been present most abundantly in the environment.³⁾ Due to the adverse effects of TNT and RDX on humans and other natural receptors,^{4,5)} the U.S. Environmental Protection Agency (EPA) has established drinking water health advisory of 2 ug/L for lifetime exposure to TNT and RDX.⁶⁾

TNT is a nitroaromatic explosive with three nitro groups are attached to the toluene ring (Figure 1). The strongly electron-withdrawing nature of nitro-groups in TNT causes a negative inducing effect on the carbon-nitrogen bond and makes the oxygen atoms on the nitro-groups highly electron rich.²⁾ The high electron density

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on the three nitro-groups hinders an electrophilic attack on the ring, resulting in the observed low chemical and biological oxidation of the ring. At the same time, the nitro-groups are highly susceptible to reductive transformation. On the other hand, the presence of three nitro-groups in TNT depletes the electron density of the ring making it a strong π acceptor and allows the ring to undergo π - π or n - π interactions with suitable electron donors.²⁾ The reduced electron density of the ring suggests that the ring is subject to nucleophilic attack by a strong nucleophile such as hydroxide ion (OH⁻).

RDX is a cyclic nitramine with alternating carbon and nitrogen atoms and with nitro-groups bonded to the three ring-nitrogen atoms (Figure 1). The RDX molecule is in a chair configuration: two axial nitro-groups and a single equatorial nitro group per molecule. RDX behaves as a strong Lewis acid, reacting with electron-donating compounds such as OH⁻ that act as base or nucleophile depending on the reaction conditions via the E2 mechanism where proton abstraction and double bonds formation take place simultaneously. Also, nucleophilic substitution of nitro groups by hydroxide ion can occur to cause the RDX molecule to become unstable and thus amenable to further degradation.⁷⁾

Nucleophilic alkaline hydrolysis has been reported to be a potential alternative remediation technology for explosives-contaminated water.⁸⁻¹²⁾ However, these researches were on the determination of hydrolytic kinetics in batch settings. Study on alkaline hydrolysis in a continuous feed system has not been reported and such

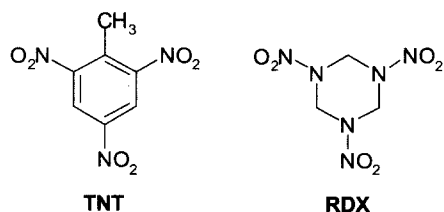


Figure 1. Structure of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).

investigation is in need. This study was conducted to assess the effectiveness of alkaline hydrolysis using a continuous flow stirred-tank reactor (CFSTR) as an ex-situ remediation technology for groundwater contaminated with high explosives TNT and RDX.

MATERIALS AND METHODS

Chemicals

TNT and RDX were obtained from the Halston Army Ammunition Plant, Kingsport, TN, USA. The calibration standards for TNT, RDX and their potential transformation products were purchased from SUPELCO (EPA 8330 Energetic Materials Kit). The potential byproducts tracked by high performance liquid chromatography (HPLC) for TNT alkaline hydrolysis were: 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene, nitrobenzene, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2-nitrotoluene, and 4-nitrotoluene. For RDX alkaline hydrolysis, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) were analyzed. Sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), acetonitrile (CH₃CN), and other chemicals used in the experiment were purchased from Fisher Scientific.

Continuous Flow Stirred-Tank Reactor (CFSTR)

The reactor (BioFlo[®] 3000, New Brunswick Scientific Co., Inc.) was filled with 10 L of reverse osmosis water and stirred at 200 rpm. The solution was initially dosed with 50% NaOH solution to raise the starting solution pH to 11.0, 11.5, and 11.9. The highest pH in the CFSTR was limited to 11.9 because the maximum controllable pH by the BioFlo pH controller was pH 12, with a dead band of 0.1 pH unit. The reaction temperature was kept constant at 25 ± 1°C with a PolyScience Chiller (Model 6305). TNT solution (1 mg/L) was continuously

added to the reactor at flow rates of 5.0, 10.0 and 14.3 L/day, corresponding to HRTs of 2, 1, and 0.7 days, respectively. During the experiment, the reaction pH was maintained constant by the automatic addition of 0.1N H₂SO₄ and 0.2N NaOH solutions by the pH controller. Liquid samples were collected and analyzed for TNT and transformation products as described below. The reaction was continued until three reactor volumes (30 L) had been flushed through the reactor. The same experimental approach was applied for RDX alkaline hydrolysis, except for the flow rate of 18.5 L/day (i.e., 0.54-day HRT) instead of 14.3 L/day. Two experiments were replicated for both TNT and RDX alkaline hydrolysis to assure data quality and showed very close similarity between replicates.

To assure complete mixing, a non-reactive chloride (Cl⁻) tracer was flushed through the CFSTR under the same experimental condition as that used for the alkaline hydrolysis. The experimental *F*-distribution was identical to the theoretical *F*-distribution where a relative concentration of 63.2% was achieved at an HRT of unity. The *F*-distribution is defined as the fraction of input that has left the CFSTR at any time.¹³⁾ Therefore, the CFSTR used was a completely mixed reactor without short-circuiting.

The OH⁻ concentration in the reactor decreased due to dilution with the influent water. Therefore, blank systems (i.e., without explosives) at three different pH levels (11.0, 11.5, and 11.9) were run in order to quantify the amount of OH⁻ added to the reactor to counteract dilution effects only. To ensure that explosives were transformed only by alkaline hydrolysis, a control system was run at pH 6. The explosives concentration profile followed the same *F*-distribution as the non-reactive Cl⁻, indicating that there was neither significant explosives sorption to the CFSTR unit nor substantial losses such as photodegradation during the experiment.

Using the first-order kinetics, the material-balance equation of explosives transformation for

a CFSTR can be expressed as follows:

$$V \frac{dC}{dt} = Q(C_0 - C) - kCV \quad (1)$$

where, *V* is the reactor volume (L), *Q* is the flow rate (L/day), *k* is the pseudo first-order explosives transformation rate constant (min⁻¹) and *C*₀ and *C* are the influent and effluent explosives concentration (mg/L), respectively.¹³⁾ Under nonsteady-state conditions, Eq. (1) changes to

$$\frac{dC}{C_0 - (1 + \theta k)C} = \frac{dt}{\theta} \quad (2)$$

where, $\theta (= V/Q)$ is the HRT (day). Putting *U* as *C*₀/(1 + θk) *C* and integration of Eq. (2) leads to

$$\frac{C}{C_0} = \alpha (1 - e^{-\beta t}) \quad (3)$$

where, α is $1/(1 + \theta k)$ and β is $1/(\alpha \theta)$. Eq. (3) was used to fit the effluent explosives concentration data from the CFSTR over the reaction period of alkaline hydrolysis using nonlinear regression.

Under steady-state conditions, Eq (1) reduces to

$$\frac{C}{C_0} = \frac{1}{1 + k\theta} \quad (4)$$

Eq. (4) was used to determine the *k* values and the half-life periods of explosives, *t*_{1/2} was calculated using the *k* values (i.e., *t*_{1/2} = 0.693/*k*).

Analysis

The effluent was sampled at predetermined times and quenched immediately with 0.1N H₂SO₄ to make aliquots acidic (pH 3 to 5). The acidic quenching did not extraneously destroy explosives, nor were there any additional

breakdown products in the acid-quenched solution. This is consistent with previous results where RDX was not destroyed in the quenched acidic solution (pH \sim 1.5).⁸⁾ Following this, samples were diluted 1:1 with CH₃CN. Analysis for explosives and their transformation products were performed by injecting 25 μ L of the samples into a DIONEX HPLC and quantified by comparison to high purity standards. The HPLC consisted of a DIONEX P580 pump, a DIONEX ASI-100 autosampler and a DIONEX UVD 340U UV/VIS detector monitored at 230 and 254 nm. Chromeleon 6.40 chromatography software was used for data analysis. Chemical separation was achieved using a SUPELCOSIL LC-CN column for RDX samples and LC-18 column for TNT samples at 25°C, with a particle size of 5 μ m and a 25 cm x 4.6 mm ID. The mobile phase was 25% methanol-75% water (v/v) for RDX samples and 50%-50% for TNT samples at a flow rate of 1.0 mL/min.

The potential hydrolysis byproducts, such as nitrite (NO₂⁻), nitrate (NO₃⁻), formate (HCOO⁻) and oxalate (C₂HO₄⁻) from both TNT and RDX alkaline treatment, and Cl⁻ from the controls were analyzed using a DIONEX ion chromatograph (IC) equipped with an ASRS-ULTRA 4 mm column. Chemical separation and detection was achieved using an IONPAC AS11 guard column (4 mm x 50 mm), an AS11 analytical column (4 mm x 250 mm), and a DIONEX CD20 conductivity detector (1.25 μ L internal volume). The gradient elution was conducted with 100 mM NaOH, reagent grade water, and 5 mM NaOH at 1.5 mL/min by a DIONEX GP40 gradient pump. Initial concentration of the mobile phase was 90% (v/v) water and 10% 5mM NaOH, which was maintained for 2.5 min. The concentration of the mobile phase was changed to 100% 5mM NaOH over 3.5 min, then changed over 14 min to 70% 5 mM NaOH and 30% 100 mM NaOH. The concentration of the mobile phase was returned to the original concentration over 7 min after the analytical run. The sample (500 μ L) was automatically injected with a DIONEX automated sampler. The

instrument was calibrated using standard anionic solutions.

UV/VIS spectral analysis was conducted with a Hewlett Packard 8453 with a diode array detector with a 1-nm resolution. The instrument was equipped with UV/VIS HPChem software and a jacketed 1 cm quartz sample cell that was thermostated by connection to a recirculating water bath to maintain a given temperature. "Apparent" color without filtering or centrifuging the samples was measured spectrophotometrically with the HACH Platinum-Cobalt Standard Method.¹⁴⁾

RESULTS AND DISCUSSION

Explosives Removal Extents and Rates

The kinetics and treatability were a function of both the reaction pH and HRT: the higher reaction pH and longer HRT, the greater explosives reduction was occurred. The best TNT alkaline hydrolysis was achieved with the 2-day HRT and reaction pH of 11.9, resulting in a 73% removal (i.e., 1 mg/L \rightarrow 0.27 mg/L) (Figure 2). On the contrary, only 11% TNT destruction was observed with the 0.7-day HRT and reaction pH of 11.0 (Figure 3). The best RDX reduction was achieved at a 99% removal with the 2-day HRT and reaction pH of 11.9, whereas only 23% RDX destruction was observed with the 0.54-day HRT and reaction pH of 11.0 (Figures 2 and 3). In general, the extent of nucleophilic alkaline reduction was greater for RDX than TNT at the same experimental conditions.

The k values for TNT alkaline hydrolysis at steady state conditions were determined using Eq. (4) to be in the range of 0.9×10^{-4} to 1.0×10^{-3} min⁻¹, corresponding to the values of $t_{1/2}$ of 5.3 to 0.5 days, respectively (Table 1). For RDX alkaline hydrolysis, the k values ranged from 3.8×10^{-4} to 2.5×10^{-2} min⁻¹, corresponding to the values of $t_{1/2}$ of 1.3 to 0.02 days, respectively. Therefore, faster rates were achieved at the longer HRT and greater reaction pH for both TNT and RDX hydrolysis. Generally,

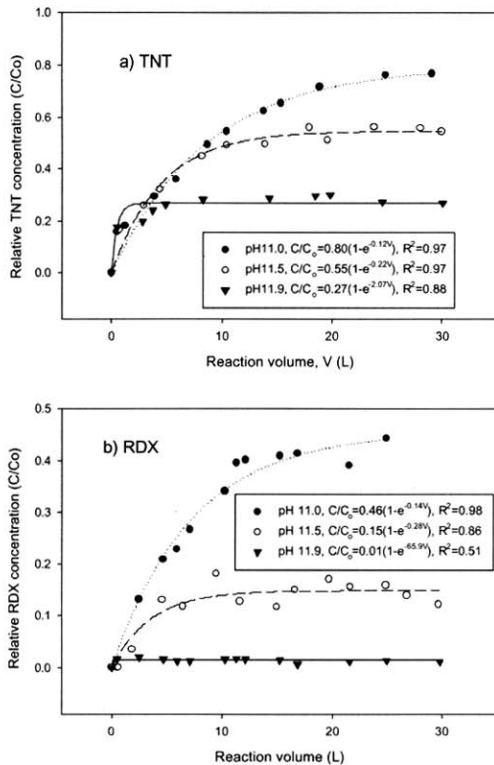


Figure 2. Representative plots of removal trend of TNT (a) and RDX (b) alkaline hydrolysis in the CFSTRs at the 2-day HRT. Eq. 3) was used to fit the effluent explosive concentration data over the reaction volume using nonlinear regression. It should be noted that very low correlation efficiency (R^2) for RDX alkaline hydrolysis at the reaction pH of 11.9 was due to the spontaneous reduction of RDX to 0.01 mg/L effluent concentration at the very early stage (i.e., spontaneous steady-state condition).

Table 1. Pseudo first-order destruction rate constants, k (min^{-1}) and half-life, $t_{1/2}$ (days) from TNT and RDX alkaline hydrolysis in CFSTRs under steady-state conditions

	Reaction pH	0.7-d HRT ^a		1-d HRT		2-d HRT	
		k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$
TNT	11.0	1.2×10^{-4}	4.0	1.5×10^{-4}	3.2	0.9×10^{-4}	5.3
	11.5	3.9×10^{-4}	1.2	3.4×10^{-4}	1.4	2.9×10^{-4}	1.7
	11.9	7.9×10^{-4}	0.6	1.1×10^{-3}	0.4	1.0×10^{-3}	0.5
RDX	11.0	3.8×10^{-4}	1.3	4.8×10^{-4}	1.0	4.2×10^{-4}	1.1
	11.5	1.3×10^{-3}	0.4	1.4×10^{-3}	0.4	2.0×10^{-3}	0.2
	11.9	2.5×10^{-3}	0.2	6.5×10^{-3}	0.1	2.5×10^{-2}	0.02

^a0.54-d HRT for RDX alkaline hydrolysis.

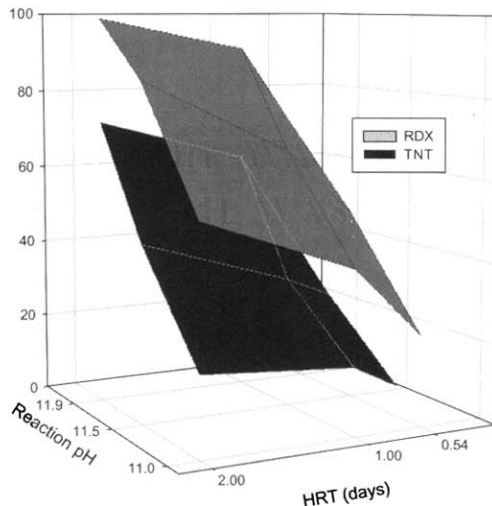


Figure 3. Comparison of removal efficiencies of nucleophilic alkaline hydrolysis for TNT and RDX in CFSTRs.

the rate of nucleophilic alkaline reduction was faster for RDX than TNT at the same experimental conditions.

Production of Hydrolysates

Possible TNT transformation products were not detected by HPLC. This absence of byproducts indirectly indicated complete loss of aromatic structure of TNT and/or the compounds were present below the method detection limit.¹²⁾ IC analysis also detected no organic acids and nitrogenous species which might come from TNT hydrolysis. In this regard, the initial TNT concentration increased to 10 mg/L and treated at the reaction pH of 11.9 and 2-day HRT. The results indicated that C_2HO_4^- was the main

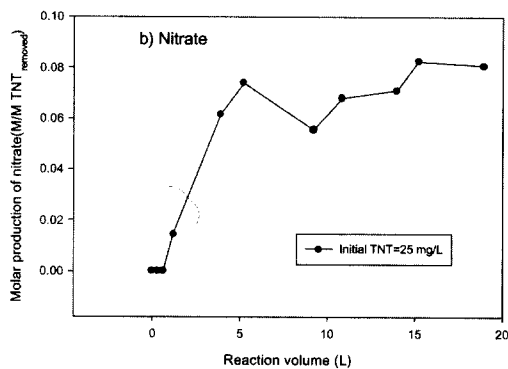
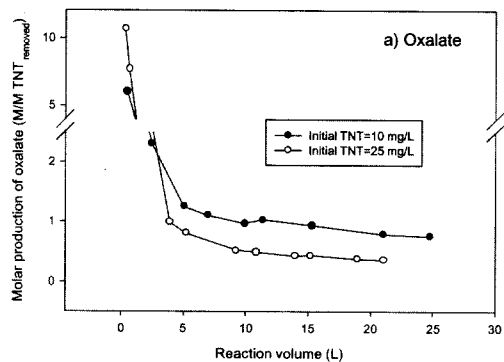


Figure 4. Molar production of oxalate (a) and nitrate (b) during TNT alkaline hydrolysis at the reaction pH of 11.9 and 2-day HRT with the influent TNT concentration of 10 and 25 mg/L. Nitrate was not detected with 10 mg/L TNT.

hydrolysate during TNT alkaline hydrolysis (Figure 4). Under steady-state condition, the molar yield (M/M TNT_{removed}) of oxalate was calculated to be 0.9. Limited amount of TNB was also produced at molar yields of 8.0×10^{-4} , which could be formed by the photocatalytic cleavage of the carbonmethyl bond rather than nucleophilic alkaline attack to the aromatic system.¹⁵ Nitrogenous species were still not detected. The initial TNT concentration further elevated to 25 mg/L and treated at the reaction pH of 11.9 and 2-day HRT. Under steady-state condition, the molar yield (M/M TNT_{removed}) of C₂H₂O₄⁻ was calculated to be 0.4. At this elevated TNT concentration, NO₃⁻ produced at molar yield of 0.07 with negligible TNB at molar yield of 1.2×10^{-3} (Figure 4).

In case of RDX alkaline hydrolysis, hetero-

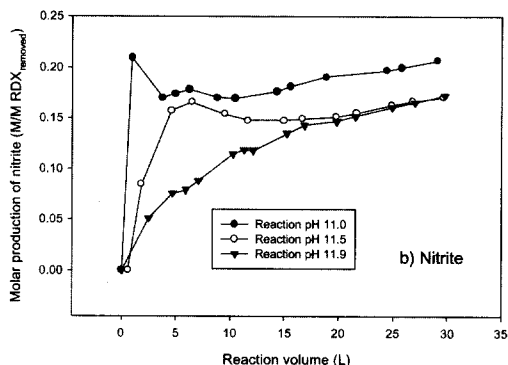
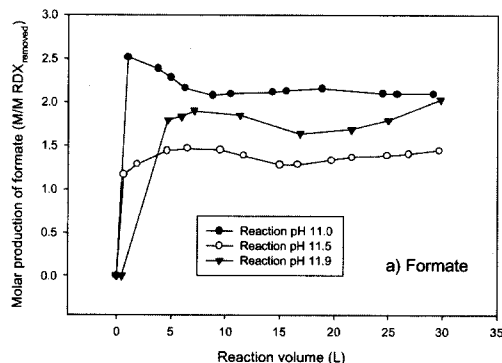


Figure 5. Representative plot of molar production of formate (a) and nitrite (b) during RDX alkaline hydrolysis at the 2-day HRT.

cyclic RDX byproducts such as TNX, DNX and MNX were not detected by HPLC either. Instead, HCOO⁻ and NO₂⁻ were detected by IC (Figure 5). Such production of HCOO⁻ and NO₂⁻ is consistent with previously published results: molar yields (M/M RDX_{removed}) of 1.5 HCOO⁻ and 1.5 NO₂⁻¹⁰ and 0.7 HCOO⁻ and 1.1 NO₂⁻¹¹. In the current study at the 2-day HRT, the molar yields of HCOO⁻ and NO₃⁻ were at 1.8, and 0.2, respectively. When the CFSTR was operated at a shorter 0.54-day HRT, more HCOO⁻ was produced at molar yield of 2.4 and less NO₂⁻ at 0.1. It remains unclear at this time why the current study produced more HCOO⁻ and less NO₂⁻ than the reported values. However, different operational conditions appear to attribute to the dissimilar results. For instance, the current study was conducted at 25°C in CFSTR systems, whereas the reported experi-

ments were performed in batch systems at 50-80°C¹⁰ and 25-45°C¹¹.

Color Development During TNT Alkaline Hydrolysis

Color production was observed when 1 mg/L TNT concentration was treated in the CFSTR. However, the intensity was not so strong to quantify during the time course of experiment.

In this regard, the kinetics of color production in the CFSTR was determined with 10 mg/L initial TNT concentration at the reaction pH

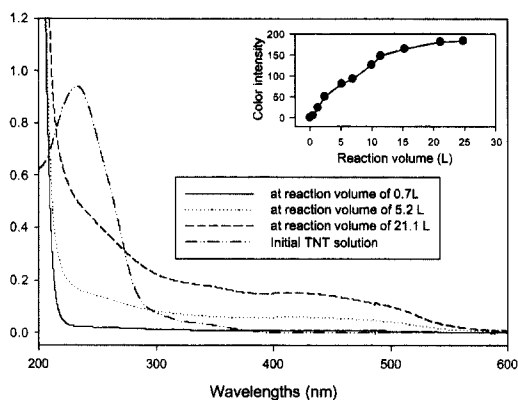


Figure 6. UV/VIS spectra during TNT alkaline hydrolysis at the reaction pH of 11.9, 2-day HRT and initial TNT concentration of 10 mg/L. Color intensity (in the inset figure) was monitored in the same experimental condition. One color unit is equivalent to 1 mg/L platinum as chloroplatinate ion.¹⁴

11.9 and 2-day HRT. UV/VIS spectra obtained did not show a featuring peak. However, the spectra indicated the presence of dissimilar color-forming intermediates that absorbed specific wavelengths of light and thereby produced different visual colors (Figure 6). Yellow, orange, and red colors were observed over the wavelength range of 380 to 460 nm, 380 to 500 nm, and 440 to 560 nm, respectively.¹⁶ Azo- and azoxy-compounds are also generated by spontaneous intermolecular condensation of nitroso- and hydroxylamino-intermediates of TNT,¹⁷ resulting in the appearance of varying colors in the visible range. The color intensity monitored strengthened the observation of increasing colorization, resulting in a gradual increase to reach a plateau at the color unit of 190.

Total and Net Alkaline Demand

The total and net alkaline demands (TAD and NAD, M OH-/M explosive_{removed}) were determined in the CFSTR treating 1 mg/L explosive influent at the three different reaction pHs to provide information pertinent to design and cost estimation for implementation of alkaline hydrolysis for on-site remediation of explosives-contaminated groundwater (Table 2). The TAD for TNT alkaline hydrolysis was determined to be, on average, 4600, 1500, and 550, when the CFSTR was operated at the pH of 11.9, 11.5, and 11.0, respectively. The amount of OH

Table 2. Total and net alkaline demands (mole of OH⁻ consumed per mole of explosive removed) in the CFSTR

	Reaction pH	Total OH ⁻ demand ^a			Net OH ⁻ demand ^b		
		0.7-d HRT ^c	1-d HRT	2-d HRT	0.7-d HRT ^c	1-d HRT	2-d HRT
TNT	11.0	650	480	530	300	150	190
	11.5	1400	1400, 1700 ^d	1520	470	520, 810 ^d	470
	11.9	5000, 5100 ^d	4200	4000	1900, 1900 ^d	1200	1100
RDX	11.0	670, 730 ^d	510	530	160, 200 ^d	100	120
	11.5	1500	1500, 1500 ^d	1300	320	430, 430 ^d	410
	11.9	3500	2900	2700	1.5	1.3	1.2

^a OH⁻ amount titrated for both removing explosive and keeping the pH constant against the influent flow.

^b OH⁻ amount titrated for removing explosive only.

^c 0.54-d HRT for RDX alkaline hydrolysis.

^d Values from the replicate.

required to keep the pH constant against the dilution of the influent flow (i.e., blank system without TNT) was obtained experimentally. Therefore, the NAD was calculated as follows:

$$\text{Net OH}^- \text{ Demand} = \left(\frac{M \text{ OH}^-_{\text{treatment}} - M \text{ OH}^-_{\text{blank}}}{M \text{ Explosive}_{\text{removed}}} \right) \quad (7)$$

where, $M \text{ OH}^-_{\text{treatment}}$ is the mole of OH^- titrated in the active treatment and $M \text{ OH}^-_{\text{blank}}$ was the mole of OH^- titrated in the blank system. The NAD for TNT alkaline hydrolysis was determined to be, on average, 1500, 610, and 210, when the CFSTR was operated at the pH of 11.9, 11.5, and 11.0, respectively.

Likewise, TAD and NAD for RDX alkaline hydrolysis was determined. When the CFSTR was operated at pH 11.5, NAD for RDX alkaline hydrolysis was determined to be approximately 390. Such demand was three times greater than the approximate 130 NAD when the system was operated at pH 11.0. However, when the RDX hydrolysis was conducted at pH 11.9, only about 1.5 NAD was used for removing one mole of RDX. On the other hand, TAD was obtained to be 3030, 1440, and 580, on average, for the reaction pH of 11.9, 11.5, and 11.0, respectively. Therefore, it was construed that as long as the reaction pH was kept high enough, such as pH 11.9 in this study, the system did not require much more OH^- beyond that used for completing hydrolysis of RDX and its byproducts. Instead, OH^- demand in such a system was mainly used for compensating the OH^- dilution by the influent flow.

In comparison, more alkali was demanded for TNT alkaline hydrolysis than RDX alkaline hydrolysis, despite less amount of TNT was destructed than RDX. This phenomenon indirectly implies that TNT is more resistant to nucleophilic alkaline attack than RDX. Another implication may include that nucleophilic alkaline hydrolysis of TNT occurs in a different

fashion from that of RDX, through which more alkali is required for the destruction of TNT transformation products.

Comparative Reactivity in Nucleophilic Alkaline Hydrolysis of TNT and RDX in Conjunction to Potential Degradation Pathway

Both TNT and RDX are known to have great reactivity toward alkaline nucleophilic reaction. Between the two high explosives, the reactivity of RDX with nucleophilic alkaline hydrolysis was greater than that of TNT. TNT is highly susceptible to nucleophilic attack by OH^- because its depleted electron density on the ring, which is caused by the nitro-groups.²⁾ Despite it is vulnerable to nucleophilic attack, the external nucleophilic attack to the electrons in the TNT aromatic ring could be still hindered by the steric effects caused by the presence of three nitro groups and one methyl group. In addition, there is a possibility of producing relatively stable hydroxydinitrotoluenes (HADNTs) by external nucleophilic attack. HADNT can undergo Bamberger rearrangement, in which $-\text{OH}$ in $-\text{NHOH}$ group shifts to the aromatic ring, which, in turn, can give rise to catechol-like intermediates before the ring cleavage. The production of 3-hydroxy-2,4,6-TNT was postulated as a result of Meisenheimer complexation,¹²⁾ in which OH^- and the nitro group are still attached to the same carbon atom before the nitro group is eliminated. It is, therefore, believed that more alkali is required for TNT alkaline hydrolysis than RDX alkaline hydrolysis because of more diverse and complicating degradation intermediates that would also demand nucleophile for their transformation. Combining the experimental results from the current study and the information from the literatures, the dominant processes leading to the loss of TNT in nucleophilic alkaline hydrolysis were ring cleavage and dimerization, resulting in the productions of C_2HO_4^- and color-forming azoxy compounds, respectively.

RDX is also vulnerable to nucleophilic reac-

tion via the bimolecular E2 mechanism, in which a proton is removed by OH⁻ from the relatively acidic methylene hydrogens resulting in the double bond between carbon and nitrogen both are in the ring and, simultaneously, NO₂⁻ is removed from the adjacent ring nitrogen.⁷⁾ RDX has a triaxial chair conformation so that the attacking nucleophile can easily approach from the rear side of RDX molecule as the removed hydrogen and nitro group leave from the front. The initial elimination process by nucleophilic attack makes very unstable transient intermediate 1,3,5-triaza-3,5-dinitrocyclohex-1-ene which undergoes fast ring cleavage at 10⁵-time faster hydrolytic rate than RDX.^{7,11)} It is, therefore, construed that once the bimolecular elimination process occurs by the initial nucleophilic attack, nucleophilic attack quickly decompose the nitramine ring to produce ring-cleaved intermediates, such as 4,6-dinitro-2,4,6-triaza-hexanal,¹⁸⁾ which are, in turn, attacked by OH⁻ to produce HCOO⁻ and nitrogenous compounds detected in the current study. Therefore, the loss of RDX in nucleophilic alkaline hydrolysis is initiated with E2 mechanism and denitration, which further cause rapid ring cleavage and further hydrolysis to form the final products such as HCOO⁻. It should be, however, noted that the alkaline degradation pathways of both TNT and RDX were not individually studied in the current study. This is currently being investigated to further support the proposed pathways.

CONCLUSIONS

Nucleophilic alkaline hydrolysis was evaluated at the different reaction pHs and HRTs in CFSTR to assess the effectiveness of alkaline hydrolysis as an ex-situ groundwater remediation contaminated with high explosives. The results indicated that both TNT and RDX alkaline hydrolysis in CFSTR had a strong dependence on the reaction pH and HRT and the extent and rate of removal efficiency of RDX was much greater and faster, respectively, than those of TNT. This was believed to be due to the

different structural characteristics, such as conformation and steric effects, and degradation pathway between TNT and RDX. The production of formate and oxalate for alkaline hydrolysis of RDX and TNT, respectively, indicated that their rings were cleaved by alkaline hydrolysis. Experimental observation also suggested that, unlike RDX alkaline hydrolysis, TNT alkaline hydrolysis occur through the production of color-forming intermediates. Less amount of alkali was demanded for RDX alkaline hydrolysis than TNT alkaline hydrolysis, probably because of more diverse and complicating degradation intermediates that would also demand nucleophile for their transformation.

Overall, nucleophilic alkaline hydrolysis can be a promising ex-situ treatment technology for remediation of high explosives-contaminated groundwater, especially for remediation of RDX-contaminated groundwater. Secondary treatment would be required to neutralize the alkalinity and to lower the pH of the effluent to a level acceptable for discharge. Further research is therefore warranted to address economics, design guidance and application protocols of nucleophilic alkaline hydrolysis before implementation of such treatment system at a field site.

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REFERENCES

- Rosenblatt, D. H., Burrows, E. P., Mitchell, W. R., and Parmer, D. L., "Organic Explosives and Related Compounds," *The Handbook of Environmental Chemistry, Volume 3, Part G*, Hutzinger, O. (Ed.), Springer-Verlag, (1991).
- Spain, J. C., "Biodegradation of nitroaromatic compounds," *Annu. Rev. Microbiol.*, **49**, 523~555 (1995).
- Walsh, M. E., Jenkins, T. F., Schnitker, P. S., Elwell, J. W. and Stutz, M. H., US Army Cold Regions Research and Engineering Laboratory, CRREL Special Report 93-5. Hanover, NH (1993).
- Peres, C. M. and Agathos, S. N., "Biodegradation of nitroaromatic pollutants: from pathways to remediation," *Biotechnology Annual Review*, **6**, 197~220 (2000).
- Won, W. D., DiSalvo L. H., and Ng, J., "Toxicity and mutagenicity of 2,4,6-trinitrotoluene and its metabolites," *Appl. Environ. Microbiol.*, **31**, 576~580 (1976).
- US EPA, 2002 Edition of the Drinking Water Standards and Health Advisories. Office of Water, EPA 822-R-02-038. Washington, DC (2002).
- Jones, W. H., "Mechanism of the homogenous alkaline decomposition of cyclomethylenetrinitramine: Kinetics of consecutive second- and first-order reactions. A polarographic analysis for cyclomethylenetrinitroamine" *J. Am. Chem. Soc.* **76**, 829~835 (1954).
- Croce, M. and Okamoto, Y., "Cationic micellar catalysis of the aqueous alkaline hydrolyses of 1,3,5-triaza-1,3,5-trinitrocyclohexane and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane," *J. Org. Chem.*, **44**(13), 2100~2103 (1979).
- Emmrich, M., "Kinetics of the alkaline hydrolysis of 2,4,6-trinitrotoluene in aqueous solution and highly contaminated soils," *Environ. Sci. Technol.*, **33**(21), 3802~3805 (1999).
- Heilmann, H. M., Wiesmann, U. and Stenstrom, M. K., "Kinetics of the alkaline hydrolysis of high explosives RDX and HMX in aqueous solution and adsorbed to activated carbon," *Environ. Sci. Technol.*, **30**(5), 1485~1492 (1996).
- Hoffsommer, J. C., Kubose, D. A., and Glover, D. J., "Kinetic isotope effects and intermediate formation for the aqueous alkaline homogenous hydrolysis of 1,3,5-triaza-1,3,5-tribitrocyclohexane (RDX)," *J. Phys. Chem.*, **81**(5), 380~385 (1977).
- Karasch, C., Popovic, M., Qasim, M. and Bajpai, R. K., "Alkali hydrolysis of trinitrotoluene," *Appl. Biochem. Biotechnol.*, **98-100**, 1173~1185 (2002).
- Vesilind, P. A., Introduction to environmental engineering, PWS Publishing Company, Boston, MA (1997).
- HACH, DR/2000 Spectrophotometer Procedures Manual, Hach Company, Loveland, CO (1991).
- Pennington, J. C., Thorn, K. A., Inouye, L. S., McFarland, V. A., Jarvis, A. S., Lutz, C. H., Hayes, C. A. and Porter, B. E., Explosives conjugation products in remediation matrices: Final report. Strategic Environmental Research and Development Program Technical Report SERDP-99-4 (1999).
- Bruce, P. Y., Organic Chemistry, Prentice-Hall, Inc., NJ (1995).
- Rieger, P. G. and Knackmuss, H. J., "Basic Knowledge and Perspectives on Biodegradation of 2,4,6-Trinitrotoluene and Related Nitroaromatic Compounds in Contaminated Soil," *Biodegradation of Nitroaromatic Compounds*, Spain J. C. (Ed.), Plenum Press, New York, (1995).
- Balakrishnan, V. K., Halasz, A., and Hawari, J., "Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX, and CL-20: New insights into degradation pathways obtained by the observation of novel intermediates," *Environ. Sci. Technol.*, **37**, 1838~1843.