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High Explosives Alkaline Hydrolysis in Continuous Stirred Tank Reactor

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Abstract
This study was conducted to assess the feasibility of alkaline hydrolysis of high explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using a continuous stirred tank reactor as an alternative ex-situ groundwater remediation technology. Results showed that 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 at the reaction pH of 11.9 and 2-day HRT, 99% and 73% reduction for RDX and TNT, respectively, was achieved. 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 byproducts from alkaline hydrolysis of RDX and TNT, respectively, indicative of ring cleavage. Therefore, alkaline hydrolysis was tested to be an alternative treatment technology for remediation of high explosives-contaminated groundwater.

Key words
Alkaline hydrolysis, Continuous stirred tank reactor, Formate, Oxalate, RDX, TNT

1. Introduction

Manufacturing, assembling, loading, and disposal of explosive compounds and range training have generated widespread contaminations with explosives and their derivatives (Rosenblatt et al., 1991; Spain, 1995). 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 (Walsh et al., 1993). Due to the adverse effects of TNT and RDX on humans and other natural receptors (Peres and Agathos, 2000; Won et al., 1976), the U.S. Environmental Protection Agency (EPA) has established drinking water health advisory of 2 ug/L for lifetime exposure to TNT and RDX (US EPA, 2002).
TNT is a nitroaromatic explosive with three nitro groups are attached to the toluene ring (Figure 1). The high electron density 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 (Spain, 1995). The

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reduced electron density of the ring suggests that the ring is subject to nucleophilic attack by a strong nucleophile such as hydroxide ion (OH^-).

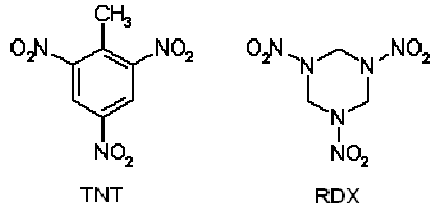

Figure 1. Structure of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX).

RDX is a cyclic nitramine with alternating carbon and nitrogen atoms and with nitro-groups bonded to the three ring-nitrogen atoms (Figure 1). 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 OH^- can cause the RDX molecule to become unstable and thus amenable to further degradation (Jones, 1954).

Alkaline hydrolysis in batch settings has been reported to be a potential alternative remediation technology for explosives-contaminated water (Croce and Okamoto, 1979; Emmrich, 1999; Heimann et al., 1996; Hoffsommer et al., 1977; Karasch et al., 2002). However, study on alkaline hydrolysis in a continuous feed system has not been reported and such investigation is in need. This study was conducted to assess the feasibility and effectiveness of alkaline hydrolysis using a continuous stirred tank reactor (CSTR) as an alternative ex-situ remediation technology for groundwater contaminated with high explosives TNT and RDX.

2. Materials and Methods

2.1 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-dinitrotolene, 2-amino-4,6-dinitrotoluene, 2,4-dinitrotolene, 2,6-dinitrotoluene, 2-nitrotolene, and 4-nitrotolene. 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. Other chemicals used in the experiment were purchased from Fisher Scientific.

2.2 Continuous stirred tank reactor (CSTR)

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 CSTR 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 H_2SO_4 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.

2.3 Analysis

The effluent was sampled at predetermined times and quenched immediately with 0.1N H_2SO_4 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 ~1.5) (Croce and Okamoto, 1979). Following this, samples were diluted 1:1 with CH_3CN. Analysis for explosives and their transformation products were performed by injecting 25 μL of the samples into a DIONEX high performance liquid chromatograph and quantified by comparison to high purity standards.
The potential hydrolysis byproducts, such as nitrite (NO_2^-), nitrate (NO_3^-), formate ($HCOO^-$) and oxalate ($C_2HO_4^-$) from both TNT and RDX alkaline treatment, and Cl^- from the controls were analyzed using a DIONEX ion chromatograph. 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. "Apparent" color without filtering or centrifuging the samples was measured spectrophotometrically with the HACH Platinum-Cobalt Standard Method (HACH, 1991).

3 Results and Discussion

3.1 Control and blank systems

To assure complete mixing, a non-reactive chloride (Cl^-) tracer was flushed through the CSTR 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 (Vesilind, 1997). Therefore, the CSTR 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 CSTR unit nor substantial losses such as photodegradation during the experiment.

3.2 Kinetic modeling

Using the first-order kinetics, the material-balance equation of explosives transformation for a CSTR can be expressed as follows:

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

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_o and C are the influent and effluent explosives concentration (mg/L), respectively (Vesilind, 1997). Under nonsteady-state conditions, Eq. (1) changes to

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

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

$$\frac{C}{C_o} = \alpha\left(1 - e^{-\beta t}\right) \qquad (3)$$

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 CSTR over the reaction period of alkaline hydrolysis using nonlinear regression.
Under steady-state conditions, Eq (1) reduces to

$$\frac{C}{C_0} = \frac{1}{1+k\theta} \tag{4}$$

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., $t_{1/2}=0.693/k$).

3.3 Extents and rates of explosives removal

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

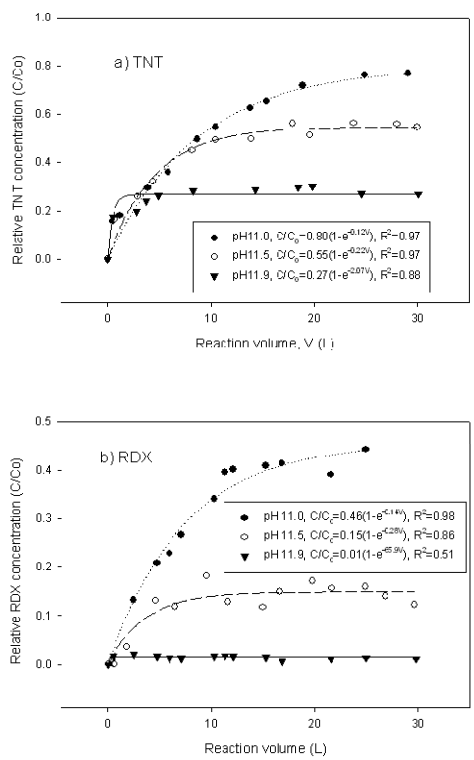

Figure 2. Representative plots of removal trend of TNT (a) and RDX (b) alkaline hydrolysis in the CSTRs at the 2-day HRT. Eq. 3) was used to fit the effluent explosive concentration data over the reaction volume using nonlinear regression. It should be noted that very low correlation efficiency (R^2)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

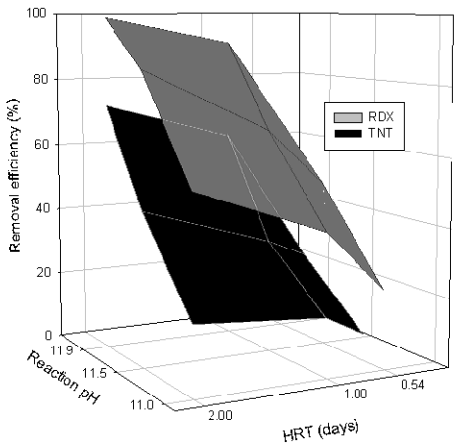

Figure 3. Comparison of removal efficiencies of nucleophilic alkaline hydrolysis for TNT and RDX in CSTRs.

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 CSTRs 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

[a] 0.54-d HRT for RDX alkaline hydrolysis.

3.4 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 (Karasch et al., 2002). 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 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 carbon–methyl bond rather than nucleophilic alkaline attack to the aromatic system (Pennington, 1999). 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 $C_2HO_4^-$ was calculated to be 0.4. At this elevated TNT concentration, NO_3^- 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, heterocyclic RDX byproducts such as TNX, DNX and MNX were not detected by HPLC either. Instead, $HCOO^-$ and NO_2^- were detected by IC (Figure 5). Such production of $HCOO^-$ and NO_2^- is consistent with previously published results: molar yields (M/M $RDX_{removed}$) of 1.5 $HCOO^-$ and 1.5 NO_2^- (Heilmann et al., 1996) and 0.7 $HCOO^-$ and 1.1 NO_2^- (Hoffsommer et al., 1977). In the current study at the 2-day HRT, the molar yields of $HCOO^-$ and

NO_3^- were at 1.8, and 0.2, respectively. When the CSTR was operated at a shorter 0.54-day HRT, more $HCOO^-$ was produced at molar yield of 2.4 and less NO_2^- at 0.1. It remains unclear at this time why the current study produced more $HCOO^-$ and less NO_2^- 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 CSTR systems, whereas the reported experiments were performed in batch systems at 50-80°C (Heilmann et al., 1996) and 25-45°C (Hoffsommer et al., 1977).

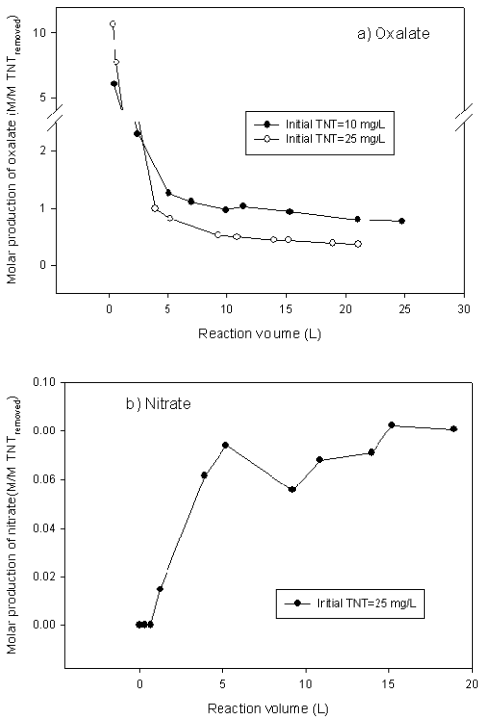

Figure 4. Molar production of oxalate (a) and nitrate (b) during TNT alkaline hydrolysis at the reaction pH of 11.9 and 2-day HRT with the influent TNT concentration of 10 and 25 mg/L. Nitrate was not detected with 10 mg/L TNT.

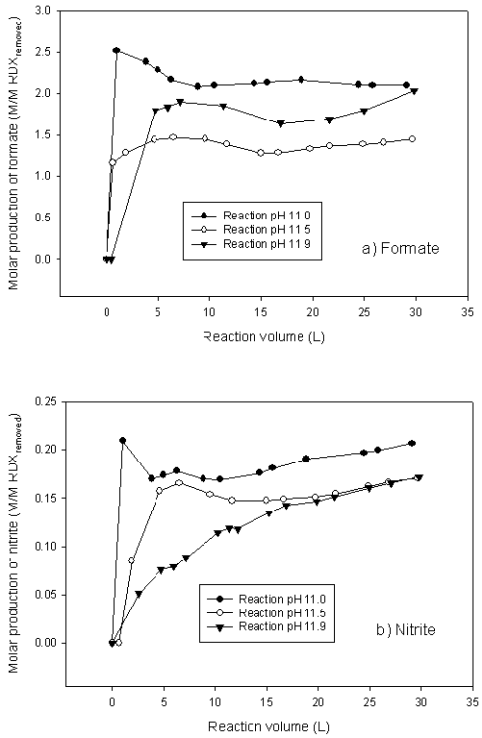

Figure 5. Representative plot of molar production of formate (a) and nitrite (b) during RDX alkaline hydrolysis at the 2-day HRT.

3.5 Color development during TNT alkaline hydrolysis

Color production was observed when 1 mg/L TNT concentration was treated in the CSTR. 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 CSTR was determined with 10 mg/L initial TNT concentration at the reaction pH 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. 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 (Bruce, 1995). Azo- and azoxy-compounds are also generated by spontaneous intermolecular condensation of nitroso- and hydroxylamino-intermediates of TNT (Rieger and Knackmuss, 1995), 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.

3.6 Total and net alkaline demand

The total and net alkaline demands (TAD and NAD, M OH^-/M $explosive_{removed}$) were determined in the CSTR 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 CSTR was operated at the pH of 11.9, 11.5, and 11.0, respectively. The amount of OH^- 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:

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

where, M $OH^-_{treatment}$ is the mole of OH^- titrated in the active treatment and M OH^-_{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 CSTR was operated at the pH of 11.9, 11.5, and 11.0, respectively.

Table 2. Total and net alkaline demands (mole of OH^- consumed per mole of explosive removed) in the CSTR

	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; and [d] Values from the replicate.

Likewise, TAD and NAD for RDX alkaline hydrolysis was determined. When the CSTR 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.

3.7 Comparison of the reactivity of TNT and RDX in alkaline hydrolysis

The reactivity of RDX with nucleophilic alkaline hydrolysis was greater than that of TNT. TNT is highly susceptible to nucleophilic attack by OH^- because depleted electron density on its ring, which is caused by the nitro-groups (Spain, 1995). Despite it is vulnerable to nucleophilic attack, the external nucleophilic attack to the π 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 hydroxydinitrotoluens (HADNTs) by external nucleophilic attack. HADNT can undergo Bamberger rearrangement, in which -OH in –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 (Karasch et al., 2002), 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 reaction 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, NO_2^- is removed from the adjacent ring nitrogen (Jones, 1954). 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 10^5-time faster hydrolytic rate than RDX (Jones, 1954; Hoffsommer et al., 1977). It is, therefore, construed that once the bimolecular elimination process occurs by the initial nucleophilic attack, nucleophillic attack quickly decompose the nitramine ring to produce ring-cleaved intermediates, such as 4,6-dinitro-2,4,6-triaza-hexanal (Balakrishnan et al., 2002), 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.

4 Conclusions

Alkaline hydrolysis was evaluated at the different reaction pHs and HRTs in CSTR to assess the feasibility and 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 CSTR 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 dissimilar degradation pathways 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, alkaline hydrolysis was found to be an alternative 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 alkaline hydrolysis before implementation of such treatment system at a field site.

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