Degradation of high energetic and insensitive munitions compounds by Fe/Cu bimetal reduction

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ABSTRACT

A reductive technology based on a completely mixed two-phase reactor (bimetallic particles and aqueous stream) was developed for the treatment of aqueous effluents contaminated with nitramines and nitro-substituted energetic materials. Experimental degradation studies were performed using solutions of three high energetics (RDX, HMX, TNT) and three insensitive-munitions components (NTO, NQ, DNAN). The study shows that, on laboratory scale, these energetic compounds are easily degraded in solution by suspensions of bimetallic particles (Fe/Ni and Fe/Cu) prepared by electro-less deposition. The type of bimetal pair (Fe/Cu or Fe/Ni) does not appear to affect the degradation kinetics of RDX, HMX, and TNT. The degradation of all components followed apparent first-order kinetics. The half-lives of all compounds except NTO were under 10 min. Additional parameters affecting the degradation processes were solids loading and initial pH.

1. Introduction

The production of energetic materials results in the generation of explosives-laden waste streams which require treatment prior to discharge into the environment. Such waste streams often contain a multitude of high-explosive and insensitive-munitions compounds, and degradation products thereof. Some of these compounds may be ecotoxic and persistent in the environment, and some have been classified as class C "Possible Human Carcinogen" by the United States Environmental Protection Agency.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, RDX) is a white crystalline solid, soluble in acetone and acetonitrile, but very poorly soluble in water (about 35–45 mg/L at room temperature). RDX is the most important high explosive for military applications in the United States. RDX is a heterocyclic nitramine with chemical stability similar to that of trinitrotoluene (TNT) but sensitivity to mechanical impact and explosive power

superior to those of TNT and other explosives. Since World War II, RDX has been used widely in a variety of military and civil activities around the world, resulting in the contamination of groundwater, surface water, sediments, and soils [1]. There are estimated 12,000 sites in the United States contaminated by high explosives owing to production activities, field usage, and disposal of munitions materials or their combustible products. Soil concentrations often exceeding 3000 mg/kg [2] and levels of 11–14 mg/L in groundwater [3] surrounding munitions plants are reported for RDX and High Melt Explosive (HMX). Chemically, HMX is a higher nitramine homolog of RDX. HMX has similar energetic properties to those of RDX, and can form as a by-product during RDX manufacture. HMX also dissolves very slightly in water; it is photodegradable and relatively non-volatile.

TNT is a white, slightly yellowish crystalline solid, poorly soluble in water (100–200 mg/L at room temperature), but soluble in acetone and benzene [4]. It is a widely used high explosive, both alone and, because of its low melting point (80 °C), as a matrix binder for other explosives, often RDX and HMX. The abiotic transformation of TNT in anaerobic soil environments has been demonstrated in buffered batch tests with montmorillonite and Fe^{2+} [5]. Reduction

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products of TNT have been assessed to possess comparable toxicity to that of the parent compound [6].

Nitrotriazolone (3-nitro-1,2,4-triazol-5-one, NTO) is a white crystalline compound soluble in water (12.8 g/L at 19 °C) producing yellow solutions. Its high aqueous solubility renders adsorption-based technologies ineffective for the treatment of wastewater generated during NTO manufacturing. Several alternative methods have been reported, focusing on advanced oxidation processes and/or biodegradation [7–10]. Preliminary batch experiments conducted in our laboratory, using 0.5 N solutions of NaOH, proved alkaline hydrolysis ineffective for NTO removal for treatment times up to 2 h.

Nitroguanidine (NQ) is a nitramine compound that serves as an oxidizer in triple-base propellants, and also reduces flash and temperature during deflagration. Nitroguanidine has an aqueous solubility ranging between 2.6 and 5.0 g/L, depending on the reporting source. In aqueous solution NQ hydrolyzes to NH_3, N_2O, and CO_2 at pH greater than 10. Alkaline hydrolysis is strongly pH dependent, and at 25 °C the NQ half-life ranges from 8 years to 7.5 h between pH 7 and 13, respectively. NQ has been reported to be non-degradable aerobically but partially degradable through anaerobic co-metabolism [11]. Carbon adsorption and ion exchange have also been reported as potential treatments for NQ [12].

2,4-dinitroanisole (DNAN) is a nitroaromatic compound poorly soluble in water (632 mg/L) and readily soluble in various organic solvents (ethanol, ether, acetone, benzene). Boddu et al. [13] have reported the removal characteristics of DNAN through adsorption on variably treated activated carbons. Reportedly, DNAN is converted to diaminoanisole in anaerobic fluidized bioreactors [14]. Experiments in our laboratory have shown that DNAN can be degraded successfully to dinitrophenol by alkaline hydrolysis. An Arrhenius expression was obtained for the apparent first-order rate constant (k') with a pre-exponential constant (A) of 2.24×10^{18} min^{-1} and activation energy (E_a) of 121.8 kJ/mol.

Most of the available technologies for the treatment of soil and water contaminated with high explosives employ biological and physical/chemical methods. The effectiveness of these methods varies. Anaerobic treatment rarely leads to the full degradation of the parent compounds, and frequently the daughter products are, in terms of toxicity, of equal or higher concern than the parent compound. Adsorption-based treatment technologies are rather expensive because the spent carbon must be disposed of as a hazardous waste.

Bimetallic particles with iron as the principal metal have been effective in degrading various organic and inorganic compounds. While treatment with bimetallic particles has not been thoroughly studied, it is believed to have several potential advantages over traditional zero-valent iron (ZVI) treatment, including faster reaction kinetics and slower deposition of corrosion products on the particle surface [15]. Several studies have indicated that iron-palladium bimetallic particles have been effective in treating nitroso- and nitro-compounds at ambient pressure and temperature [16,17]. The secondary metals used – copper, nickel, palladium, etc. help to catalyze the reaction and decrease oxide formation on the iron surface [15]. Transition metals, e.g. copper, are effective at inducing and promoting iron corrosion by forming a galvanic couple between the iron (anode) and the respective metal (cathode) with ambient water acting as the salt bridge [15]. Dissolution of the metal occurs at the anodic sites, releasing ions that can then form rust on the iron surface [18]. A thin film of oxyhydroxides develops on the ZVI and results in a cycle of oxidation, recrystallization, and precipitation [19]. The effectiveness of ZVI is strongly influenced by the formation of precipitates on the iron surface [19]. When the film of oxyhydroxides grows on the iron surface, the iron becomes less effective because there are fewer active sites and the galvanic cell loses its strength. It is believed that the addition of halide salts extends the life of the ZVI and makes it more effective as the halide ions are able to penetrate the pores in the oxide layer, dispersing it and making it more permeable [18]. Ghauch and Tuqan [15] were able to fit kinetic data using a pseudo-first-order model for the degradation of chlorothalonil, with copper and palladium being the most effective. Increasing the concentration of palladium to 10% (w/v), i.e. above catalytic amounts, caused a very large drop in the k_{obs} value. This was attributed to an "over-coating" of the iron particle which effectively turned the iron particle into a palladium particle with an iron core – this was analogous to what was observed during our studies with nanoscale iron (data not shown). Ghauch and Tuqan's study found the most effective dosing level to be 1% Cu and 1% palladium. Additionally, chloride and bromide salts have been shown to be pitting and corrosion promoters [18]. Kim et al. [18] examined the hypothesis that halide salts promote degradation of high explosives and extend the life of ZVI. Degradation of RDX and HMX in aqueous solutions was significantly faster with the addition of chloride and bromide salts. RDX showed complete degradation within 12 h when halide salts were added, and only 30% degradation after 12 h when ZVI was used alone. HMX degraded completely within 48 h with the addition of halide salts, and showed little to no change in the same amount of time when ZVI was used alone. Additionally, at any given salt concentration, Cl$^-$ was more effective than Br$^-$, most likely due to the lower pH of the $CaCl_2$ solutions attributed to ion pairing and greater acidification. Fuller [20] obtained similar results to Kim [18] using nickel catalysts to degrade explosives in water solutions, and found that RDX and HMX rapidly degraded to below detection under acidic conditions.

The goal of this research was to study the degradation of high explosives and insensitive-munitions components using bimetal-particle reduction that degrades the target compounds within reasonable treatment time. This study (a) evaluates the feasibility of bimetallic zero-valent iron–copper (Fe/Cu) and iron–nickel (Fe/Ni) particles for the treatment of three high explosives (in laboratory prepared solutions and industrial pinkwater samples) and three insensitive munitions, and (b) investigates the reaction kinetics and the factors affecting the degradation rates during treatment.

2. Materials and methods

The experimental program involved the following steps: (a) preparation and characterization of the bimetal substratum: micron-sized iron particles were plated with secondary metals (Cu and Ni) by cold electrolytic deposition. The surface loading was controlled by the strength of the plating solution and the contact time. Bimetallic particles were characterized using BET surface area, and metal content. (b) Bench-scale experiments: this phase focused on determining the reaction kinetics of RDX, HMX, TNT, NTO, DNAN and NQ and sought to identify the various factors affecting their decomposition. Standards for TNX (>99.0% pure), DNX (59% pure), and MNX (99.5% pure) were purchased from SRI International (Menlo Park, CA). Work standards for RDX, MNX, DNX, and TNX were prepared by diluting stock solutions with acetonitrile to desired concentrations. All stock and work solutions were stored at 4 °C.

2.1. Materials

RDX (90% purity, 10% HMX) and HMX were supplied by US ARMY TACOM/ARDEC (Picatinny Arsenal, NJ). Industrial grade iron particles HC-200 (70–80 μm particle size, 2.8–3.2 g/cm^3 bulk density) were obtained from Hepure Technologies (Wilmington, DE). Dissolved explosives calibration standards in acetonitrile were purchased from Restek Corporation (Bellefonte, PA). All compounds were 98% pure. RDX standards (99.4% purity) dissolved in methanol

and acetonitrile (1:1 v/v), were purchased from AccuStandard, Inc. (New Haven, CT).

2.2. Preparation and characterization of bimetal particles

A series of preliminary experiments dealt with practical, procedural and analytical aspects of the iron bimetal particle preparation, coating, and characterization. A typical bimetal particle preparation procedure comprised the following steps: (1) An acid-wash with 1 M nitric acid to remove ferric oxide impurities from the iron surface; (2) DI water wash to remove residual acid; (3) absolute-ethanol wash to remove residual water and prevent corrosion; (4) cold plating of the iron particles in copper/nickel solutions; (5) vacuum filtration of the Fe/Cu and Fe/Ni bimetal particles; (6) three absolute-ethanol washes; (7) storage under nitrogen to prevent oxidation. Thus prepared, the bimetal particles were characterized and subsequently used in batch kinetic and pilot plant studies. The various procedures used in preliminary experiments are described in detail elsewhere [21].

The BET and Langmuir specific surface areas of the particles prepared following the procedure above described were determined using a Micromeritics surface analyzer model ASAP 2010 (Micromeritics Corporation, Norcross, GA, USA) with nitrogen as the adsorbing gas. ICP-OES (inductively coupled plasma optical emission spectroscopy) (Varian Vista MPX, Palo Alto, CA) was used to determine the specific amounts of iron, copper, and nickel in the particles following acid digestion. The amount of oxygen present was determined indirectly by mass balance.

2.3. Analytical methods

2.3.1. HPLC

The energetic compounds and, in the case of RDX, degradation products were analyzed using a high-performance liquid chromatograph (HPLC) (Varian Inc. Palo Alto, CA, equipped with a ProStar 410 Auto-sampler and a 330 UV–vis PDA detector). For the analysis of NTO and NQ, a Thermo Scientific Hypercarb^{TM} (porous graphite) 5 μm 4.6 mm × 150 mm column was used. The eluent was an isocratic mixture water: [acetonitrile + 0.1% trifluoroacetic acid] 85:15 (v/v), pumped at 1 mL/min. The injection volume was 5 μL of sample. The analytical wavelengths were 286 nm for NQ and 316 nm for NTO, respectively. At these conditions, NQ elutes at 3.5 min, and NTO – at 9.7 min. For the analysis of DNAN, RDX, HMX, TNX, DNX, and, MNX, a Dionex Acclaim® E1 5 μm 120 Å 4.6 mm × 250 mm column was used. For RDX, MNX, DNX, and TNX, analyzed and quantified together, the eluent was an isocratic mixture methanol:water 50:50 (v/v), pumped at 1 mL/min; the injection volume was 10 μL of sample; the analytical wavelength was 254 nm. At these conditions, TNX elutes at 7.9 min, DNX at 9.1 min, MNX at 10.9 min, and RDX at 12.6 min. For the analysis of DNAN and HMX, the eluent was an isocratic mixture methanol:water 70:30 (v/v), pumped at 1 mL/min; the analytical wavelength was 284 nm for DNAN and 254 nm for HMX, respectively; the injection volume was 5 μL; DNAN elutes at 9.7 min, and HMX at 6.0 min under these conditions. Blank samples and known concentration standards were periodically run for QA/QC purposes.

3. Results and discussion

3.1. Characterization of the bimetal particles

The ICP-OES analysis results shown in Table 1 indicate that the amount of copper deposited on the iron surface is consistently higher than that of nickel, although the experimental conditions and concentrations of the stock solutions used were identical.

Table 1
Elemental composition of bimetallic particles (average of two samples).

Sample	Fe (%)	Ni (%)	Cu(%)	Oxygen^a (%)	Fe:Cu	Fe:Ni
Fe/Ni	60.6	0.6	NA	38.8	NA	101.0
Fe/Cu	76.0	NA	9.7	13.9	7.9	NA

NA: non applicable.
^{a} Oxygen determined by mass difference.

The results for the surface characterization (BET and Langmuir) for both types of particles are presented in Table 2. The BET and Langmuir specific surfaces area for the Cu-plated particles were larger than for the Ni-plated particles. The reasons for the dissimilarities in the secondary (i.e., Cu or Ni) metal deposition and in the specific surface areas as an in-depth characterization of the bimetallic particles (i.e., SEM, AFM) are beyond the scope of the present work.

3.2. Kinetic experiments

Experimental runs using coated iron bimetallic particles were performed to derive kinetic information. The experiments were conducted using synthetic solutions prepared from industrial grade RDX. HMX is a by-product of RDX manufacture. Thus, HMX destruction kinetics was followed during the experiment using industrial grade RDX solutions.

3.2.1. Degradation of high explosive compounds (RDX, HMX, TNT) in pure compound experiments

The experiments were carried out using laboratory prepared solutions of the target compounds (60 mL aqueous samples containing 600 mg bimetallic particles; 1% solid/liquid (S/L) loading, and pH adjusted to 3 with glacial acetic acid). The selection of the S/L ratio was based on preliminary test runs (data not shown) and on available information in the technical literature [22]. To assess the effect that the type of galvanic pair may have on the degradation of the high energetics, two different bimetal particulate suspensions were used, namely Fe/Cu and Fe/Ni. The aquatic solubility of each target compound determined the choice of its initial concentration. The pH of the samples after treatment was in the range of 4–5. The collected samples were acidified with acetic acid to pH 3 prior to HPLC analysis in order to prevent iron precipitation in the HPLC column. Typical time-concentration profiles are shown in Fig. 1. The

Table 2
Surface area characterization of Fe bimetallic particles.

| Copper/iron bimetal	
BET results	
BET surface area (m^2/g)	2.585 (±0.027)
VM (cm^2/g)@ STP	0.594
Correlation coefficient	0.999
Molecular cross-section (nm^2)	0.162
Langmuir results	
Langmuir surface area (m^2/g)	3.800 (±0.123)
VM (cm^2/g) @ STP	0.872
Correlation coefficient	0.997
Molecular cross-section (nm^2)	0.162
Nickel/iron bimetal	
BET results	
BET surface area (m^2/g)	1.573 (±0.004)
VM (cm^2/g)@ STP	0.361
Correlation coefficient	0.999
Molecular cross-section (nm^2)	0.162
Langmuir results	
Langmuir surface area (m^2/g)	2.435 (±0.052)
VM (cm^2/g) @ STP	0.559
Correlation coefficient	0.997
Molecular cross-section (nm^2)	0.162
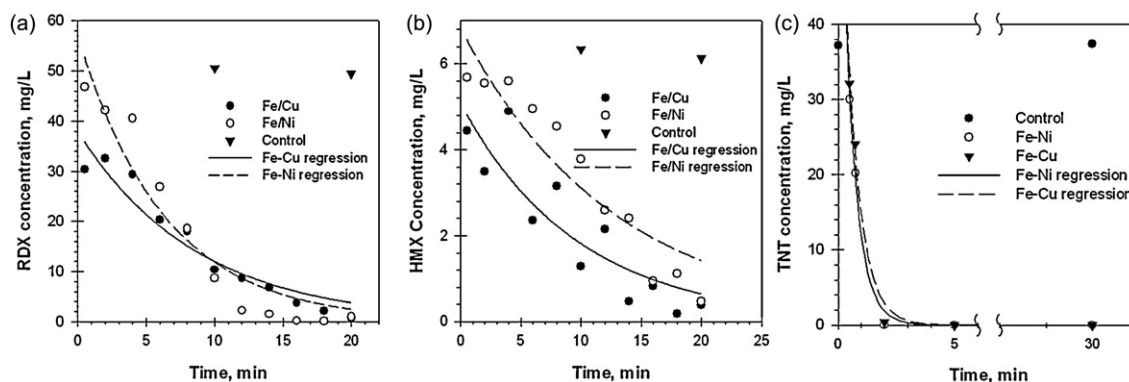
Fig. 1. (a) RDX, (b) HMX and (c) TNT concentration-time profiles using 1% Fe/Ni or Fe/Cu bimetal particles in synthetic solutions (experiments were performed in duplicate).

experimental data were used to compute the kinetic constants for the degradation of energetic materials in the presence of bimetallic particles. A pseudo-first-order kinetic expression was used for the calculations

$$\frac{dC}{dt} = -k'C \tag{1}$$

where C is the concentration of energetic material (i.e., RDX, HMX, and TNT) and k' represents the apparent first-order degradation constant (min^{-1}). The rate constants k', obtained by non-linear regression of the time-concentration experimental data, are presented in Table 3, along with the correlation coefficients and computed half-lives for RDX, HMX and TNT. The results shown in Fig. 1 indicate that RDX degrades effectively in less than 30 min when its aqueous solution of an approximate initial concentration of 50 mg/L is treated with 1% bimetal Fe/Cu or Fe/Ni suspensions. The data strongly suggest that RDX is consumed according to an apparent first-order model (R^2 of 0.974 and 0.960 for Fe/Cu and Fe/Ni, respectively), resulting in a half-life of less than 6.0 min. Based on the pseudo-first-order degradation constants, the type of bimetal pair (Fe/Cu or Fe/Ni) does not appear to affect the degradation kinetics of RDX appreciably. This finding was also observed for HMX and TNT. However, due to concerns over nickel regulations in aquatic systems, Ni metal was eliminated as a coating option; only Fe/Cu particles were used in subsequent experimental runs. No degradation was observed in the control samples, as evidenced by the virtually unchanged RDX concentration in them over a time period corresponding to the treatment time. HMX and TNT follow degradation patterns similar to that of RDX. The apparent first-order kinetic constants for all three compounds are given in Table 3, along with the respective correlation coefficients and computed half-lives. RDX degradation by ferrous bimetals proceeds via successive reduction steps leading to complete mineralization. Byproduct formation included MNX, DNX and TNX, all of which degrade completely in less than 30 min. A series of runs were carried out to further study the degradation of RDX and its reduction products. The experiments were performed using 1% S/L copper-

coated iron particles. Typical results from these experiments are shown in Fig. 2, with cubic sp line lines added for visual clarity.

Evidently, the RDX disappearance follows first-order kinetics according to the equation ($R^2 = 0.995$):

$$C_{RDX} = 18.2 \ exp(-0.766t) \tag{2}$$

where C_{RDX} represents the RDX concentration at time t and the pre-exponential value the fitted initial RDX concentration. The degradation of RDX results in the gradual generation of the mono-, di-, and tri-nitroso derivatives, namely MNX, DNX and TNX. The simultaneous detection of the three degradation products does not conform to a strictly sequential transformation pathway according to the scheme:

$$RDX \rightarrow MNX \rightarrow DNX \rightarrow TNX \tag{3}$$

However, the fact that the concentrations tend to attain peak values successively (at 1, 3, and 5 min respectively for MNX, DNX and TNX) may to some extent indicate a preferential reductive pathway.

Fig. 3 presents the concentration–time profiles of carbon in RDX, overall product-carbon (sum of the concentration of carbon in MNX, DNX, and TNX) and total-carbon (the sum of the former two). The additiveness of RDX-carbon and product-carbon to yield the total carbon clearly verifies the RDX reductive transformation to MNX, DNX and TNX. Accordingly, a comparison of the initial RDX carbon (3.5 mg/L) to the total carbon (3.7 mg/L) immediately after mixing the sample with the Fe/Cu bimetal suspension, verifies the carbon balance within the error of the analytical method. From the plot in Fig. 3 it is evident that the RDX carbon degradation follows
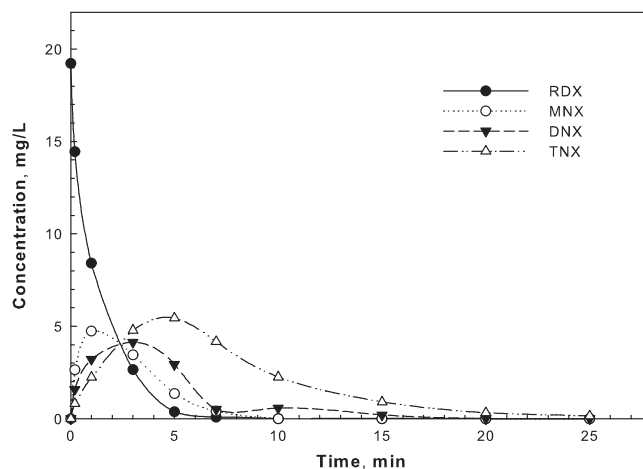
Table 3
Pseudo first order degradation constants and half-lives for RDX, HMX, and TNT for two types of bimetal (Fe/Ni and Fe/Cu). Values in parenthesis represent the standard error for the estimated rate constant.

Experimental run	k' (min^{-1})	Half-life (min)	R^2
Synthetic RDX solution Fe/Cu	0.115(0.015)	6.0	0.974
Synthetic RDX solution Fe/Ni	0.158(0.023)	4.4	0.960
Synthetic HMX solution Fe/Cu	0.103(0.023)	6.7	0.928
Synthetic HMX solution Fe/Ni	0.079(0.012)	8.8	0.969
Synthetic TNT solution Fe/Cu	1.630(0.225)	0.4	0.992
Synthetic TNT solution Fe/Ni	1.873(0.186)	0.4	0.996

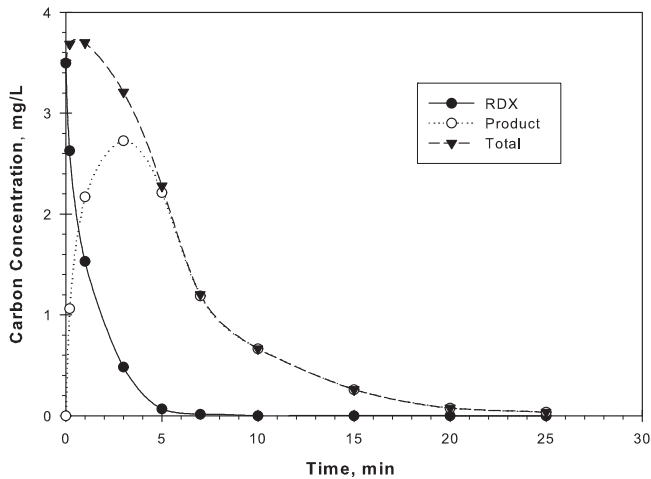**Fig. 2.** Concentration-time profiles of RDX and by-products (MNX, DNX, and TNX) using 1% S/L Fe/Cu bimetal particles.

Fig. 3. Concentration–time profiles of RDX carbon, product carbon and total carbon using 1% Fe/Cu bimetal particles.

Fig. 4. Kinetics of degradation of TNT, RDX, and HMX in pink water treated with 3% load of Fe/Cu particles.

first-order kinetics, while product carbon reaches a maximum at about 3.5 min and soon afterwards diminishes according to first-order kinetics, virtually merging with the total carbon curve. The first-order RDX carbon degradation is described by the following equation ($R^2 = 0.995$):

$$C_{RDX-C} = 3.32 \ \exp(-0.766t) \tag{4}$$

resulting, as expected, in the same rate constant as RDX concentration disappearance given by Eq. (2). The disappearance of the total carbon also follows first-order kinetics expressed by the equation ($R^2 = 0.982$):

$$C_{TC} = 3.93 \ \exp(-0.139t) \tag{5}$$

where C_{TC} is the total-carbon concentration representing the aggregate effect of the disappearance of RDX, as well as the generation and subsequent disappearance of the product carbon. This explains the significantly reduced value of the total carbon degradation constant ($0.139 \, min^{-1}$) compared to the RDX carbon constant ($0.766 \, min^{-1}$).

3.2.2. Degradation of high explosive compounds (RDX, HMX, TNT) in pink water

A series of batch experiments were performed to determine the feasibility of bimetal treatment to degrade the target compounds in 'real-life' waste streams and to assess possible synergistic/antagonistic effects. Pinkwater is a waste stream generated at munitions manufacturing and filling facilities. This wastewater was selected because it contains all three target compounds,
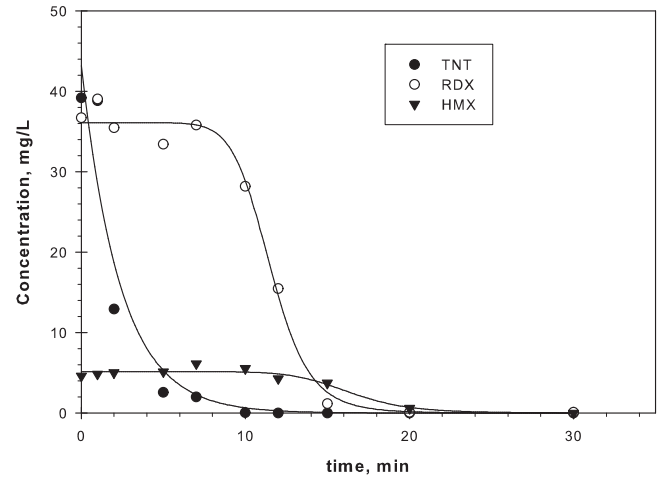
heretofore investigated individually. Since the overall organic load in pinkwater is significantly higher than that of the pure-compound experiments, the loading of coated iron particles was increased to 3% (by weight) based on preliminary tests. The initial pH of the pinkwater was 3.61; it was adjusted to 2.96 by adding 1 mL of 1 M acetic acid to vials containing 60 mL of pinkwater. Then, 1.8 g (3%) of Cu coated iron particles were added. The initial concentrations of target compounds in the pinkwater were 36.37 mg/L, 4.98 mg/L and 46.20 mg/L, for RDX, HMX and TNT, respectively. Experiments were run in two replicates with sampling times ranging from 1 to 30 min. An important objective of this study was to establish whether the degradation of each of the target compounds is affected by the presence of other energetic compounds. The results for these runs, presented in Fig. 4, indicate that TNT degrades via first-order kinetics according to the equation ($R^2 = 0.948$):

$$C_{TNT} = 43.21 \ \exp(-0.420t) \tag{6}$$

TNT reaches non-detectable concentration in about 2 min. The value of the rate constant for TNT ($0.420 \, min^{-1}$) in the pinkwater experiment is significantly lower compared to that determined in the pure-compound experiments ($0.630 \, min^{-1}$), even though the S/L ratio in the former was triple that of the latter (3% compared to 1%). Similar to TNT, RDX and HMX exhibit first-order decay which, however, materializes after lag periods of approximately 7 and 12 min, respectively. Fitting first-order rate expression to the data after the respective lag times, the following equations are obtained for RDX ($R^2 = 0.934$) and HMX ($R^2 = 0.919$):

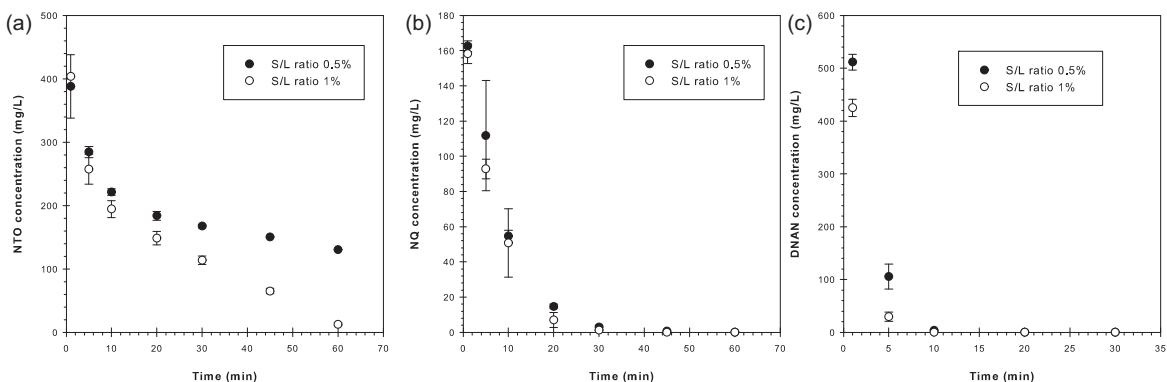$$C_{RDX} = 43.05 \ \exp(-0.081t) \tag{7}$$

Fig. 5. Effect of the Fe/Cu solids-to-liquid ratio on (a) NTO, (b) NQ, and (c) DNAN destruction at initial pH 3. Average and standard deviation of two replicates.
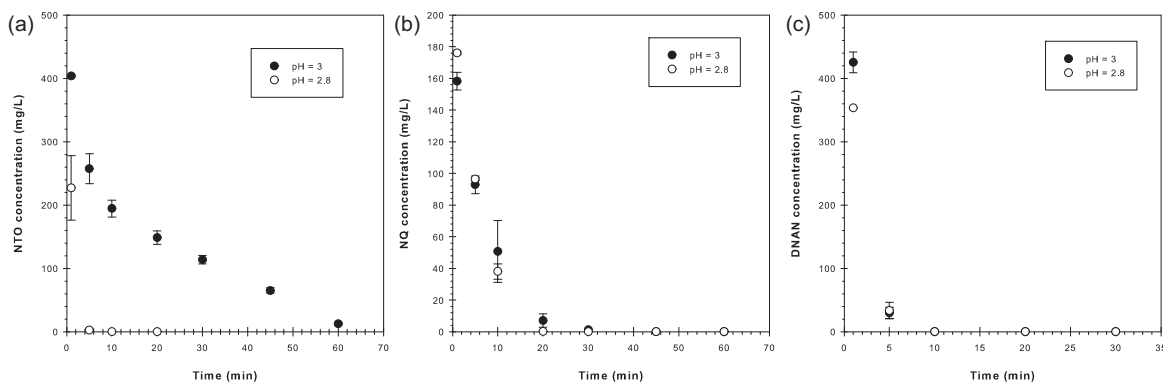
Fig. 6. Effect of initial pH on (a) NTO, (b) NQ, and (c) DNAN destruction at Fe/Cu solids-to-liquid ratio 1%. Average and standard deviation of two replicates.

$$C_{HMX} = 5.82 \exp(-0.042t) \tag{8}$$

The values of the rate constants for RDX ($0.081\,\mathrm{min^{-1}}$) and HMX ($0.042\,\mathrm{min^{-1}}$) in the pinkwater are lower than those obtained in the pure-compound experiments and presented in Table 3. This finding suggests some kind of inhibitory behavior partly due to the increased organic loading or possibly from antagonistic interactions among compounds present. The observed lag times also indicate some type of unidentified interactions and may suggest a specific preference order of each energetic for the bimetal surface. More specifically, TNT appears to have a high preference for the bimetal surface, thereby degrading first. RDX proceeds to exponential degradation but only when TNT is exhausted after the lag time of 7 min. Similarly, HMX concentration remains virtually unchanged for a lag period of 12 min until all RDX is consumed; only then does HMX degrade exponentially.

3.3. Kinetic experiments of insensitive-munitions compounds (NTO, DNAN, NQ) – effect of the bimetal S/L ratio

Preliminary experiments were carried out to assess the feasibility of reductive treatment of three novel munitions components, NTO, DNAN, and NQ. Two sets of experiments were conducted to assess the effect of the S/L ratio on the degradability of the three compounds. The data are presented in Fig. 5a–c. Evidently all three compounds are amenable to reductive degradation according to pseudo-first-order kinetics. The apparent rate constants for all compounds and conditions determined are presented in Table 4. The first-order model describes the destruction of all three compounds satisfactorily (R^2 greater than 0.975). Based on apparent rate constant values, NTO, the compound with the highest solubility among the three compounds, exhibits the slowest degradation rate of all three compounds. The degradation rate of DNAN is the highest (3–5 times greater than that of NQ), even though the solubility of this compound is roughly one order of magnitude lower than that of NQ. This indicates that amenability to reductive treatment is dictated by the chemical nature of the organic compound rather than its solubility. It appears that aromatics exhibit a high affinity for bimetal reductive treatment, a fact that was also verified

in the case of the three high explosives (TNT, RDX, HMX) where TNT was clearly more degradable compared to the heterocyclic non-aromatic nitramines (RDX and HMX). In the case of NTO, the two attempted S/L ratios (0.5% and 1.0%) resulted in doubling of the rate constant (0.021, 0.049 $\mathrm{min^{-1}}$). This agrees with the fact that the pseudo-first-order rate constant is a lumped parameter which takes into account the surface area of particles per volume of solution. In the case of NQ and DNAN, the effect of the S/L ratio on the value of the rate constant was less pronounced. For NQ, the pseudo-first order constants were 0.100 and 0.134 $\mathrm{min^{-1}}$ respectively for S/L ratios of 0.5% and 1.0%, while for DNAN the values were 0.591 and 0.667 $\mathrm{min^{-1}}$ respectively for the 0.5% and 1.0% S/L ratios. It appears that the effect of the S/L ratio diminishes with increasing values of the pseudo-first-order reaction rate constant.

3.4. Kinetic experiments of insensitive munitions compounds (NTO, DNAN, NQ) – effect of the initial pH

Kinetic experiments were conducted to determine the effect of the initial pH on the reductive degradation of the three munitions compounds. This study was deemed necessary as NTO is an organic acid of considerable strength ($pK_a = 3.76$) [14], unlike NQ and DNAN, which are practically non-ionogenic. A value of NTO $pK_a = 3.52$ determined experimentally from a titration curve of NTO with a standard solution of NaOH is in agreement with the reported value. The results for the two sets of experiments conducted at initial pH values of 3.0 and 2.8 are shown in Fig. 6a–c. Accordingly, a decrease of initial pH from 3.0 to 2.8 results in substantially higher degradation rates for NTO reaching non-detectable values within 2 min. This suggests that the undissociated NTO form exhibits a higher affinity for reduction sites than the ionic form. An initial pH drop from 3.0 to 2.8 improves the affinity of NTO for reduction sites by favoring the molecular over the ionic form from 3.3 to 5.2 times. In addition, the lower pH favors the corrosion rate of iron producing Fe^{2+} and electrons necessary for the reduction of NTO. Conversely, an initial pH drop by 0.2 units does not appear to have a significant effect on the degradation rates of NQ and DNAN.

4. Conclusions

Bimetal iron-copper particles are highly effective for treating waste streams containing numerous energetic and munitions components, present both alone and together. The type of bimetal pair (Fe/Cu or Fe/Ni) does not appear to affect the degradation kinetics of RDX, HMX, and TNT. In pure compound experiments, the degradation process is successfully described by an apparent first-order model. Based on the results, the two nitroaromatic compounds investigated (TNT and DNAN) are more prone to iron-copper bimetal reductive treatment, with half-lives of less than

Table 4
Apparent first-order constants and half-life for munitions components (NTO, NQ, DNAN) at pH 3. Values in parenthesis represent the standard error of the estimated rate constant.

	k ($\mathrm{min^{-1}}$)		Half-life (min)	
	S/L 0.5%	S/L 1.0%	S/L 0.5%	S/L 1.0%
NTO	0.021(0.005)	0.049(0.009)	33.0	14.1
NQ	0.100(0.009)	0.134(0.006)	6.9	5.2
DNAN	0.591(0.008)	0.667(0.005)	1.2	1.0

2 min. NTO proved to be the most resistant to reductive treatment among all compounds studied. The half-life of NTO can be considerably shortened by a proper adjustment of the experimental conditions (i.e. solids-to-liquid ratio and the initial pH). Experiments with "real life" wastes containing mixtures of RDX, HMX and TNT indicate that the nitroaromatic structure of TNT exhibits a high preference for the metal surface, causing that compound to degrade first. Under these conditions, reductive degradation of the other components initiates after a lag time has elapsed.

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