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Iron-Mediated Remediation of RDX-Contaminated Water and Soil under Controlled Eh/pH

J. SINGH, S. D. COMFORT,* AND
P. J. SHEA

School of Natural Resource Sciences, University of Nebraska, Lincoln, Nebraska 68583-0915

Soil and water contaminated with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a serious environmental problem at several active and abandoned munitions production facilities. Zero-valent iron (Fe^0) can effectively remediate RDX-contaminated soil and water. The objective of this study was to manipulate Eh and pH for enhanced Fe^0-mediated destruction of RDX. This was accomplished by monitoring RDX destruction under controlled Eh-pH conditions (Eh: −300 to +150 mV; pH: 2−10). Decreasing Eh and pH increased RDX destruction in aqueous solution. Treating 20 mg of RDX L^{-1} (90 μM) under a static Eh of −150 mV and pH 7 with 20 g of Fe^0 L^{-1} removed 95% of the RDX within 4 h; no RDX was detected after 8 h. Treating a soil slurry (20% solids; 510 mg RDX kg^{-1} soil) with 20 g of Fe^0 L^{-1} at an Eh of −150 mV and pH 7 increased RDX destruction by 24% over the unbuffered control and resulted in 99% RDX destruction within 24 h. Adding 4.2 mM sodium sulfide (in lieu of a static Eh) under similar conditions resulted in 93% RDX loss within 24 h. Results indicated that lowering Eh and maintaining neutral pH during Fe^0 treatment can increase RDX destruction in contaminated soil and water.

Introduction

During World War II, the manufacture and testing of high explosives at ammunition production facilities occurred at several U.S. and European locations (*1*, *2*). Explosive-laden wastewater generated during ordnance production was often discharged directly into drainage ditches, local streams, and settling lagoons. These past disposal practices have caused serious environmental problems for regulatory agencies and created formidable challenges in designing remediation treatments. Major soil and water contaminants often include nitroaromatics (TNT), nitrate esters (nitroglycerin, nitrocellulose), and heterocyclic nitramines (RDX and HMX). Among these compounds, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) is of particular environmental concern because it is generally resistant to microbial transformations in aerobic soils (*3*, *4*) and is readily leachable (*4*, *5*). While RDX is nonmutagenic (*6*), the presence of RDX in drinking water creates toxicological concerns because ingestion of RDX adversely affects the central nervous system, gastrointestinal tract, and kidneys (*7*). RDX has also been found to be toxic to some green algae (*8*) and freshwater fish (*9*).

Developing cost-effective and environmentally sound treatment technologies for explosive-tainted water and soil has been a current focus of environmental research (2, *10*−*12*). Elemental iron (Fe^0) is an avid electron donor and has been used in the remediation of contaminated groundwater because of its low cost and nontoxicity (*13*). Through studies on the dehalogenation of chlorinated methanes, Matheson and Tratnyek (*14*) proposed three reduction mechanisms, with direct electron transfer at the metal interface as the most probable reaction pathway. Other studies have indicated the importance of surface bound Fe(II)-species as electron donors or electron-transfer mediators in redox transformations of organic compounds (*15*−*17*). Klausen et al. (*15*) demonstrated that surface bound Fe(II) on iron (hyr)oxide surfaces or surface coatings plays an important role in the reductive transformation of nitroaromatic compounds, while unbound Fe(II) species were not reactive.

Other researchers have used Fe^0 as the bulk reductant for the reduction of nitroaromatics compounds to anilines (*18*), which can be further degraded biologically (*19*) or incorporated into natural organic matter via enzyme-catalyzed coupling reactions (*20*, *21*). While the use of Fe^0 to treat nitroaromatic compounds has received attention, far less effort has been directed at the use of Fe^0 for treating heterocyclic nitramines, the second major class of contaminants often found at munitions production facilities. Recently, we demonstrated the effectiveness of Fe^0 to reduce RDX concentrations in contaminated water and soil (*22*, *23*). Treating an aqueous RDX solution (32 mg L^{-1}) with 10 g of Fe^0 L^{-1} resulted in 100% destruction within 72 h (*23*).

Optimizing treatment of RDX-contaminated soil and water with Fe^0 requires an understanding of the redox potential and pH necessary for efficient destruction. This requires an appreciation for the thermodynamic stabilities of the dominant iron species in soils under varying Eh/pH conditions. In the soil−water environment, oxidative dissolution of iron metal is coupled to reduction of suitable oxidants. Although contaminant reduction is the primary goal, competition for electrons will occur from additional oxidants in the soil slurry such as dissolved O_2, H_2O, and other inorganic electron scavengers (e.g., NO_3^-, SO_4^{2-}). The corrosion of Fe^0 and related iron species results in a net increase in pH, which favors iron hydrolysis reactions (*24*). Oxidation of Fe^{2+} yields Fe^{3+} which leads to rapid precipitation of ferric (oxy)hydroxides (*25*). In agitated soil slurries, it is likely that dissolved O_2 will initially dominate and control the rate of Fe^0 and Fe^{2+} oxidation. By lowering the oxygen concentration prior to Fe^0 addition, more efficient contaminant destruction may be achieved. Moreover, by reducing or buffering the pH of the Fe^0-H_2O suspension, contaminant destruction rates should increase because less $Fe(OH)_{3(s)}$ will precipitate and protons are provided for reductive transformations. Manipulation of the Eh/pH could also affect the fate and extent of the surface bound Fe(II)-species and subsequently influence the redox transformations of organic compounds.

In this paper, we describe the use of Fe^0 to remediate RDX-contaminated water and soil. Our objective was to use an Eh-pH stat to determine the effects of varying Eh/pH on RDX destruction rates in water and soil.

Materials and Methods

Chemical Reagents and Soil. Technical grade RDX was obtained from the U.S. Biomedical Research and Development Laboratory (Frederick, MD). Carbon-14 ring-labeled RDX (154 MBq mmol^{-1}) was custom-synthesized by NEN Research Products (Boston, MA). Analytical standards of RDX were obtained from the Indian Head Division, Naval Surface Warfare Center (Indian Head, MD). Degreased zero-valent

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* Corresponding author phone: (402)472-1502; fax: (402)472-7904; e-mail: scomfort@unl.edu.

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TABLE 1. Characteristics of RDX-Contaminated Soil Obtained from the Former Nebraska Ordnance Plant near Mead, NE

soil property	unit	RDX-contaminated soil
soil pH (1:1, H_2O)		5.9
organic carbon	%	1.6
cation exchange capacity	$cmol_c\ kg^{-1}$	15.4
sand	%	30
silt	%	46
clay	%	24
extractable RDX	$mg\ kg^{-1}$	510

iron (ca. 40 mesh) was obtained from Fisher Scientific (Pittsburgh, PA) and used as purchased. We determined the surface area of this iron was 111 $m^2\ g^{-1}$ using the ethylene glycol monoethyl ether (EGME) method (*26*); analysis of similar iron by an outside laboratory determined the surface area was 1.87 $m^2\ g^{-1}$ using the BET method.

RDX-contaminated soil (0−15 cm) was obtained from a drainage ditch adjacent to a munitions production building at the abandoned Nebraska Ordnance Plant (NOP), near Mead, NE. The predominant soil type in the vicinity of the NOP is classified as a Sharpsburg (fine, montmorillonitic, mesic, Typic Argiudoll). Prior to experimentation and analysis, the soil was air-dried and ground to pass through a 2-mm sieve. Physicochemical properties of the soil were determined (Table 1) and included: pH, organic matter content, cation exchange capacity (*26*), and particle size distribution by the hydrometer method (*27*).

Eh-pH Stat. Laboratory experiments were conducted with a bench-scale Eh-pH stat system; details of system components and circuitry are described elsewhere (*28*). In brief, this system allowed for independent and dual control of Eh and pH inside a reaction cell. The reaction cell was a two-piece custom glass container. The lower section housed the RDX solution or soil slurry (working volume 500−600 cm^3); the upper section contained five glass-threaded sockets (7 mm i.d.) that housed a pH and redox electrode, acid/base feed, gas inlet, and a gas outlet line. In addition, a central 18-mm (i.d.) socket housed a stainless steel stirring rod powered by an electric motor.

The redox potential in the reaction cell was controlled by a potentiostat (*28*). This circuitry monitored the analogue signal from the combination redox probe (Corning, Bigflats, NY) and, based on the operator's preselected Eh, relayed an electrical signal to one of two solenoid valves, which allowed gas to pass into the reaction cell from cylinders containing compressed air or H_2/Ar (3%/97%). This potentiostat maintained the redox potential within ±20 mV of the set value. A redox standard solution [39.21 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 48.22 g of $FeNH_4(SO_4)_2 \cdot 2H_2O$, and 56.2 mL of concentrated H_2SO_4 dissolved in 1 L of H_2O] was used to periodically check the performance of the redox probe (*29*). This solution has an Eh of +476 mV when measured using Ag/AgCl reference electrode and saturated KCl as the fill solution.

A Metrohm Titrino (Model 718S, Brinkmann Instruments Inc., Westbury, NY) was used to measure and regulate the pH within the reaction cell. The pH stat continuously titrated into the reaction cell to maintain a set pH by dispensing small volumes of acid (HCl) or base (NaOH) until the preset pH was reached.

RDX Solution/Fe^0 Experiments. All RDX solutions were treated with 20 g of Fe^0 L^{-1} (2%,w/v; particle size ca. 40 mesh). Each experiment used 500 mL of a 20 mg RDX L^{-1} prepared in an 8 mM NaCl matrix and spiked with ^{14}C-labeled RDX (90 Bq mL^{-1}). No nutrients or cofactors were added to the aqueous RDX solution, and no efforts were made to control the sterility of the solution. All experiments monitored changes in RDX concentration and ^{14}C-activity with time. The initial unbuffered experiment monitored changes in both Eh and pH with time following the addition of Fe^0. Subsequent experiments controlled either Eh (+150, 0, −150, and −300 mV), pH (2, 4, 6, 8, and 10), or both (Eh = −150 mV, pH = 6; Eh = −150 mV, pH = 7). Solutions were continuously agitated by a mechanical stirrer. At selected times throughout the 24-h experiments, 1.2-mL aliquots were removed, transferred to 1.5-mL polypropylene microcentrifuge tubes, and centrifuged at 15 000*g* for 10 min. RDX was quantified by HPLC using a Keystone Betasil NA column (Keystone Scientific Inc., Bellefonte, PA) with an isocratic mixture of methanol and H_2O (25:75) at a flow rate of 1.0 mL min^{-1} and spectrophotometric detection at 254 nm. Carbon-14 in the aqueous solution was determined by mixing 1 mL of sample with 6 mL of Ultima Gold cocktail and quantification by liquid scintillation counting (LSC) using a Packard 1900TR Liquid Scintillation Counter (Packard Instr. Co., Downers Grove, IL).

RDX Concentration and Iron Aging Experiments. The effects of RDX concentration on destruction rates were determined by varying the initial RDX concentration (C_o = 1, 2.5, 5, 10, 20 mg of RDX L^{-1}) and plotting relative concentrations (C/C_o) versus time. Nonlinear regression (Sigma Plot, Jandel Corp., San Rafael, CA) was used to determine psuedo-first-order rate constants in all experiments. All experiments were conducted under static Eh/pH conditions (−150 mV and pH 7).

To determine the effects of iron aging on RDX destruction rates, general procedures were followed (C_o = 20 mg of RDX L^{-1} + 2% Fe^0), but we reseeded RDX into the reaction vessel at either 2, 4, or 6 h following the Fe^0 addition. This reseeding was performed in three separate experiments by adding between 4 and 5 mL of 2000 mg of RDX L^{-1} (in methanol) to the reaction vessel so that the RDX concentration was increased to its initial concentration (C_o = 20 mg of RDX L^{-1}). All experiments were conducted under static Eh/pH conditions (−150 mV and pH 7).

Soil Slurry Experiments. Slurries of RDX-contaminated soil (20% solids; 510 mg of RDX kg^{-1} soil) were equilibrated for 12 h prior to treatment with 2% Fe^0 (w/v). Treatments included four sets of Eh and pH conditions: (i) control = unbuffered Eh/pH; (ii) unbuffered Eh, pH = 7.0; (iii) Eh = 0 mV, pH = 7.0; and (iv) Eh = −150 mV, pH = 7.0. Samples were taken throughout the 24 h experiment and analyzed by HPLC for solution RDX concentrations as described above. The slurries were allowed to settle for 2 to 3 days, the supernatant was discarded, and residual soil from each experiment was air-dried. Subsamples of soil (2 g) were extracted with 10 mL of acetonitrile by sonication for 18 h at 30 °C to determine extractable RDX.

Sodium Sulfide Experiments. To eliminate the requirement of H_2/Ar gas mixture and the potentiostat, sodium sulfide ($Na_2S \cdot 9H_2O$) was used to lower the redox potential in the reaction cell. Treatments included 0.1% (w/v) sodium sulfide alone (control) and sodium sulfide + Fe^0. The pH of both treatments was buffered at 7 with the pH-stat. One additional treatment used 0.2 M KH_2PO_4 buffer (pH 7) in place of the pH-stat. Experimental procedures and sampling protocols were similar to experiments described above.

Results and Discussion

RDX Solution/Fe^0 Experiments. It is not uncommon for soils located around munitions production facilities to contain precipitated or solid-phase RDX (*4*). Adding water to these soils results in saturated solutions (i.e., RDX solubility limit is reached). Consequently, remediating RDX-contaminated soils will require a treatment that can continuously remove high concentrations of RDX from solution.

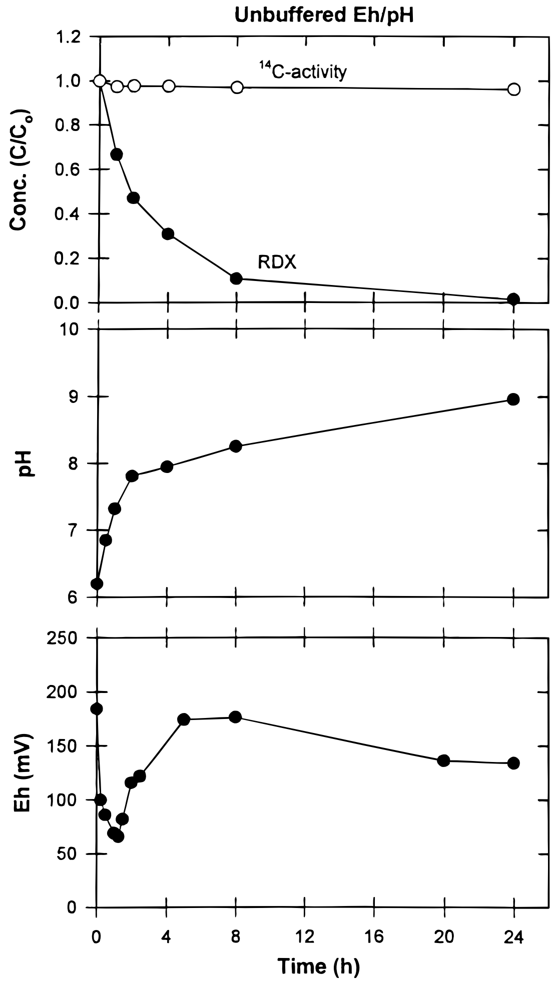

FIGURE 1. Changes in RDX, ^{14}C-activity, Eh, and pH with time following addition of 20 g Fe^0 L^{-1} (2%,w/v) to a 20 mg RDX L^{-1} aqueous solution.

Adding 2% Fe^0 (w/v) to a 20 mg RDX L^{-1} solution rapidly decreased RDX concentrations within the first 4 h and resulted in 98% removal by 24 h (Figure 1). Tracking solution ^{14}C-activity indicated little change following the addition of Fe^0 and indicates that the Fe^0-induced transformation products were not retained by the iron surface, nor precipitated, or lost from the reaction chamber as a gas; this observation is consistent with earlier reports (*23*).

The loss of RDX from Fe^0 treatment can in part be explained by the formation of nitroso degradates. In a previous study (*23*), we demonstrated that following a 24-h treatment of 20 mg of RDX L^{-1} with 10 g of Fe^0 L^{-1} (1% Fe^0 w/v, vs 2% as in this study), the mono-, di-, and trinitroso degradates of RDX collectively accounted for 26% of the RDX lost from solution. After 24 h, this amount decreased as the RDX concentration continued to decrease and nitroso products disappeared (*23*). Although a near complete (100%) balance of ^{14}C was also observed in this study, a similar N-balance was not obtained. Monitoring NH_4^+ released into solution revealed that it constituted 17.5% of the RDX-N added. This indicates the formation of unidentified C−N intermediates, other than the nitroso degradates, was formed from the treatment of RDX with Fe^0.

Temporal monitoring of pH and Eh in the present study indicated a steady rise in pH from 6.2 to 8.3 during the first 8 h and then a gradual increase to pH 9 by 24 h (Figure 1). This increase in pH is explained by the oxidative dissolution of iron metal resulting from the reaction of Fe^0 with dissolved O_2 [eq 1] and H_2O [eq 2].

$$2Fe^0 + O_2 + 4H^+ \rightleftarrows 2Fe^{2+} + 2H_2O \qquad (1)$$

$$Fe^0 + 2H_2O \rightleftarrows Fe^{2+} + H_2 + 2OH^- \qquad (2)$$

In both reactions, H^+ are consumed so that the pH rises and significant amounts of OH^- appear. Under reducing conditions ferrous hydroxide ($Fe(OH)_{2(s)}$) can precipitate, which with time can decompose to magnetite (Fe_3O_4) (*30*). In the unbuffered system, however, the solution was continuously agitated (aerated), and the formation of $Fe(OH)_{2(s)}$ was likely short-lived as changes in Eh occurred.

Monitoring Eh following the addition of Fe^0 indicated a rapid drop in Eh from 184 mV to approximately 70 mV within 1 h (Figure 1). This rapid decrease was followed by an increase in Eh to near ambient conditions (174 mV) within 5 h. After 5 h, the Eh remained relatively constant until 8 h; thereafter a slight decrease in Eh corresponded with a one unit rise in pH (Figure 1).

The rapid decrease in Eh during the first 1 h can be readily attributed to the oxidation of Fe^0 during aerobic corrosion [eq 1]. While ferrous species were being generated, both Eh and pH of the unbuffered system steadily increased. It is well established that if the solution pH is much above 6, dissolved oxygen causes rapid oxidation of Fe^{2+} and precipitation of ferric hydroxide [eq 3] (*24*, *31*).

$$Fe^{2+} + {}^{1}/_{4}O_2 + {}^{5}/_{2}H_2O \rightleftarrows Fe(OH)_{3(s)} + 2H^+ \qquad (3)$$

The rate law for oxidation of dissolved Fe^{2+} can be expressed as

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2 P_{O_2} \qquad (4)$$

where $k \approx 8.0 \times 10^{13}$ min^{-1} atm^{-1} mol^{-2} L^2 at 20 °C and P_{O_2} is the partial pressure of O_2 (*24*, *31*). Therefore, the rate of ferrous iron oxidation is first-order with respect to oxygen and Fe^{2+} and second-order with respect to OH^-. The strong relationship between Fe^{2+} oxidation and pH [eq 4] indicates that Fe^{2+} will not persist for more than a few minutes in aerated solutions with pH ≥ 7 (*24*, *31*). In our unbuffered experiments, the pH was above 7 and rising at the time when the Eh had reached a minimum ($t = 1$ h, Eh = 70 mV). Therefore, ferric hydroxides were rapidly being produced. The observed increase in Eh after 2 h is likely coupled to the passivation of the Fe^0 and the continuous mixing (aeration) of the solution.

Considering the observed fluctuations in Eh and pH during Fe^0 treatment of aqueous RDX, our approach to maximize RDX destruction rates was to first buffer either Eh or pH with the Eh-pH stat and then buffer both Eh and pH for enhanced RDX destruction. It should be noted that the use of an Eh/pH-stat allowed us to control the Eh/pH of the bulk solution (suspension), not the iron interface, which likely was dominated by the Fe^0/Fe^{2+}couple. Other electrochemical cell techniques, such as use of a rotating disk electrode (*32*) would be needed to adjust the potential at the iron interface.

Treating a 20 mg RDX L^{-1} solution with 2% Fe^0 (w/v) under four redox potentials (+150, 0, −150, and −300 mV) resulted in greater RDX destruction rates with decreasing Eh (Figure 2A). While RDX destruction increased when Eh was lowered from +150 to 0 mV, minimal differences were observed between the 0 and −150 mV redox settings, and destruction rates were essentially identical between the −150 and −300 mV treatments (Figure 2A). Because pH was not buffered, the initial pH of 6.2 for the RDX solution increased to between 8.8 and 9.4 at 24 h for the various redox settings. Small differences in RDX destruction rates at the lower Eh settings are likely explained by the thermodynamic stability

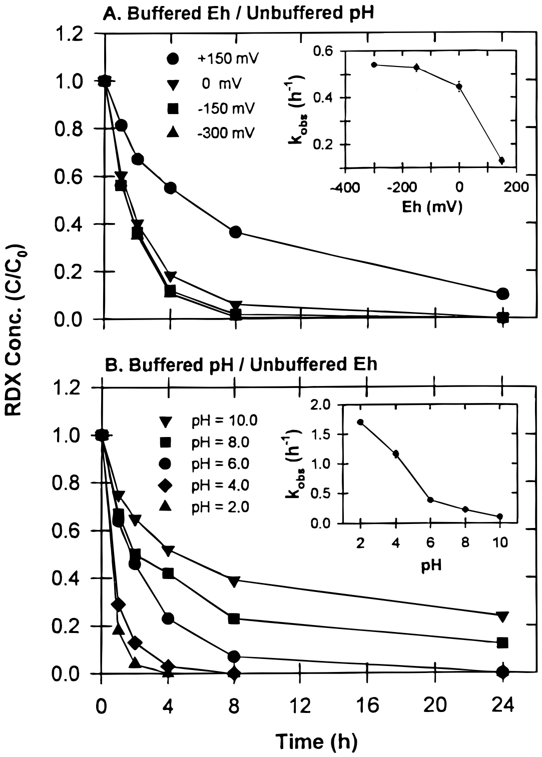

FIGURE 2. Changes in RDX concentration following Fe^0 treatment under buffered: (A) Eh (+150, 0, −150, and −300 mV) and (B) pH (10, 8, 6, 4, 2).

of the various iron species. The Eh/pH stability diagram for the Fe^0-H_2O system (*14*) indicates that at near neutral pH, ferric iron reduction occurs at approximately +150 mV (vs SHE). In the unbuffered control, and at our highest redox setting (+150 mV vs Ag/AgCl), the formation of rust ($Fe(OH)_{3(s)}$) was readily visible during our 24 h experiment; at the lower Eh settings, the redox potential was below the stability field for $Fe(OH)_{3(s)}$ formation and this corresponded with less differences in RDX destruction rates (Figure 2A).

Results from controlled pH experiments indicated a steady increase in RDX destruction with decreasing pH (Figure 2B). No RDX was detected in solution after 4 h at pH 2, but about 24% of the initial RDX remained after 24 h at pH 10. With reference to pH and within the confines of the experimental treatments, pH 2 resulted in the greatest rate of RDX destruction. However, because pH 2 would be difficult to maintain in a large-scale treatment, especially with subsoils typical for Nebraska (high carbonate concentrations), we chose pH 6 and 7 as appropriate values for further study. This was also based on the fact that a near-neutral pH would be more favorable for subsequent biotic-mediated transformations of the products generated from Fe^0 treatment of RDX. We previously demonstrated that Fe^0 increased the cumulative $^{14}CO_2$ released from a static soil microcosm containing ^{14}C-RDX (16% without Fe^0 vs 61% with Fe^0) (*23*). Therefore, there is evidence to indicate that Fe^0-treated RDX products are more biodegradable than parent RDX.

Following separate evaluations of Eh and pH effects on RDX destruction rates, Eh and pH were simultaneously controlled in the reaction cell. An Eh of −150 mV combined with pH 6 or 7 was evaluated for this purpose. As much as 96% of the initial RDX was lost within 4 h under these experimental conditions, with no appreciable differences between pH 6 and 7 (Figure 3). Changes in ^{14}C-activity with time were mild for most treatments, with the exception of the −150 mV/unbuffered pH treatment, where approximately 12% of the ^{14}C-activity was lost from solution. The lack of significant ^{14}C sorption indicates that reactive sites on the iron surface were not likely blocked by sorption of organic solutes. This has not been the case with Fe^0 treatment of some other contaminants, e.g., atrazine (*33*).

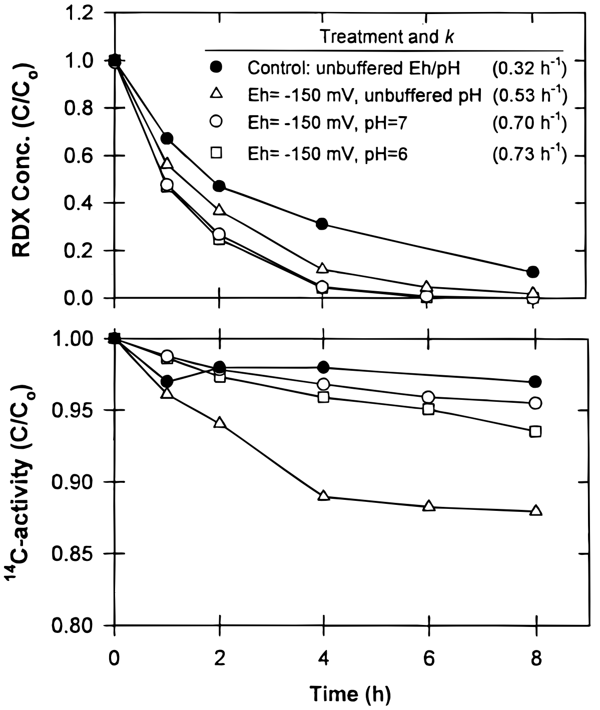

FIGURE 3. Changes in RDX concentrations and ^{14}C-activity under controlled Eh/pH conditions.

RDX Concentration and Iron Aging Experiments. The effects of RDX concentration and duration of Fe^0 in H_2O (aging) were evaluated. Johnson et al. (*34*) reported that initial transformations rates of CCl_4 were concentration dependent in experiments using a high CCl_4 to Fe^0 ratio. By comparison, Orth and Gillham (*35*) found pseudo-first-order kinetic constants for trichloroethylene were not concentration dependent in systems with a much lower range of solute concentrations. Using initial concentrations of 20, 10, 5, 2.5, and 1.0 mg of RDX L^{-1} and a constant Eh/pH (−150 mV, pH 7), we observed an increase in the rate constants for RDX loss from 0.70 (SE = 0.02) h^{-1} (20 mg of RDX L^{-1}) to 1.01 (SE = 0.04) h^{-1} (1.0 mg of RDX L^{-1}) (Figure 4A). Although rate constants increased at lower RDX concentrations, the observed differences indicated that the first-order decay rate constants were not strongly dependent on RDX concentration. Allen-King et al. (*36*) reported concentration-dependent rate constants for CCl_4 reduction in a fresh Fe^0-H_2O system but observed no affect of CCl_4 concentration after the Fe^0 was exposed to water for 2.7 days.

Because RDX-contaminated soils often contain solid-phase RDX, it is likely that soil solutions will become continuously replenished with RDX. This high RDX concentration in soil coupled with Fe^0 oxidation with time will undoubtedly affect relative RDX destruction rates. By reseeding RDX into the initial solution, the effects of iron aging on RDX destruction were evaluated. Transformation rates were slowed when RDX was reseeded at 2, 4, or 6 h (Figure 4B). Initially, approximately 50% of the RDX was transformed within 1 h. When RDX was reseeded at 6 h, subsequent RDX loss within the next 1 h was only 31%. Corresponding pseudo-first-order rate constants decreased from 0.67 to 0.39 h^{-1} (Figure 4B). Several researchers have reported the effects of iron aging on contaminant destruction rates (*34, 36−37*). Most often, a physical mechanism, such as blockage by precipitates, irreversible sorption of degradation products,

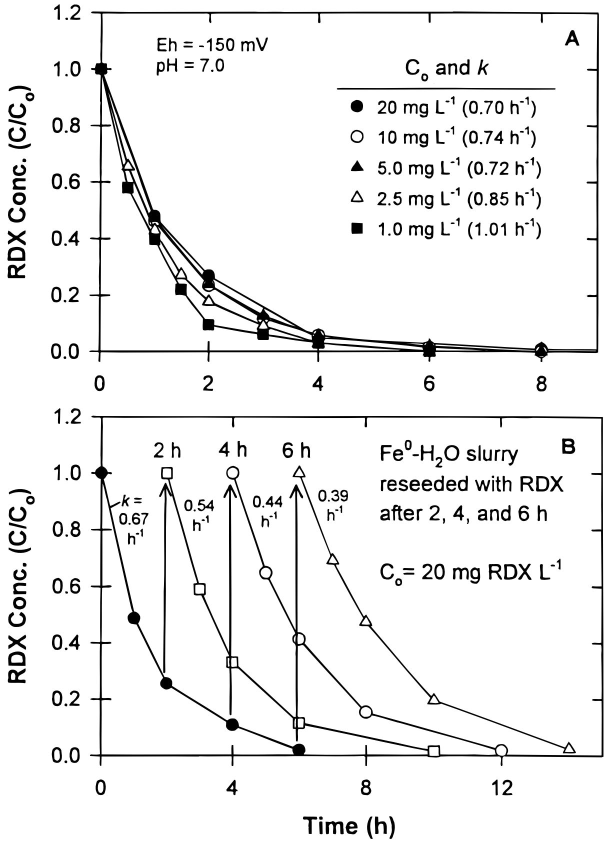

FIGURE 4. Changes in RDX concentrations following Fe^0 addition: (A) effects of initial RDX concentration on pseudo first-order destruction rates; and (B) effects of iron aging on RDX destruction rates. The figure indicates results from three experiments where RDX was reseeded into the reaction cell after 2, 4, and 6 h.

or corrosion are offered as explanations. Because earlier experiments showed no loss of solution ^{14}C with time, we can exclude sorption of organic degradates to the iron surface as one source for the decrease in RDX destruction rates with time. The observed decrease in rate constants indicates that although Eh/pH conditions were controlled for enhanced RDX destruction, corrosion and passivation of the iron surface likely influenced RDX destruction rates.

Soil Slurry Experiments. Before adding Fe^0, RDX-contaminated soil (510 mg of RDX kg^{-1}) was prepared as a slurry (100 g soil:500 mL water) and equilibrated for 12 h. Soil analysis revealed a textural class of a loam with a pH of 5.9 (Table 1). This soil was obtained from a drainage ditch adjacent to a munitions production building at the Nebraska Ordnance Plant (Mead, NE). Drainage ditches were routinely used as conduits for disposal of munitions-laden wastewater during plant operations. Consequently, these soils are severely contaminated. Dissolution of solid RDX and desorption of RDX from this soil resulted in an initial solution concentration of approximately 32 mg of RDX L^{-1} and an acetonitrile-extractable soil concentration of 350 mg of RDX kg^{-1}. By manipulating Eh and pH in the soil slurry, the Fe^0-mediated destruction of RDX could be enhanced. In the unbuffered control, a 75% decrease in total RDX was observed in the soil slurry after 24 h (Table 2). Lowering the Eh to 0 mV and maintaining neutral pH further reduced the total RDX by 86% (Table 2). Applying Fe^0 to the slurry that had an Eh of −150 mV and a pH of 7 resulted in a 99% reduction in total RDX (solution RDX + extractable RDX); this treatment reduced RDX concentration below the USEPA remediation goal for the Nebraska Ordnance Plant (5.8 mg of RDX kg^{-1}). Therefore, as observed in RDX solution experiments, using 2% Fe^0 (w/v) under controlled Eh and pH conditions was highly effective in remediating the RDX-contaminated soil.

Sodium Sulfide Experiments. While enhanced RDX destruction in our bench-scale reactor was achieved at an Eh = −150 mV and pH = 7, these conditions would be more difficult to achieve at the field scale using similar equipment (i.e., H_2/Ar gases). As an alternative to the Eh-stat, we chose sodium sulfide ($Na_2S \cdot 9H_2O$; 4.2 mM) as an oxygen scrubber to chemically lower the Eh of the soil slurry. Yu and Bailey (*38*) reported an Eh of −481 mV for an aqueous 0.24 M sodium sulfide solution. Previous researchers have used $Na_2S \cdot 9H_2O$ as an oxygen scrubber in media used to grow methanogenic bacteria (*39*). Initial experiments using $Na_2S \cdot 9H_2O$ as a control (with no buffering of pH) resulted in 80% reduction in RDX concentration from aqueous solution within 24 h (data not shown). Most of this RDX loss, however, was attributed to alkaline hydrolysis because the solution pH increased from 6.3 to 11.6 within 1 min after adding $Na_2S \cdot 9H_2O$ and remained above pH 11 throughout the experiment. RDX is known to undergo alkaline hydrolysis via attack of the base on the acidic hydrogens of the RDX methylene groups (*40*) to form 1,3,5-triaza-3,5-dinitrocyclohex-1-ene, which under further hydrolysis can yield NO_2^-, N_2O, NH_3, and N_2 (*41*−*43*). When the pH was buffered at 7, $Na_2S \cdot 9H_2O$ had no effect on RDX transformation in aqueous solution (data not shown) or in the soil slurry (Figure 5).

Using $Na_2S \cdot 9H_2O$ in combination with Fe^0 to treat RDX-contaminated soil (pH = 7) decreased the total RDX in the soil slurry by 93% (Table 2). When the soil slurry pH was controlled with the phosphate buffer rather than the pH Stat, total RDX decreased by 89%. These RDX destruction rates are less than those achieved with the Eh-pH stat but greater than those observed in the unbuffered control (75% destruction, Table 2). Although the $Na_2S \cdot 9H_2O$ was effective in initially lowering the Eh from 160 to −110 mV, it could not

TABLE 2. RDX Remaining after 24 h Treatment of Contaminated Soil (510 mg RDX kg^{-1}) with Fe^0 (2% w/v) under Varying Eh/pH Conditions

experimental treatments	RDX left in solution (mg L^{-1})	extractable RDX (mg kg^{-1})	total RDX remaining[a] (mg kg^{-1})	RDX lost[b] (%)
		Eh-pH Experiments		
control (unbuffered Eh/pH)	14.1 (0.04)[c]	56 (0.46)	126 (0.03)	75 (0.05)
Eh = unbuffered; pH 7	7.9 (0.11)	29 (0.44)	68 (0.06)	86 (0.11)
Eh = 0 mV; pH 7	6.4 (0.05)	22 (0.15)	54 (0.04)	89 (0.08)
Eh = −150 mV; pH 7	0.5 (0.01)	1.2 (0.01)	3.9 (0.05)	99 (0.01)
		Na_2S Experiments[d]		
Na_2S+Fe^0 (pH stat)	4.6 (0.06)	11 (0.19)	34 (0.48)	93 (0.09)
Na_2S+Fe^0 (0.2 M KH_2PO_4)	7.5 (0.03)	17 (0.36)	54 (0.50)	89 (0.10)

[a] Total RDX equals RDX left in solution plus soil extractable RDX. [b] RDX lost = 100% − [(total RDX remaining ÷ 510 mg RDX kg^{-1}) × 100]. [c] Values in parentheses represent sample standard deviations ($n = 2$). [d] $Na_2S \cdot 9H_2O$ concentration was 0.1% (w/v) and pH was buffered at 7 with the pH stat or 0.2 M KH_2PO_4.

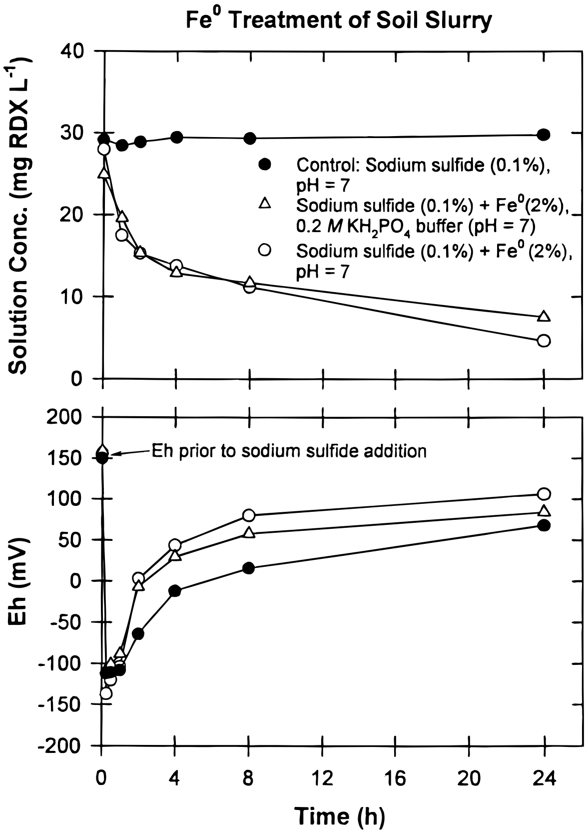

FIGURE 5. Changes in RDX concentration and Eh following treatment of a soil slurry with Fe^0. Eh was lowered by $Na_2S{\cdot}9H_2O$ addition, and pH was controlled by the pH-stat or phosphate buffer.

continuously maintain the low Eh (Figure 5) and likely explains why less RDX destruction was observed. However, a complicating factor, not initially considered was the effect of a reduced sulfur species on the iron speciation. Similarly, iron complexation with phosphate pH buffer may have led to precipitation. These factors could also have contributed to less RDX destruction than those obtained with the Eh/pH stat.

In summary, RDX destruction by zero-valent iron in aqueous solution and soil slurries was greatly enhanced by decreasing Eh and pH. Results from our experiments provide Eh/pH ranges for enhanced RDX destruction by zero-valent iron. Treating soil slurries containing 20% solids with 2% Fe^0 (w/v) under Eh = −150 mV and neutral pH completely remediated a RDX-contaminated soil (510 mg of RDX kg^{-1}) within 24 h. Controlling Eh/pH increased overall RDX destruction in a soil slurry by 24% over the unbuffered Eh/pH system. In lieu of the Eh/pH stat, sodium sulfide and buffer solutions effectively lowered Eh and maintained neutral pH in the soil slurry. These manipulations enhanced the short-term effectiveness of Fe^0 to remediate a RDX-contaminated soil.

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