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PII: S0269-7491(97)00081-X

Environmental Pollution, Vol. 97, No. 1-2, pp. 55-64, 1997
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0269-7491/97 $17.00 + 0.00

REMOVAL OF TNT AND RDX FROM WATER AND SOIL USING IRON METAL

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(Received 16 October 1996; accepted 26 May 1997)

Abstract

Contaminated water and soil at active or abandoned munitions plants is a serious problem since these compounds pose risks to human health and can be toxic to aquatic and terrestrial life. Our objective was to determine if zero-valent iron (Fe^0) could be used to promote remediation of water and soil contaminated with 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). As little as 1% Fe^0 (w/v) removed 70 mg TNT litre^{-1} from aqueous solution within 8 h and removed 32 mg RDX litre^{-1} within 96 h. Treating slurries (1:5 soil:water) of highly contaminated soil (5200 mg TNT and 6400 mg RDX kg^{-1} soil) from the former Nebraska Ordnance Plant (NOP) with 10% Fe^0 (w/w soil) reduced CH_3CN-extractable TNT and RDX concentrations below USEPA remediation goals (17.2 mg TNT and 5.8 mg RDX kg^{-1}). Sequential treatment of a TNT-contaminated solution (70 mg TNT litre^{-1} spiked with ^{14}C-TNT) with Fe^0 (5% w/v) followed by H_2O_2 (1% v/v) completely destroyed TNT and removed about 94% of the ^{14}C from solution, 48% of which was mineralized to $^{14}CO_2$ within 8 h. Fe^0-treated TNT also was more susceptible to biological mineralization. Our observations indicate that Fe^0 alone, Fe^0 followed by H_2O_2, or Fe^0 in combination with biotic treatment can be used for effective remediation of munitions-contaminated water and soil. © 1997 Elsevier Science Ltd

Keywords: Munitions, reduction, remediation, sorption, zero-valent iron.

INTRODUCTION

Contamination of soil and water with 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a problem at sites where munitions were formerly manufactured, loaded, stored or demilitarized (Jenkins and Walsh, 1992). Past disposal practices at the former Nebraska Ordnance Plant (NOP, Mead, NE) have resulted in numerous hectares of contaminated land. TNT and RDX are still present at very high concentrations throughout the soil profile in drainage ditches adjacent to NOP facilities where the explosives were packed and loaded during World War II and the Korean War (Fig. 1). RDX, and to a lesser extent TNT, are mobile in soil and pose a risk of groundwater contamination when present at high concentrations. These and related compounds have been detected in surface water and groundwater in the vicinity of other former munitions facilities (Jerger *et al.*, 1976; Periera *et al.*, 1976; Spalding and Fulton, 1988). Cleanup is required to ensure public health and safety since many of these nitroaromatics and nitramines pose risks to human health (Sittig, 1985), and can be toxic to aquatic and terrestrial organisms (Schott and Worthley, 1974; McCormick *et al.*, 1976; Smock *et al.*, 1976; Kaplan and Kaplan, 1982; Wellington and Mitchell, 1991).

Incineration is the preferred technology for remediating munitions-contaminated soil and was recently recommended for 6400 m^3 of contaminated soil at the NOP. Although incineration is effective, it is expensive, produces unusable ash, and has poor public acceptance due to safety concerns regarding air emissions. The high cost and associated disadvantages of incineration have motivated researchers to seek more cost-effective and environmentally benign remediation alternatives.

Bioremediation of munitions-contaminated soil is often slow and may be incomplete (Boopathy *et al.*, 1994; Rieger and Knackmuss, 1995). Chemical treatments can provide efficient and environmentally acceptable remediation alternatives. In recent years, great interest has focused on using zero-valent iron metal (Fe^0) as a remediation tool (Wilson, 1995). Reynolds *et al.* (1990) found that several aliphatic halogenated hydrocarbon solvents were unstable in the presence of metallic well casings. Researchers have subsequently reported dehalogenation of a variety of compounds by iron metal. Gillham and O'Hannesin (1994) found rapid abiotic reductive dechlorination of 14 chlorinated methanes, ethanes and ethenes in the presence of Fe^0. Rapid reductive dehalogenation of atrazine (6-chloro-*N*-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) was observed in the presence of nanosize Fe^0 particles (Pulgarin *et al.*, 1995). Iron-promoted remediation processes have been successfully used in the field, including *in situ* permeable reactive walls (Blowes *et al.*, 1995; Powell *et al.*, 1995; Yamane *et al.*, 1995).

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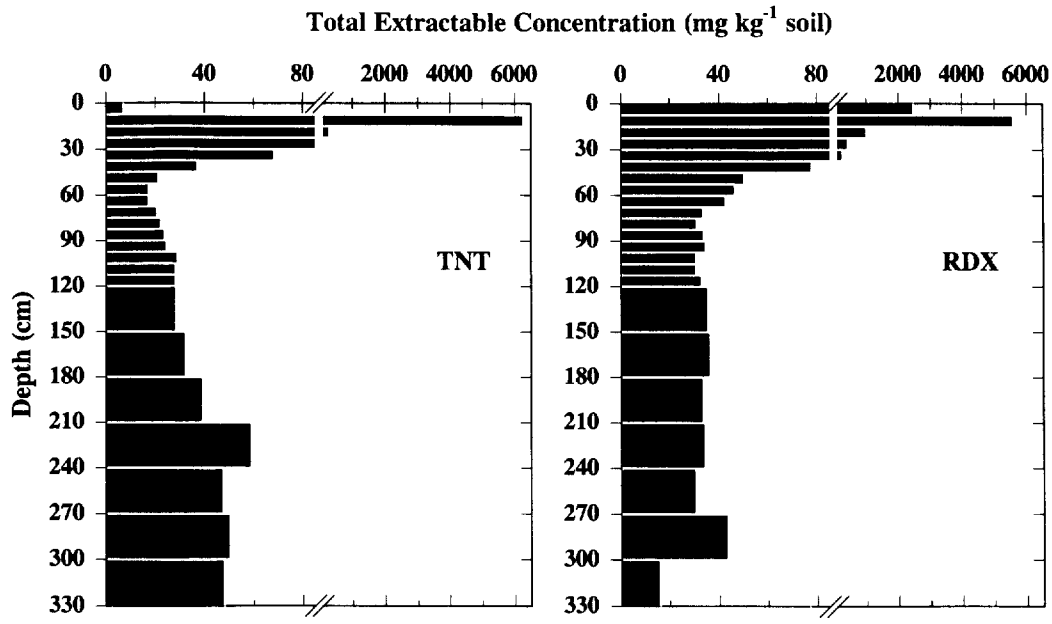

Fig. 1. Distribution of TNT and RDX in contaminated soils at the former Nebraska Ordnance Plant, Mead, NE. Bar widths delineate sampling depths.

A 1950s post-wartime process (Kastens and Kaplan, 1959) employed Fe^0 to promote reduction of trinitrobenzoic acid derived from TNT to triaminobenzene, which readily hydrolyzed to phloroglucinol (2,4,6-trihydroxybenzene) for use in photocopy and dye industries. Direct reduction of TNT with Fe^0 and acid produced methyl phloroglucinol (2,4,6-trihydroxytoluene). Jenkins and Walsh (1992) later used a zero-valent metal (Zn^0) in a Franchimont reaction to convert RDX to nitrous acid as the initial step in a colorimetric procedure for rapid RDX detection in soil. Removal of RDX nitro groups would be an important first step in the transformation of RDX to more biodegradable products. In a recent study, Agrawal and Tratnyek (1996) described nitrobenzene reduction by Fe^0 as an example of the potential for Fe^0 to remediate water contaminated with other nitroaromatics. These studies demonstrate the enormous potential of Fe^0 to remove environmental contaminants and indicate applications for remediating TNT- and RDX-contaminated water and soil.

Nitro group reduction is common among processes contributing to the environmental fate of TNT (Spanggord *et al.*, 1991). Incomplete TNT reduction, often observed in aerobic transformations, produces nitroso, hydroxylamino, and anilinic intermediates that may be highly toxic and recalcitrant. In mammalian systems, some of these compounds can form DNA adducts which may induce mutagenesis and carcinogenesis (USEPA, 1977). Condensation of the nitroso and hydroxylamino intermediates can produce potentially toxic azoxy dimers, but in soil the availability of these compounds is greatly reduced through strong binding (Bollag, 1992; Hundal *et al.*, 1997). Neither azoxybenzene nor azobenzene were detected, however, after treating nitrobenzene with Fe^0 (Agrawal and Tratnyek, 1996). Thus treatment with Fe^0 may promote more efficient TNT transformation and detoxification than biotic remediation treatments alone.

Chemical pretreatment can facilitate subsequent biodegradation of some recalcitrant or toxic xenobiotics (Scott and Ollis, 1995). Lee and Carberry (1991) reported reduced toxicity and increased biodegradation of phenolic compounds in wastewater after treatment with Fenton reagent (Fe^{2+} + H_2O_2). Pretreatment with Fenton reagent also resulted in a 50% reduction in toxicity and increased degradability of *o*-cresol and 2,4-dinitrophenol by anaerobic bacteria (Wang *et al.*, 1992). We hypothesize that Fe^0, or Fe^0 in combination with H_2O_2, could be used to transform TNT and RDX to products that are strongly bound, less toxic, or more biodegradable in the soil-water environment.

The objective of our research was to determine how Fe^0 could be used to remediate water and soil contaminated with TNT and RDX. Abiotic treatments included Fe^0 alone or in combination with H_2O_2; Fe^0 was also evaluated as a pretreatment to increase TNT biodegradation. TNT- and RDX-contaminated soils were obtained from the former NOP. Remediation goals of 17.2 mg TNT and 5.8 mg RDX kg^{-1} soil established by the United States Environmental Protection Agency (USEPA) for the NOP site (U.S. Army Corps of Engineers, 1992) were used as criteria to assess the effectiveness of the remediation treatments.

MATERIALS AND METHODS

Chemical reagents and soils

Technical grade 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were obtained from the U.S. Biomedical Research and Development Laboratory (Fort Detrick, Frederick, MD). ^{14}C-ring labeled TNT (137 MBq $mmol^{-1}$) and RDX (154 MBq

$mmol^{-1}$) were custom-synthesized by NEN Research Products (Boston, MA). Analytical standards of TNT, RDX, 2-amino-4,6-dinitrotoluene (2ADNT), and 4-amino-2,6-dinitrotoluene (4ADNT) were obtained from the Indian Head Division, Naval Surface Warfare Center (Indian Head, MD). Hexahydro-1,3,5-trihydroxy-1,3,5-triazine was obtained from Aldrich (Milwaukee, WI). Fine-grained (~40 mesh) zero-valent iron metal (Fe^0) was obtained from Fisher Scientific (Pittsburgh, PA). The specific surface area of Fe^0 was $3.3\,m^2\,kg^{-1}$ as determined using ethylene glycol monoethyl ether (Soil Survey Staff, 1984).

TNT- and RDX-contaminated soils were obtained from two drainage ditches adjacent to munitions production buildings at the abandoned NOP. Sharpsburg (mixed, mesic, Typic Argiudoll) is the predominant soil type in the vicinity of the NOP. Vertical cores, 122 cm long and 5.6 cm in diameter, were taken to a depth of 330 cm using a hydraulic push unit that encased cores in plastic liners (Giddings Machine Co., Fort Collins, CO). The soil was removed from the plastic liner, air dried, and ground to pass through a 2 mm sieve. Soils from the 7.5 to 15 cm depth (Table 1) were used in this study since this depth represented the highest level of contamination.

General procedures

Stock solutions of 70 mg TNT $litre^{-1}$ and 32 mg RDX $litre^{-1}$ were prepared in water and verified by high performance liquid chromatography (HPLC) using Keystone NU (TNT) and NA (RDX) columns (Keystone Scientific Inc., Bellefonte, PA) with an isocratic mixture (55:45) of CH_3OH and H_2O at a flow rate of $1\,ml\,min^{-1}$. Analytes were detected spectrophotometrically at 254 nm and quantified by comparison to high purity standards. Hexahydro-1,3,5-trihydroxy-1,3,5-triazine was identified in Fe^0-treated RDX solutions by 1-propyl esterification and GC/MS comparison with derivatized analytical standards (Sun and Pignatello, 1993). The ^{14}C-activity of stock solutions spiked with ^{14}C-ring labeled TNT or RDX was determined by liquid scintillation counting (LSC). This was accomplished by mixing a 1 ml aliquot with 6 ml Ultima Gold counting solution (Packard, Meriden, CT) and counting on a Packard 1900TR liquid scintillation counter (Packard Instrument Co., Downers Grove, IL).

Table 1. Characteristics of munitions-contaminated soils obtained from drainage ditches at the former Nebraska Ordnance Plant near Mead, NE

Soil property	Unit	TNT-contaminated soil	RDX-contaminated soil
Soil pH (1:1, H_2O)		6.5	5.9
Organic matter	%	1.5	2.8
Cation exchange capacity	$cmol_c\,kg^{-1}$	12.5	15.4
Sand	%	80	30
Silt	%	13	46
Clay	%	7	24

Various amounts of fine-grained (~40 mesh) Fe^0 were added directly to 125-ml Erlenmeyer flasks containing TNT or RDX stock solutions. The flasks were sealed with parafilm to reduce evaporation losses and agitated using an oscillating shaker at 25 ± 1°C. At preselected times, 1.2-ml aliquots were removed and transferred to 1.5-ml polypropylene microcentrifuge tubes, centrifuged at 7600 × g for 10 min, and analyzed by HPLC and LSC.

Sorption of Fe^0-treated TNT and RDX to the iron surface was determined by equilibrating ^{14}C-spiked TNT or RDX solutions with 10% Fe^0 (w/v) at 25 ± 1°C for 24 h (TNT) or 48 h (RDX). Procedures used to fractionate adsorbed ^{14}C were as previously reported (Hundal *et al.*, 1997). In brief, the Fe^0-treated solutions were centrifuged and the supernatant removed. The iron residue was washed with deionized water and sequentially extracted with 3 mM $CaCl_2$, CH_3CN, 0.5N NaOH, EDTA, nonionic surfactant (X-77, Chevron Chemical Co., San Francisco, CA), and strong alkali (10% KOH in ethanol). The 'readily available' pool consisted of ^{14}C extractable with 3 mM $CaCl_2$, while CH_3CN-extractable ^{14}C comprised the 'potentially extractable' pool (Hundal *et al.*, 1997). Bound (unextractable) ^{14}C residue was determined by combustion to $^{14}CO_2$ with a biological oxidizer (Packard Tri-Carb B306). The ^{14}C mass balance calculations indicated an average recovery of approximately 95%.

Combined reduction and oxidation

To determine the potential of Fe^0 in combination with H_2O_2 to further promote TNT and RDX destruction, 1% H_2O_2 (v/v) was added to solutions containing ^{14}C-TNT or ^{14}C-RDX at different times following treatment with Fe^0, and ^{14}C loss was monitored. Hydrogen peroxide (1% v/v) was added at 0, 1, or 4 h after equilibrating TNT or RDX with Fe^0 (5% w/v). At the end of the experiment, solution ^{14}C was determined by LSC. The ^{14}C sorbed to the iron was determined by combustion to $^{14}CO_2$ and mineralized ^{14}C-TNT or RDX was calculated from ^{14}C mass balance. Mineralization of ^{14}C-TNT and ^{14}C-RDX was confirmed in an additional experiment by measuring $^{14}CO_2$ evolution as described below.

Abiotic reduction combined with microbial degradation

Experiments were conducted to determine the effect of iron pretreatment on TNT biodegradation. A microbial inoculum was obtained from the TNT-contaminated soil by agitating 1 g soil with water (1:5 w/v) for 48 h at 25 ± 1°C. TNT stock solutions (50 ml) spiked with ^{14}C-TNT were added to four, 125-ml Erlenmeyer flasks, mixed with 49 ml of double-strength Pseudomonas minimal medium (PMM, Martin *et al.*, 1997) without glucose, and inoculated with 1 ml of the consortium. PMM was buffered at pH 7.0 and contained 40.2 mM K_2HPO_4, 22 mM KH_2PO_4, 0.4 mM $MgSO_4 \cdot 7H_2O$, and 7.6 mM $(NH_4)_2SO_4$. The flasks were placed in a bioreactor and $^{14}CO_2$ and volatile ^{14}C emissions were monitored daily as described below. $^{14}CO_2$ produced from untreated ^{14}C-TNT and Fe^0-treated TNT were

compared. TNT or Fe^0-treated TNT served as the sole carbon source or glucose was included to determine if a readily available substrate could enhance TNT mineralization. Since TNT mineralization may be limited by sorption and nonavailability of transformation products, in some experiments EDTA was added as a releasing agent. To eliminate possible deleterious effects of excess iron on the microorganisms, an additional experiment was conducted in which the iron was removed from the solution (by filtration) and only the treated solution was used.

Microbial respiration experiments were performed in the dark using an eight-flask bioreactor at 30°C. In this reactor, CO_2-free air was bubbled through inert bubblers into 125-ml Erlenmeyer flasks and continuously swept into three, 20-ml collection vials connected in series. The first two traps contained 18 ml of xylene-based scintillation counting solution (Scintiverse E, Fisher Scientific, Pittsburgh, PA) and were used to collect volatile ^{14}C products; the last trap collected $^{14}CO_2$ in a mixture of 10:40:50 (v/v/v) ethanolamine, methanol, and Scintiverse E. All collection vials were replaced every 24 h and ^{14}C was determined by LSC. Mass balance was determined from total ^{14}C recovered as volatilized ^{14}C, $^{14}CO_2$, ^{14}C remaining in solution, and ^{14}C associated with the microbial biomass (in treatments where Fe^0 was removed after treatment) upon termination of the experiment. The ^{14}C associated with the microbial biomass was determined by oxidizing the biomass (combustion) to $^{14}CO_2$ in a biological oxidizer (Packard Tri-Carb B306). The $^{14}CO_2$ was trapped in a mixture (3:2 v/v) of Carbosorb and Permafluor (Packard) and quantified by LSC.

Treatment of contaminated soil slurries

Slurries (1:5 w/v soil:water) of TNT- or RDX-contaminated soils were prepared in 50-ml Teflon centrifuge tubes using 2 g soil and 5, 10, and 15% Fe^0 (w/w). The tubes were agitated on an oscillating shaker at 25 or 45 ± 1°C for 1, 2, 4, 6, 12, 24, 72 and 96 h. Each treatment (Fe^0 concentration and sampling time) consisted of four experimental units (replicates). At each sampling, the tubes were centrifuged, supernatant was removed, and TNT or RDX in the supernatant was quantified by HPLC. The remaining soil was extracted with CH_3CN (1:5 w/v) by vortexing for 1 min and sonicating for 18 h at 30°C. TNT or RDX remaining after Fe^0 treatment was determined from that remaining in solution and that extracted with CH_3CN. The effect of Fe^0 in combination with 1% H_2O_2 (added in one dose or four, 1/4 doses at 12 h intervals) on TNT and RDX removal and destruction was also determined using the same procedures.

RESULTS

Removal and transformation by Fe^0

Treating an aqueous solution of TNT (70 mg litre^{-1}) with various Fe^0 concentrations indicated that as little as 1% Fe^0 (w/v) completely removed TNT from solution within 8 h of contact time (Fig. 2). HPLC analysis revealed production of monoaminodinitrotoluenes (2ADNT and 4ADNT) during the initial 30 min of Fe^0 treatment, which later disappeared, indicating further transformation or adsorption to the iron surface. The ^{14}C mass balance, however, indicated no

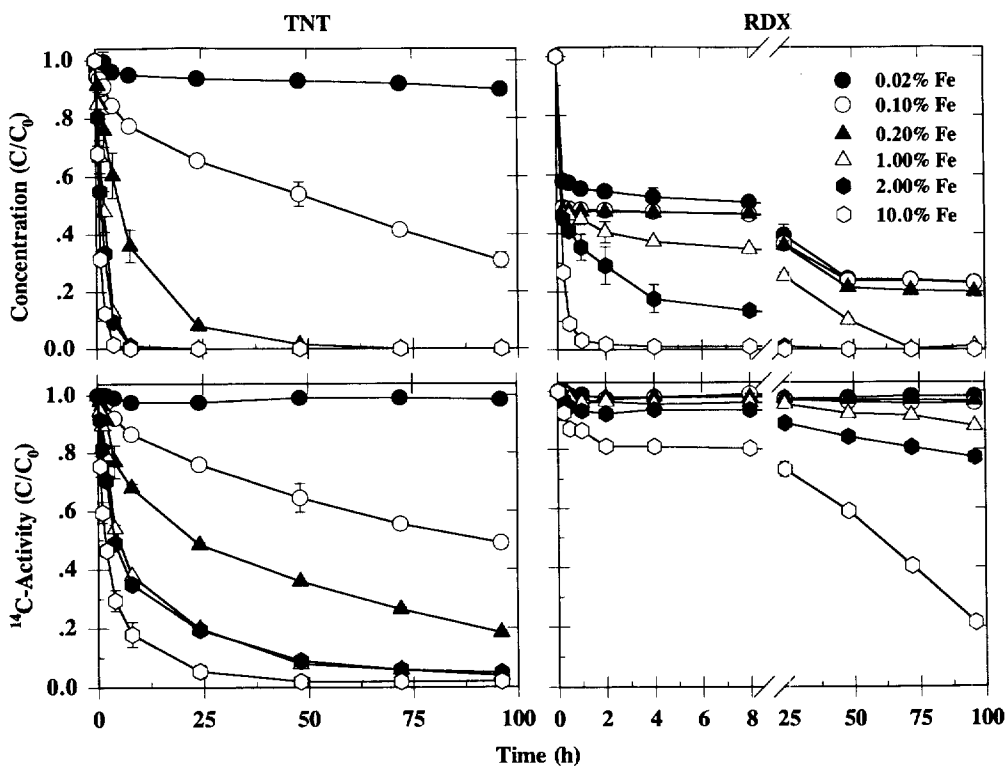

Fig. 2. TNT and RDX transformation as affected by Fe^0 concentration (% w/v) at 25°C.

TNT mineralization to CO_2. Likewise, no volatilized ^{14}C was detected in these experiments or any subsequent experiment. Most of the ^{14}C added as ^{14}C-TNT was removed from solution within 48 h (Fig. 2), indicating the TNT transformation products were adsorbed to the iron. TNT removal was very slow when only 0.1% Fe^0 (w/v) was used and not significant when Fe^0 was decreased to 0.02% (Fig. 2).

Treating RDX solution (32 mg RDX litre^{-1}) with 1% Fe^0 (w/v) also resulted in near complete removal of RDX from solution, but only after 96 h (Fig. 2). RDX loss was initially rapid, but slowed with time. All of the RDX was removed within 4 h by 10% Fe^0 (w/v); however, in contrast to ^{14}C-TNT, about 20% of the ^{14}C added as ^{14}C-RDX remained in solution at 96 h. When less Fe^0 was used (<2%), almost all of the ^{14}C remained in solution (Fig. 2). This indicates that the products of Fe^0-treated RDX are water soluble and have less affinity for the iron surface than the TNT transformation products.

Fractionation of adsorbed ^{14}C after Fe^0 treatment

Approximately 98% of the ^{14}C added as ^{14}C-TNT was adsorbed by the iron within 24 h of equilibration with 10% Fe^0 (w/w). Only 0.6% of the adsorbed ^{14}C was extractable with 3 mM $CaCl_2$ ('readily available' pool) and 0.3% was removed with CH_3CN ('potentially available' pool) (Fig. 3). Nonionic surfactant and EDTA removed little of the adsorbed ^{14}C. Subsequent extraction with 0.5N NaOH removed about 35% of the adsorbed ^{14}C and 19% was extractable with 10% KOH in ethanol. About 37% of the adsorbed ^{14}C was unextractable (irreversibly bound) after these exhaustive extractions.

Approximately 63% of the ^{14}C added as ^{14}C-RDX was adsorbed to the iron within 48 h after treatment with 10% (w/v) Fe^0, of which 6.5 and 0.7% was extractable with 3 mM $CaCl_2$ and CH_3CN, respectively (Fig. 3). About 46% of the adsorbed ^{14}C was extracted with 0.5N NaOH, 10% KOH in ethanol removed about 10%, and approximately 29% was unextractable. These observations indicate that the iron-adsorbed products of Fe^0-treated TNT were more strongly retained than the RDX products.

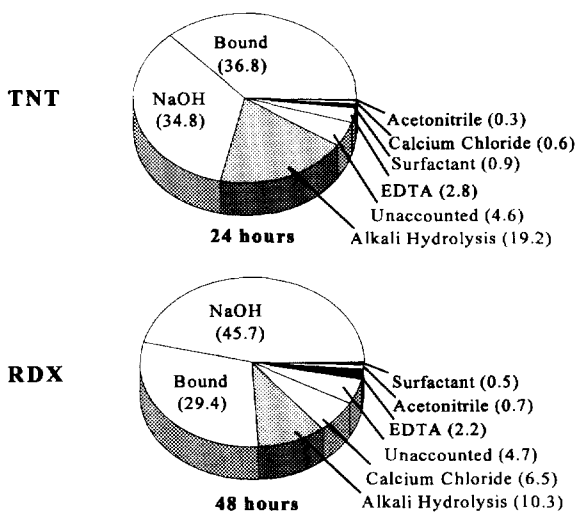

Fig. 3. Fractionation of ^{14}C-TNT and ^{14}C-RDX adsorbed to the iron surface after equilibrating for 24 and 48 h.

Sequential reduction and oxidation

The possibility of abiotically reducing, then oxidizing TNT and RDX in solution was explored. Treating a ^{14}C-TNT solution with Fe^0 (5% w/v) followed by H_2O_2 (1% v/v) after 0, 1, and 4 h resulted in similar ^{14}C loss from solution (Fig. 4). However, differences were observed in percent mineralization among treatments (data not shown). Adding H_2O_2 simultaneously with Fe^0 resulted in 46% loss of ^{14}C as $^{14}CO_2$ within 8 h and 47% was sorbed to the iron. Delaying H_2O_2 addition 1 h after Fe^0 resulted in similar $^{14}CO_2$ loss (48%) and sorption (45%) to iron. When H_2O_2 addition was delayed 4 h, TNT mineralization decreased to 29% and sorbed ^{14}C increased to 68%. This indicates initial reduction of TNT produces products that are susceptible to oxidation. With time, however, these products become strongly sorbed and may not be readily available for subsequent oxidation.

In contrast to TNT, more ^{14}C-RDX was lost from solution (Fig. 4) and RDX mineralization increased (data not shown) when H_2O_2 addition was delayed. At 96 h after simultaneous addition of Fe^0 and H_2O_2, 12% of the added ^{14}C was sorbed to the iron surface and 33% was lost as $^{14}CO_2$. Delaying H_2O_2 addition for 1 h similarly resulted in 10.5% sorbed and 37% mineralized, but 52% was mineralized (19.5% sorbed) when H_2O_2 was added 4 h after treatment with Fe^0. These data, combined with results previously presented (Fe^0 treatment of RDX, Fig. 2) indicate that reductive transformation of RDX results in products that are not strongly sorbed by Fe^0 and more readily oxidized than those from Fe^0-treated TNT.

Abiotic reduction combined with microbial degradation

Fe^0-treated TNT was more biodegradable than untreated TNT in liquid media inoculated with a microbial consortium obtained from TNT-contaminated soil. Iron pretreatment increased TNT mineralization, as evidenced from a higher daily $^{14}CO_2$ flux (Fig. 5) and cumulative $^{14}CO_2$ production (Fig. 6). Adding EDTA after Fe^0 treatment resulted in a 1 day burst in $^{14}CO_2$ (Fig. 5); evolved $^{14}CO_2$ was similar in magnitude to ^{14}C released during sequential extraction of adsorbed ^{14}C-TNT residue with EDTA (Fig. 3). We hypothesize that the observed evolution of $^{14}CO_2$ after adding EDTA resulted from mineralization of TNT transformation intermediates displaced from the iron surface; no $^{14}CO_2$ burst occurred when the same amount of carbon contained in the EDTA was added as glucose. However, adding more glucose (1600 mg C litre^{-1}) sustained mineralization at about 0.1% day^{-1} for the duration of the experiment (Fig. 5). This indicates that a readily available alternative carbon source can promote TNT biodegradation after pretreatment with Fe^0. Mineralization was also greater when iron was removed

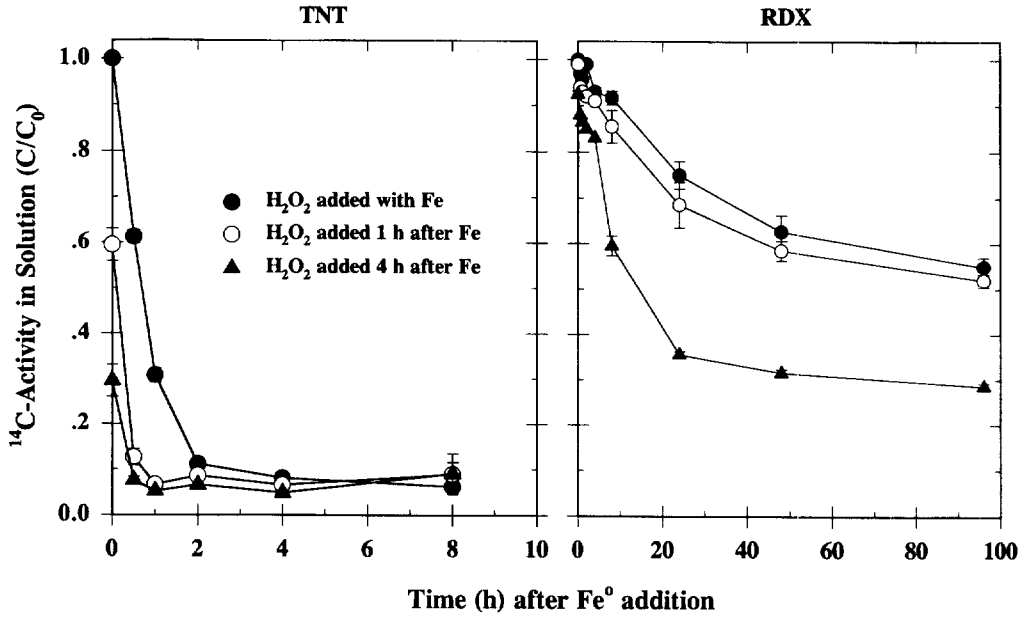

Fig. 4. Combined reduction and oxidation of TNT. The H_2O_2 was added after 0, 1, and 4 h of equilibration with Fe^0.

after treatment and only the supernatant was used in the microbial respiration experiments (Figs 5 and 6). Less mineralization in the presence of iron can be attributed to reduced availability of TNT transformation products sorbed to the iron surface.

Cumulative mineralization was greatest (*ca* 12%) when the iron was removed after the TNT was completely transformed (Fig. 6). Adding EDTA or glucose to Fe^0-amended TNT solution resulted in 6% mineralization, while only 0.5% mineralization of untreated TNT was observed. Greater mineralization of Fe^0-treated TNT indicates transformation to more biodegradable products.

Treatment of contaminated soil slurries

Equilibrating slurries of TNT- and RDX-contaminated soil (5200 mg TNT kg^{-1} and 6400 mg RDX kg^{-1}) with 10% Fe^0 (w/w soil) at 45°C decreased CH_3CN-extractable TNT and RDX concentrations below USEPA remediation goals (17.2 mg TNT and 5.8 mg RDX kg^{-1} soil) for the NOP site within 24 and 48 h, respectively (Fig. 7). TNT was removed from the soil slurries more

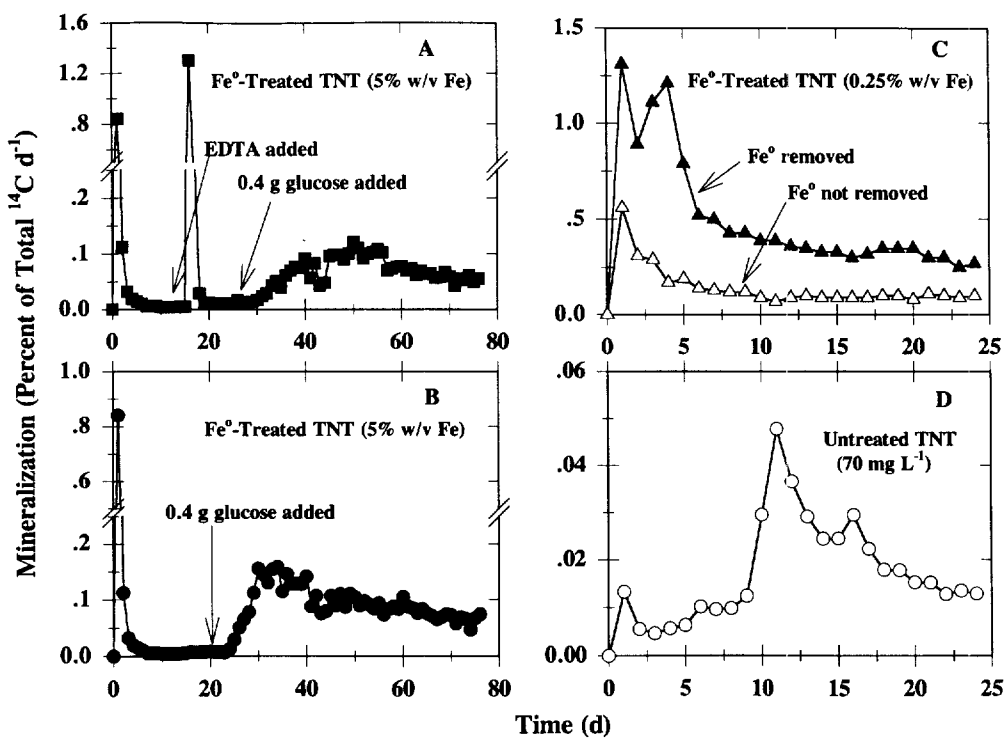

Fig. 5. Comparative mineralization of Fe^0-treated TNT and untreated TNT in *Pseudomonas* minimal medium by a microbial consortium obtained from munitions-contaminated soil. The effects of EDTA and glucose additions, and iron removal are indicated.

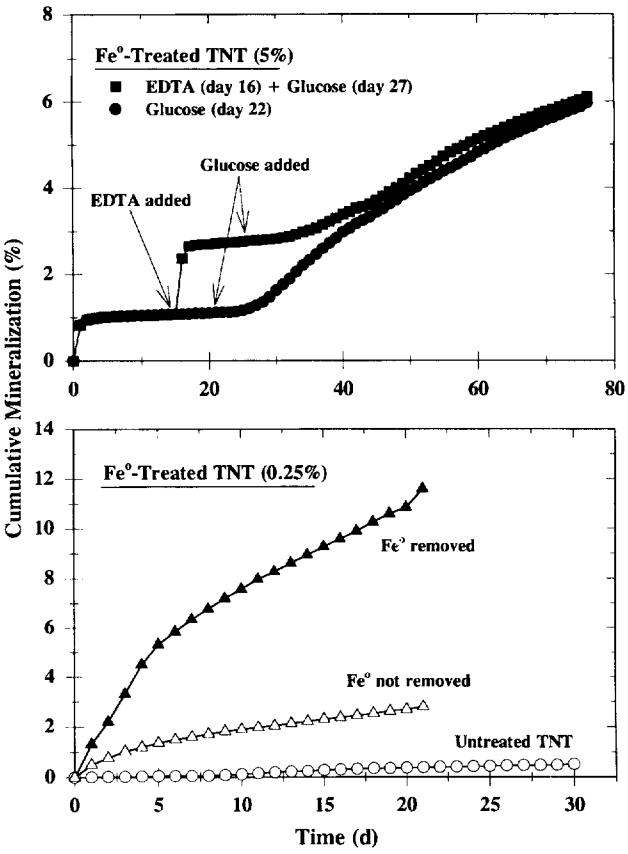

Fig. 6. Cumulative mineralization of Fe^0-treated TNT and untreated TNT in *Pseudomonas* minimal medium by a microbial consortium obtained from munitions-contaminated soil.

rapidly than RDX and the treatment was less effective at 25°C (data not shown). Less contaminated soils required less time and Fe^0 to achieve remediation goals for the NOP site (data not shown).

Acetonitrile-extractable TNT was reduced below the USEPA remediation goal in contaminated soil slurries within 48 h at 25°C when 15% Fe^0 (w/w soil) was used in combination with a single addition of 1% H_2O_2 (Fig. 8). Splitting the 1% H_2O_2 into four, 1/4 doses at 12 h intervals was more effective than one addition and less iron (10%) was required to reduce CH_3CN-extractable TNT below the remediation goal. When Fe^0 was used in combination with 1% H_2O_2 (added in one dose or four increments at 12 h intervals), 5% Fe^0 was sufficient to reduce CH_3CN-extractable RDX below 5.8 mg kg^{-1} soil within 48 h (Fig. 8). In these highly contaminated NOP soils, the USEPA remediation goals for TNT and RDX were not achieved during the time frame of our experiments with low concentrations of Fe^0 (0.5, 1.0, and 2.0%), with or without 1% H_2O_2.

DISCUSSION

TNT and RDX are labile in the presence of Fe^0 and rapidly disappear from solution as a result of transformation and sorption onto the iron surface. In soil slurries, TNT and RDX were destroyed more rapidly at 45°C than at 25°C. This may be due to increased diffusion, higher solubility of TNT and RDX, and faster reaction kinetics at the higher temperature (Bier, 1997; Li *et al.*, 1997).

Reduction of nitroaromatic compounds by Fe^0 or Fe^{2+} has been previously reported (Haderlein and Schwarzenbach, 1995; Klausen *et al.*, 1995; Agrawal and Tratnyek, 1996). Agrawal and Tratnyek (1996) recently concluded that nitroreduction by Fe^0 was controlled by mass transfer, since they observed little effect of nitroaromatic ring substitution or solution pH on reduction rate constants. They also observed that nitraromatic destruction was linearly correlated to the square root of the mixing rate. In our experiments, only small amounts of monoaminodinitrotoluenes (2ADNT and 4ADNT) were detected during the first 30 min of treating TNT with Fe^0. These products later disappeared, indicating rapid transformation and sorption to the iron surface. By comparison, most of the ^{14}C was

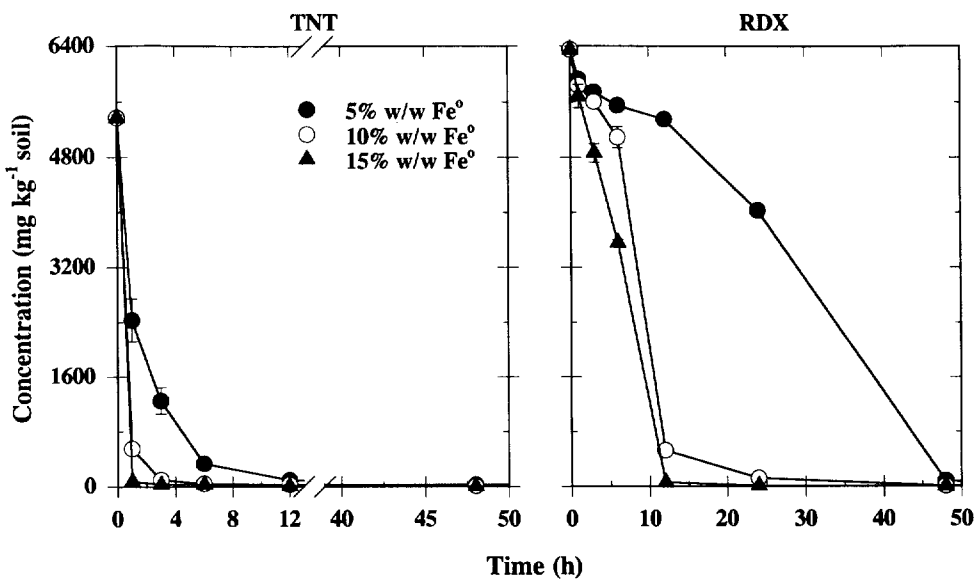

Fig. 7. Acetonitrile-extractable TNT and RDX concentrations following treatment of contaminated soil slurries with Fe^0 at 45°C.

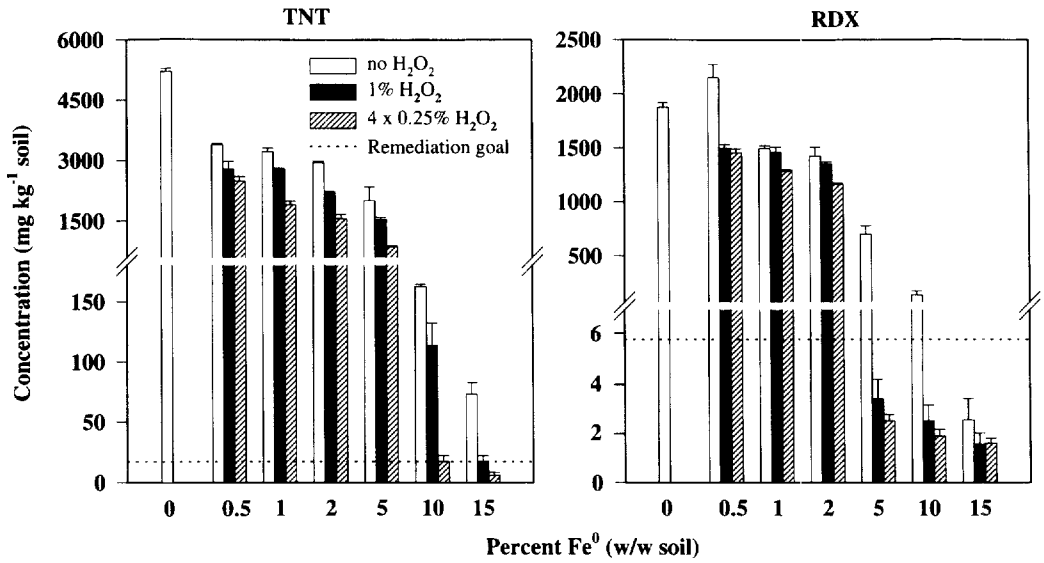

Fig. 8. Acetonitrile-extractable TNT and RDX concentrations 48 h after treating soil slurries with Fe^0 and Fe^0 + 1% H_2O_2. The H_2O_2 was added as a single dose or four, 1/4-doses at 12 h intervals.

present in solution after treating ^{14}C-RDX with Fe^0, which indicates that the products of Fe^0-treated RDX are more water soluble and do not sorb as strongly to the iron. After complete loss of RDX (10% w/v Fe^0), 3 μmoles of N in the form of ammonium (NH_4^+) were recovered per μmole of RDX, corresponding to 50% of the RDX-N. No nitrite or nitrate was recovered from the treated solution. Reduction of RDX and hydrolysis may produce hexahydro-1,3,5-trihydroxy-1,3,5-triazine, tentatively identified in our sample by GC/MS. This compound decomposes in mildly acidic solution yielding formic acid and ammonia (Smolin and Rapoport, 1959). In contrast to RDX, only about 17% of the total TNT-N was recovered as NH_4^+ after complete loss of TNT, which indicates that the products of Fe^0-treated TNT are adsorbed to the iron surface with some of the nitrogen moieties intact.

The nature of the ^{14}C from Fe^0-treated ^{14}C-TNT that could not be extracted from the iron is unknown. Haderlein and Schwarzenbach (1995) postulated formation of electron donor acceptor (EDA) complexes between nitroaromatics and oxyhydroxides on mineral surfaces, which provide electrons to the nitroaromatic compound. Considering that iron oxides will form at the surface of Fe^0 metal during nitroaromatic reduction, similar EDA complexes may occur. Sequential extractions of the iron after treatment with Fe^0 indicate stronger binding of the TNT transformation products to the iron surface than those from Fe^0-treated RDX. Iron treatment may increase formation of bound residue from TNT in soils, as anilines generated from reduction of aromatic NO_2 groups can covalently bind to polyphenols or quinones in organic matter (Bartha and Hsu, 1974; Calderbank, 1989).

While USEPA remediation goals for TNT- and RDX-contaminated soil were achieved by Fe^0 treatment at elevated temperature, our results indicate that a two-step reduction-oxidation treatment may be most efficient for remediation of TNT and RDX contamination. Nitro groups are susceptible to reduction and Fe^0 treatment produces amino degradation products, as well as Fe(II) and Fe(III) (Klausen *et al.*, 1995). Subsequent addition of H_2O_2 initiates the Fenton reaction (Fenton, 1894) and results in oxidation of reduced TNT and RDX intermediates. The resulting oxidation products are more readily degradable and the net result is increased mineralization. Timing of H_2O_2 addition in relation to Fe^0 is important since availability affects the extent of subsequent oxidation. TNT mineralization was greatest when H_2O_2 was added within 1 h of Fe^0 treatment, while more RDX was mineralized when H_2O_2 addition was delayed 4 h. The decrease in TNT mineralization when H_2O_2 addition was delayed 4 h can be attributed to lower availability of TNT and its transformation products compared to RDX and its transformation products.

Very high concentrations of explosives encountered at some sites such as the NOP can be toxic to soil microorganisms and may reduce biotransformation. Combining abiotic reduction with biodegradation can mitigate this remediation problem. Pretreatment of 70 mg TNT litre^{-1} with Fe^0 resulted in 20-fold greater mineralization than untreated TNT in liquid media, which indicates generation of more biodegradable products. Greater mineralization following removal of iron from the liquid media indicates that sorption of TNT transformation products to the iron surface reduces their availability. This observation was supported by a large burst in $^{14}CO_2$ after addition of EDTA, which may displace some of the treatment products from the iron surface. Addition of readily available carbon after Fe^0 treatment enhanced and sustained mineralization, and indicated the potential to use this remediation technology *in situ* where other sources of carbon are available or carbon amendments can be made.

The effectiveness of Fe^0 in removing TNT and RDX from contaminated soil slurries indicates that Fe^0 can be successfully used to remediate munitions-contaminated

soils. Transformation and removal of TNT and RDX from less contaminated soils would require less Fe^0 and a shorter treatment time than grossly contaminated soil. Fe^0 combined with H_2O_2 destroyed TNT and RDX in contaminated soil slurries more efficiently than Fe^0 alone and less iron was required to achieve the same level of remediation. Treating TNT with Fe^0 may also increase its biodegradability and promote detoxification in soil through sorption and bound residue formation.

ACKNOWLEDGEMENTS

Appreciation is expressed to the Great Plains-Rocky Mountain Hazardous Substances Research Center (Kansas State Univ.) project nos. 92-24 and 95-32, NSF/EPSCoR cooperative agreement EPS-9255225, and the University of Nebraska Water Center for support of this research. Publication no. 11703, Agric. Res. Div., Univ. Nebraska-Lincoln; project nos. NEB 12-230, 239, 244, and 251.

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