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

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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} ($90 \text{ }\mu\text{M}$) under a static Eh of -150 mV and pH 7 with 20 g of $\text{Fe}^0 \text{ L}^{-1}$ removed 95% of the RDX within 4 h; no RDX was detected after 8 h. Treating a soil slurry (20% solids; $510 \text{ mg RDX kg}^{-1}$ soil) with 20 g of $\text{Fe}^0 \text{ L}^{-1}$ 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.

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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 ₂ O)		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

FIGURE 1. Changes in RDX, ¹⁴C-activity, Eh, and pH with time following addition of 20 g Fe⁰ L⁻¹ (2%,w/v) to a 20 mg RDX L⁻¹ aqueous solution.

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).

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

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.

TABLE 2. RDX Remaining after 24 h Treatment of Contaminated Soil (510 mg RDX kg⁻¹) with Fe⁰ (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)
Na₂S Experiments^d				
Na ₂ S+Fe ⁰ (pH stat)	4.6 (0.06)	11 (0.19)	34 (0.48)	93 (0.09)
Na ₂ S+Fe ⁰ (0.2 M KH ₂ PO 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 Na₂S·9H₂O concentration was 0.1% (w/v) and pH was buffered at 7 with the pH stat or 0.2 M KH₂PO₄.

FIGURE 5. Changes in RDX concentration and Eh following treatment of a soil slurry with Fe⁰. Eh was lowered by Na₂S·9H₂O addition, and pH was controlled by the pH-stat or phosphate buffer.