

Enhancing oxidation of TNT and RDX in wastewater: pre-treatment with elemental iron

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Abstract Munitions manufacturing wastewater is commonly treated by adsorption to activated carbon. We are proposing a new munitions manufacturing wastewater treatment system consisting of a reductive pre-treatment process and subsequent Fenton's oxidation to mineralize energetic compounds such as TNT and RDX. The pre-treatment involves reduction of electron-withdrawing nitro groups of TNT and RDX with elemental iron. The iron-treated explosives are then oxidized by Fenton's reagent through the addition of H_2O_2 . The objective of this work is to investigate the feasibility of using elemental iron to convert TNT and RDX to reduction products which may be more oxidizable in subsequent Fenton's oxidation. Results of batch reduction experiments with elemental iron showed complete removal of TNT and RDX and formation of the reduction products within 60 minutes. Results of column experiments showed a rapid and complete removal of TNT and RDX within 9.7 minutes retention time. Fitting observed effluent concentrations to a one-dimensional advection-dispersion equation, we were able to predict the concentration profiles of TNT and RDX in the iron column and calculate the iron column length required for the desired removal. The results of Fenton's oxidation experiments showed that iron pre-treatment enhanced both the rate and extent of TNT and RDX mineralization by Fenton's oxidation.

Keywords 2,4,6-trinitrotoluene (TNT); elemental iron; Fenton's oxidation; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)

Introduction

2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, Royal Demolition Explosives) are the most widely used explosives in the world (Spain *et al.*, 2000). TNT is carcinogenic and mutagenic and is acutely toxic to microbes, algae, fish, and other organisms (Smock *et al.*, 1976; Won *et al.*, 1976). RDX is a heterocyclic nitramine that is persistent and toxic to organisms including humans (Yinon, 1990). Direct oxidation of these compounds by conventional biooxidation processes is difficult due to the presence of electron-withdrawing nitro constituents (Knackmuss, 1996). Therefore, these energetic compounds are often removed from munitions-manufacturing wastewater "pink water" by physical-chemical processes such as advanced oxidation, alkaline hydrolysis, carbon adsorption (Heilmann *et al.*, 1996; Li *et al.*, 1997; Bier *et al.*, 1999), with carbon adsorption being the most common method. This method is non-destructive and generates explosive-laden spent carbon, which is hazardous and needs to be treated or disposed of properly to avoid secondary contamination. We are proposing an innovative and potentially superior pink water treatment process involving elemental iron and Fenton's oxidation.

A large body of literature indicates that elemental iron can reductively transform a wide range of oxidized pollutants. Elemental iron has been increasingly used in recent years in permeable reactive barriers for remediation of contaminated groundwater (Gillham and O'Hannesin, 1994; Vidic and Pohland, 1996). Elemental iron has been shown to transform chlorinated solvents, Cr^{6+} , nitrate, azo dyes, nitroaromatic compounds and nitramines in water, including TNT and RDX (Orth and Gillham, 1996; Roberts *et al.*, 1996; Blowes *et al.*, 1997; Huang *et al.*, 1998; Gu *et al.*, 1998; Nam and Tratnyek, 2000; Agrawal and Tratnyek, 1996; Singh *et al.*, 1998; Oh *et al.*, 2001).

Fenton's oxidation, which utilizes ferrous ion (Fe^{2+}) and hydrogen peroxide to produce hydroxyl radical ($\cdot\text{OH}$) as a strong oxidant, has been widely used to degrade toxic and recalcitrant pollutants because of its high removal efficiencies, simple operation and a relatively low capital cost (Mohanty and Wei, 1993; Potter and Roth, 1993; Lou and Lee, 1995; Solozhenko *et al.*, 1995; Casero *et al.*, 1997; Tang and Tassos, 1997). However, recent studies suggest that Fenton's oxidation may only partially transform TNT and RDX, even with high concentrations of hydrogen peroxide ($\geq 1\%$) and ferrous ion (≥ 80 mg/L) over eight hours (Li *et al.*, 1997; Bier *et al.*, 1999).

The objective of this work is to investigate the feasibility of using elemental iron to convert TNT and RDX to reduction products which may be more oxidizable in subsequent Fenton's oxidation. We propose to utilize the ferrous ion generated during anaerobic corrosion of elemental iron to produce the hydroxyl radical through addition of hydrogen peroxide. We hypothesize that the reduction products of TNT and RDX are more readily oxidized by the hydroxyl radical to H_2O and CO_2 .

Material and methods

Chemicals

TNT (>99%) and RDX (>99%) were obtained from Holston Army Ammunition Plant (Kingsport, TN). Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was purchased from Aldrich (Milwaukee, MI). HEPES (N-[2-hydroxyethyl]piperazine-N'-[ethanesulfonic acid]) was obtained from Sigma (St. Louis, MO). Acetonitrile (HPLC grade) and H_2O_2 (30%) were purchased from Fisher Scientific (Pittsburgh, PA). All chemicals were used as received.

Master Builder iron was chosen as a representative elemental iron because it has been widely used in groundwater remediation work and its elemental composition has been determined (Reardon, 1995; Hardy and Gillham, 1996; Gu *et al.*, 1998). The iron was used as received without pre-treatment. Specific surface area of Master Builder iron was 1.29 m²/g as determined by BET adsorption method.

Batch reduction experiments

Batch reduction experiments were performed in an anaerobic glove box (95% N_2 + 5% H_2 , Coy, MI) using 8 mL borosilicate vials containing 5 mL of aqueous solution and 1 g of iron. Initial concentrations of TNT and RDX were 0.209 and 0.155 mM, respectively. Replicate vials were set up for each experiment. All solutions contained 0.1 M HEPES buffer to maintain a constant pH of 7.4 throughout the experiment. The solutions were purged in the glove box to completely remove oxygen. After iron was added, the vials were shaken in a horizontal position using an orbital shaker at a speed of 100 rpm. At different elapsed times, one of the vials was sacrificed and the supernatant was filtered through a 0.2 μm mixed cellulose membrane filter (Millipore, MA) for analysis by high performance liquid chromatography (HPLC). Acetonitrile extraction of used filters indicated that the explosives did not adsorb to the filters.

Column experiments

Column experiments were conducted using a glass column (2.5 cm id \times 30 cm L; Ace Glass, Vineland, NJ) with Teflon end fittings. The column was packed with Master Builder scrap iron and had a porosity of 0.66. To ensure anaerobic conditions, all solutions were purged with N_2 for 20 minutes prior to introduction into the column. TNT and RDX solutions were pumped into the packed column using a peristaltic pump in an upward direction at the flow rate of 10–20 mL/min. Where necessary, iron content was decreased by replacing it with Ottawa Sand (20–30 mesh, Fisher Scientific, Pittsburgh, PA) for the study.

Column modeling

The one-dimensional advection–dispersion equation with reaction was used to fit the disappearance of the parent compounds in the iron column. It was assumed that the removal of TNT and RDX from the aqueous phase was pseudo first order. Under steady-state conditions, the analytical solution for the advection–dispersion equation is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - KC = 0 \quad (1)$$

where C is the concentration of reactant or product, D is the hydrodynamic dispersion coefficient (cm^2/sec) and $D = av + D^*$ [a = dispersivity (cm) and D^* = diffusion coefficient (cm^2/sec)]. v is the average linear velocity (cm/sec), x is the effective column length (cm), and K is the fitted first-order rate constant (sec^{-1}) for the removal of the parent compounds from solution.

For a reactant with an initial condition [$C(x, 0) = 0$] and a boundary condition [$C(0, t) = C_0$, $C(\infty, t) = 0$],

$$\frac{C}{C_0} = e^{[\frac{v - \sqrt{v^2 + 4KD}}{2D}x]} \quad (2)$$

Batch Fenton's oxidation experiments

Batch oxidation experiments were conducted using 200 mL Erlenmeyer flasks to evaluate the feasibility of treating iron-treated TNT and RDX solutions through H_2O_2 addition. Each flask contained 100 mL of solution completely mixed using a magnetic stirrer. Initial pH was adjusted to 2.7–3.3 using 0.1 N H_2SO_4 to optimize Fenton's oxidation. Iron-treated TNT and RDX solutions were obtained by two methods: (1) allowing 90 g of scrap iron and 150 mL of stock solution to react for 3 hours in a 500 mL batch reactor shaken at 150 rpm in an anaerobic glove box, and (2) passing the stock solution through a 30 cm packed iron column at the flow rate of 12 mL/min. At different sampling times, a 1 mL aliquot was withdrawn, to which a drop of 6-N NaOH solution was added to quench Fenton's reaction (Tang and Chen, 1996). The following analyses were made during each experiment: (1) TNT and RDX concentrations; (2) major reaction intermediates and products; and (3) total organic carbon (TOC).

Analytical methods

TNT and RDX were analyzed with a Varian HPLC (Walnut Creek, CA) equipped with a Supelguard guard column (20×4.6 mm; Supelco, Bellefonte, PA), a SUPELCO LC-18 column (250×4.6 mm, $5 \mu\text{m}$; Supelco, Bellefonte, PA), a UV detector (2510 Varian, Walnut Creek, CA) and an isocratic pump (2550 Varian, Walnut Creek, CA). A methanol–water mixture (50/50 v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. 2,4,6-triaminotoluene (TAT) was analyzed by a HPLC with an Alltima C18 column (250×4.6 mm, $5 \mu\text{m}$; Alltech, Deerfield, IL) and an Alltima guard column (7.5×4.6 mm; Alltech, Deerfield, IL). An acetonitrile-phosphate buffer (40 mM, pH 3.2, 10/90 v/v) was used as eluent at 1.0 mL/min. The injection volume for all samples was 10 μL and the wavelength for the UV detector was 254 nm. Total organic carbon concentration was determined with a Tekmar-Dohrmann TOC analyzer (DC-190, Santa Clara, CA).

Results and discussion

Results of batch experiments

The results of the TNT and RDX reduction experiments are shown in Figure 1. TNT was completely removed in 60 minutes with scrap iron and the majority of the TNT removed

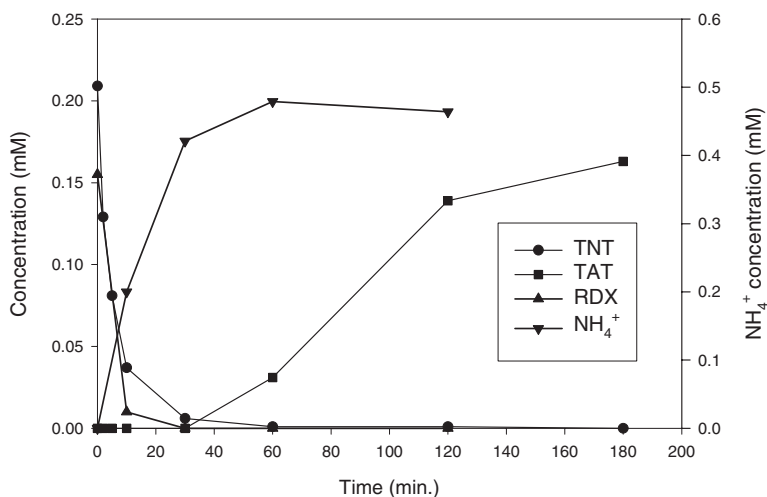


Figure 1 Transformation of aqueous TNT and RDX with master builder scrap iron

was recovered as TAT (Figure 1). Similarly, all RDX in solution was removed within 30 minutes and NH_4^+ was produced as a product (Figure 1). The results indicate that elemental iron is capable of rapidly removing TNT and RDX through reductive transformation.

Results of column experiments

Preliminary column experiments with TNT and RDX in 0.1 M HEPES solutions (pH 7.4) and deionized water (initial pH 7.7) were conducted using a 30 cm iron packed column at the flow rate of 10 mL/min. Complete reduction of TNT and full recovery of TAT was achieved in the column effluents, indicating that a 30 cm length (retention time = 9.7 minutes) is sufficient to reduce TNT regardless of buffering capacity. RDX was also completely removed under these conditions. The dispersion coefficient (α) was calculated to be 0.117 cm based on chloride tracer test using the method of Brigham (1974). Measurement of effluent concentrations of TNT and RDX using 3 cm and 5 cm column lengths at three linear velocities allowed calculation of the pseudo first-order removal rate constants (K) using the advection–dispersion–reaction equation. Figure 2 shows the results from the column experiments and concentration profiles predicted by the fitted model. For two column lengths and three linear velocities, we obtained K values of 0.0285 ± 0.003 and $0.0185 \pm 0.005 \text{ sec}^{-1}$ for TNT and RDX, respectively. At 20 cm length, TNT was completely removed at the flow rate of 20 mL/min. In the case of RDX, 30 cm of column

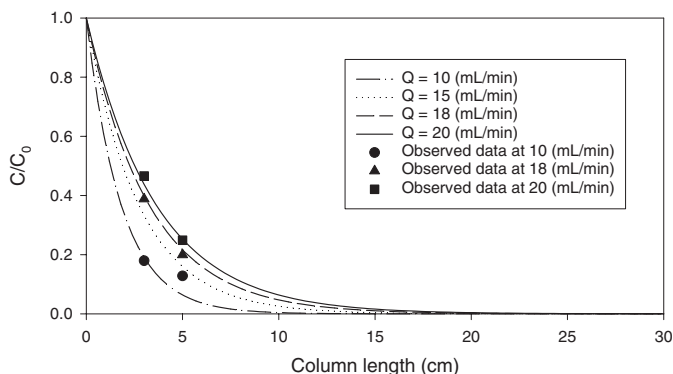


Figure 2 Observed and predicted TNT concentrations at different iron column lengths and flow rates ($K = 0.0285 \pm 0.003 \text{ sec}^{-1}$)

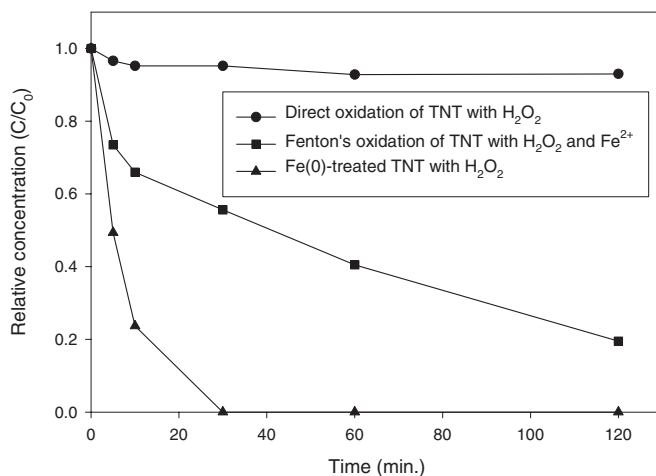


Figure 3 Concentrations of TNT or Fe(0)-treated TNT (TAT) during oxidation by 4 mM H₂O₂, 4 mM H₂O₂ and 0.8 mM Fe²⁺ (Fenton's reagent), and iron treatment followed by H₂O₂ oxidation (4 mM). Initial pH = 3.3. Initial TNT concentration = 0.19–0.22 mM

length was required to reduce RDX completely at the same flow rate (data not shown). These experiments show that this simple model may be used to predict the concentrations of these energetic compounds in the proposed iron treatment column.

Removal of Fe(0)-treated TNT and RDX with H₂O₂ addition

Figure 3 compares three different treatments of TNT: (1) addition of H₂O₂; (2) addition of Fe²⁺ and H₂O₂ (Fenton's reagent); and (3) Fe(0) pre-treatment followed by H₂O₂ addition. The addition of 4 mM H₂O₂ removed <10% of TNT in 2 hours. About 50% of TNT was removed in 30 minutes and 80% was removed in 2 hours with 4 mM H₂O₂ and 0.8 mM of Fe²⁺. In comparison, iron pre-treatment and subsequent addition of 4 mM H₂O₂ completely removed TNT and its reduction product TAT from the solution within 30 minutes. Addition of H₂O₂ by itself or with Fe²⁺ (Fenton's reagent) did not remove RDX from solution even after 2 hours. In contrast, iron pre-treatment and subsequent H₂O₂ addition completely removed RDX and a water-soluble product (data not shown).

Mineralization of iron-treated TNT and RDX with Fenton oxidation

We also quantified the extent of TNT mineralization through TOC measurement. In the presence of 40 mM H₂O₂ and 2 mM Fe²⁺, we observed 50% mineralization of TAT in 30 minutes (Figure 4). Under the same conditions, only 12% of TNT was mineralized, indicating that Fe(0) pre-treatment significantly enhanced Fenton oxidation efficiency. In the case of RDX, Fenton oxidation with 40 mM H₂O₂ and 1 mM Fe²⁺ did not mineralize RDX. On the other hand, more than 60% of Fe(0)-reduction products of RDX was mineralized in 90 minutes under the same conditions (data not shown).

Conclusions

The major results from this study can be summarized as follows:

- TNT and RDX were completely removed from the solution with elemental iron in batch and column reduction experiments.
- A simple advection–dispersion–reaction model may be used to estimate TNT and RDX concentrations in the iron pre-treatment column and to determine the column length needed to achieve the desired removal efficiency.

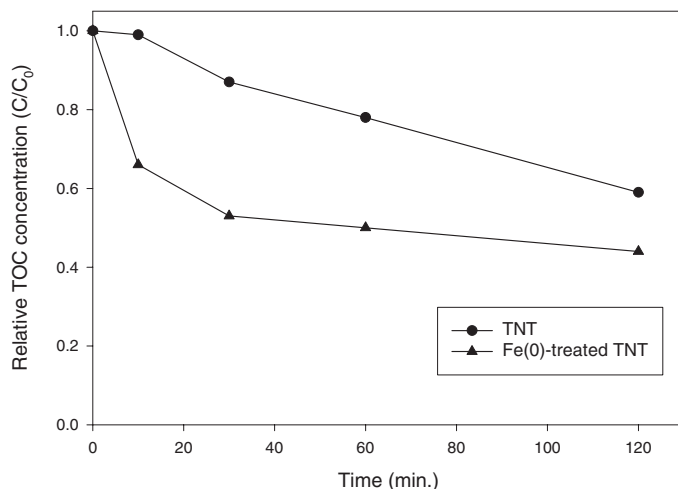


Figure 4 The changes of TOC concentrations during Fenton's oxidation with TNT and Fe(0)-treated TNT. (Initial pH = 3.1, H_2O_2 = 40 mM, Fe^{2+} = 2 mM, initial TNT concentration = 13.2–15.3 mg/L as TOC)

- Iron pre-treatment enhanced the rates and extents of mineralization of both TNT and RDX by Fenton's oxidation.

In conclusion, we demonstrated the complete reductive removal of TNT and RDX with elemental iron and the enhanced mineralization efficiency by Fenton's oxidation. Based on the results of this study, an integrated iron pre-treatment column– H_2O_2 oxidation reactor is proposed as an alternative treatment technology to completely remove and mineralize TNT and RDX in munitions manufacturing wastewater.

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