Degradation of energetic compounds using an integrated zero-valent iron-Fenton process

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Abstract: The effect of reductive treatment with elemental iron on the extent of mineralization by Fenton oxidation was studied for the explosive 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using a completely-stirred tank reactor (CSTR). The results support the hypothesis that TNT and RDX are reduced with elemental iron to products that are oxidized more rapidly and completely by Fenton's reagent. Iron pretreatment enhanced the extent of TOC removal by approximately 20% and 60% for TNT and RDX, respectively. Complete TOC removal was achieved for TNT and RDX solutions with iron pretreatment under optimal conditions. On the other hand, without iron pretreatment, complete mineralization of TNT and RDX solutions were not achieved even with much higher H_2O_2 and Fe^{2+} concentrations. The bench-scale iron treatment-Fenton oxidation integrated system showed more than 95% TOC removal for TNT and RDX solutions under optimal conditions. The proposed zero-valent iron-Fenton process was evaluated with pink water from the Iowa Army ammunition plant. Results from batch and column experiments show that TNT, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were completely removed from the pink water and that triaminotoluene (TAT) and NH_4^+ were recovered as products in reduction with zero-valent iron. By using an integrated system, $83.3 \pm 4.2\%$ of TOC was removed in a CSTR with 10 mM of Fe^{2+} and 50 mM of H_2O_2. These results suggest that the reduction products of TNT and RDX are more rapidly and completely mineralized by Fenton oxidation and that a sequential iron treatment-Fenton oxidation process may be a viable technology for pink water treatment.

1. Introduction

2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are common explosives and major constituents in wastewater from munitions-manufacturing plants (Spain et al., 2000). In 1998, 77 million pounds of explosive-laden wastewater, commonly known as pink water, were generated from munitions-manufacturing plants in the U.S (Adrian and Campbell, 1999). Concentrations of TNT and RDX in pink water were reported to be up to 51.3 and 19.7 mg/L, respectively (Yinon and Zitrin, 1993). Due to their toxicity and possible carcinogenicity (Won et al., 1976; Kaplan and Kaplan, 1982), these explosive compounds are removed from wastewater before its discharge to environment.

Conventional biological wastewater treatment processes (i.e. activated sludge system) are not efficient to treat pink water because electron-withdrawing nitro constituents in explosives inhibit the electrophilic attack by enzymes (Bruhn et al., 1987; Knackmuss, 1996). The use of chemical oxidation processes (i.e. hydroxyl radical attack) was not also effective because of the hindrance of oxidation by nitro functional groups (Schmelling et al., 1996). Consequently, costly granular activated carbon (GAC) sorption process has been commonly used for pink water treatment in munitions-manufacturing plants (Concurrent Technologies Corporation, 1995).

In efforts to develop a cost-effective pink water treatment system, studies have focused on developing biological or chemical transformation of nitro functional groups in explosives to overcome the hindrance of oxidation. Many studies showed that TNT could be biologically transformed to triaminotoluene (TAT) by pure and mixed cultures under anaerobic conditions (Preuss et al., 1993; Lewis et al., 1996; Hawari et al., 1998; Hwang et al., 2000). In theses studies, it was also found that TAT was unstable and could be transformed to phenolic products depending on pH. However, its transformation mechanism is not clear yet. Hawari and coworkers (2000) proposed that the triazine ring of RDX was cleaved through enzymatic hydrolysis to form methylenedinitramine (MDNA) and bis(hydroxymethyl)nitramine in anaerobic sludge. These compounds were further biodegraded to give formaldehyde, methanol, nitrous oxide (N_2O), and water (Hawari et al., 2000; Halasz et al, 2002).

Two-stage anaerobic-aerobic biotransformation process was also studied for the treatment of wastewater containing TNT and 2,4-dinitrotoluene (DNT) (Berchtold et al., 1995; VanderLoop et al., 1998). VanderLoop et al. (1998)

observed that reductive products of TNT and DNT from the anaerobic fluidized-bed granular activated carbon bioreactor were easily oxidized in a subsequent activated-sludge system. Similarly, RDX was easily degraded as a nitrogen source using two-stage anaerobic-aerobic system in the sequencing batch reactor (Brenner et al., 2000).

DNT and TNT were also shown to be electrochemically reduced to 2,4-diaminotoluene (DAT) and TAT, respectively (Jolas et al, 2000; Rodgers and Bunce, 2001). Rodgers and Bunce (2001) observed that electrochemical reduction products of DNT and TNT were oxidized much easier by hydrogen peroxide than DNT and TNT. They also suggested stepwise electrochemical reduction-oxidation process for treatment of DNT and TNT in munitions waste.

Elemental iron has been used for permeable reactive barrier (PRB) to remediate groundwater contaminated with chlorinated solvents and heavy metals (Orth and Gillham, 1996; Roberts et al., 1996; Blowes et al., 1997; Gu et al., 1998). It has also been shown that DNT, TNT, and RDX can be rapidly reduced to products with elemental iron (Devlin et al., 1998; Singh et al., 1998; Oh et al., 2002a; Oh et al., 2002b). Recently, several researchers used the elemental iron reduction process for the pretreatment of wastewater containing nitro aromatics and azo dyes (Mantha et al., 2001; Perey et al., 2002, Oh et al., 2003a). Pretreatment with elemental iron was suggested since elemental iron can reductively transform electron withdrawing constituents and make recalcitrant compounds more amenable for subsequent oxidation processes. Perey et al. (2002) demonstrated that the recalcitrant azo dyes can be aerobically biodegraded an activated sludge system after iron pretreatment.

In this study, we evaluated Fenton oxidation as a subsequent oxidation process following the iron pretreatment. Fenton oxidation is the most common advanced oxidation process for the treatment of organic contaminants due to its simplicity and non-selectivity (Huang et al., 1993). However, previous research showed that a large amount of H_2O_2 (a range of 0.1%) was required to remove TNT and RDX from explosive-contaminated water using Fenton oxidation and that complete mineralization of TNT and RDX was difficult to achieve in short period of time (Li et al., 1997; Bier et al., 1999). Since the reductive transformation of nitro functional groups to amino groups would lower Gibbs free energy of the compound (Schwarzenbach et al., 1993), we hypothesized that reduction with elemental iron will make refractory explosives thermodynamically more favorable for oxidation and, thus enhance the extent of degradation in Fenton oxidation. In the present study, we examined the effect of elemental iron pretreatment on the oxidation of TNT and RDX by Fenton's reagent. TNT and RDX solutions were initially reduced with elemental iron and subsequently oxidized in a laboratory-scale continuous stirred tank reactor (CSTR). Total organic carbon (TOC) concentration in a reactor effluent was used to determine the extent of degradation in the CSTR. We also demonstrated the integrated system with real pink water. By batch and column experiments, we determined the reduction of TNT, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) with zerovalent iron and evaluated the extent of TOC removal from pink water in the integrated system.

2. Material and Methods

Chemicals

TNT (>99%), RDX (>99%), and HMX (>99%) were provided by the Holston Army ammunition plant (Kingsport, TN). Pink water was provided by the Iowa Army ammunition plant (Middletown, IA). $FeSO_4 \cdot 7H_2O$ (>99%) was purchased from Sigma (St. Louis, MO) and H_2O_2 (30%) was obtained from Fisher Scientific (Pittsburgh, PA). Scrap iron used in this study was obtained from Master Builders, Inc. (Aurora, OH). Specific surface area of Master Builders iron was 1.29 m^2/g (Oh et al., 2003b). The iron was used as received without pretreatment.

Fe(0)-treated TNT and RDX

Iron-treated TNT and RDX solutions were prepared by passing solutions of TNT (0.24 mM or 20 mg/L TOC) and RDX (0.25 mM or 9.0 mg/L TOC) through a glass column (2.5 cm i.d.× 30 cm L, Ace Glass, Vineland, NJ) packed with Master Builders iron (porosity = 0.66). TNT and RDX solutions were prepared with deionized water, purged with N_2 for at least 20 minutes, and then pumped into the column using a peristaltic pump in an upward direction at a flow rate of 10 mL/min. This gave a retention time in the column of approximately 9.7 minutes. HPLC analysis of the column effluents indicated that TNT and RDX were completely transformed. TNT was fully reduced to TAT and no aminonitrotoluene intermediates were detected. The steady-state concentration of ferrous ion in the effluent was below 0.1 mg/L. The column effluents were passed through a 0.22-μm cellulose membrane filter (Millipore, Bedford, MA) to remove particles. The filtered solution was collected in a 2.5-L glass bottle and used for the Fenton oxidation experiments within three days.

Fenton oxidation in a CSTR

Fenton oxidation experiments were conducted using an acrylic, cylindrical CSTR (8.8 cm dia. × 3.5 cm effective height). Solutions of $FeSO_4 \cdot 7H_2O$ and H_2O_2, and the test solution containing TNT, RDX, or their reduction products were pumped into a CSTR using peristaltic pumps (Cole-Parmer, Vernon Hills, IL). The test solution and Fenton's reagent were mixed in the CSTR using a magnetic stirrer (950 ± 50 rpm, as measured using a tachometer). The flow rate of Fe^{2+} and H_2O_2 solutions were 0.04 mL/min and that of the test solution were 3.5 mL/min. The pH of the reaction mixture was controlled at 3.0 ± 0.1 using an automatic pH controller (Cole-Parmer, Vernon Hills, IL) with 0.1-N NaOH solution. After more than three hydraulic retention times (HRTs), CSTR effluent was collected and filtered with a glass fiber filter (1.5-mm, Whatman, Clifton, NJ) prior to TOC analysis. Preliminary result with 2 mM H_2O_2 and 2 mM Fe^{2+} showed that increasing HRT from 40 min to 2 hours did not result in meaningful increase in TOC removal for TNT (from 29.0 ± 3.0% to 31.6 ± 5.0%) and iron-treated TNT (from 51.8 ± 1.0% to 52.3 ± 0.5%). Therefore, an HRT of 1 hour was used for all CSTR experiments.

Degradation in a bench-scale integrated system

A bench-scale integrated system (similar to that shown in Fig. 1) was constructed to further evaluate the feasibility of the proposed process to mineralize TNT and RDX. The integrated system was constructed by connecting the iron column and the CSTR described previously with silicone tubing and a glass fiber filter. The same column described above was used. Deoxygenated TNT or RDX solution was pumped into the iron column at a flow rate of 3.5 mL/min. Initial concentrations of TNT and RDX solutions were 0.196 ± 0.008 mM (16.0 ± 1.2 mg/L TOC) and 0.180 ± 0.006 mM (6.5 ± 0.2 mg/L TOC), respectively. TNT and RDX solutions were passed individually through the column on a continuous basis for over two weeks to ensure steady-state conditions. The concentrations of H_2O_2 and Fe^{2+} and the mole ratio were chosen based on results of previous CSTR experiments. The concentrations of TNT and RDX, TOC, NH_4^+, and NO_3^- in the influent, iron column effluent, and CSTR effluent were monitored over time and recorded when the concentrations became constant.
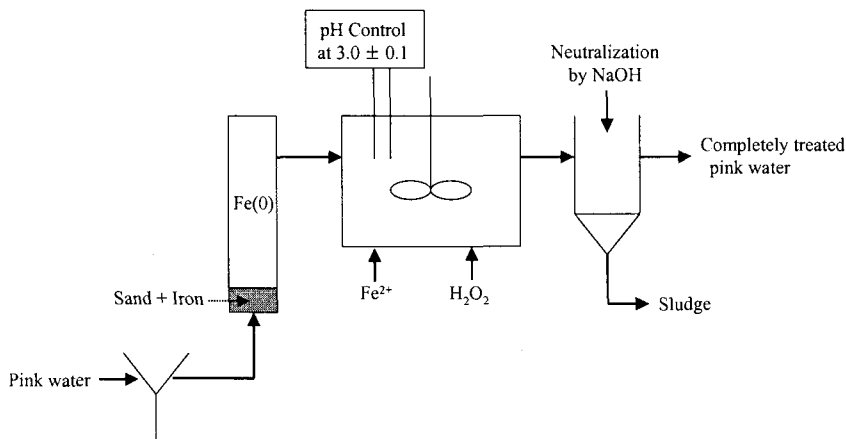

Fig. 1. A proposed Fe(0) column-Fenton oxidation integrated system for pink water treatment.

Batch and column experiments with pink water

Batch experiments were conducted 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 cast iron. Pink water contained 0.1 M HEPES buffer to maintain a constant pH of 7.4 throughout the experiments. The solution was purged in a glove box to completely remove oxygen for at least 1 day. After iron was added, the vials were shaken in a horizontal position using an orbital shaker at 100 rpm. At each sampling time, replicate vials were sacrificed and the supernatant was filtered through a 0.22-μm mixed cellulose membrane filter (Millipore, Bedford, MA) for analysis using a high performance liquid chromatograph (HPLC).

Column experiments were conducted using a glass column (2.5 cm i.d.× 30 cm L, Ace Glass, Vineland, NJ) packed with Master Builders iron. To ensure anaerobic conditions, pink water was purged with N_2 for 20 minutes prior to introduction into the column. The deoxygenated pink water was pumped into the packed column using a peristaltic pump in an upward direction at the flow rate of 3.50 ± 0.05 mL/min. The retention time in the column

was approximately 25 minutes. After more than three retention times, the column effluents were collected and passed through a 0.22-μm cellulose membrane filter (Millipore, Bedford, MA) for HPLC analysis.

Analytical methods

TNT, RDX, and HMX were analyzed using 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 μm), a UV detector (2510 Varian, Walnut Creek, CA) and an isocratic pump (2550 Varian, Walnut Creek, CA). Methanol-water mixture (55/45, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. TAT was analyzed by HPLC with an Alltima C18 column (250×4.6 mm, 5 μm, Alltech, Deerfield, IL) and an Alltima guard column (7.5×4.6 mm, Alltech). Acetonitrile-phosphate buffer (40 mM, pH 3.2, 10/90, v/v) was used as an 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. TOC concentration was determined using a Tekmar-Dohrmann TOC analyzer (DC-190 Rosemount Analytical Inc., Santa Clara, CA). NH_4^+ and NO_3^- were analyzed with an UV-vis spectrophotometer (DR2010, HACH, Loveland, CO) using the salicylate method and the cadmium reduction method, respectively (Hach Co., 1998).

3. Results and discussion

Fenton oxidation of Fe(0)-treated TNT and RDX solutions

In order to maximize the extent of TOC removal in TNT and Fe(0)-treated TNT solutions in CSTR, optimum H_2O_2 to Fe^{2+} ratio was determined with 2 mM Fe^{2+} and various H_2O_2 concentrations (Fig. 2). First of all, Fig. 2 clearly shows that the extent of TOC removal in Fe(0)-treated TNT solution was significantly higher than that the TOC removal observed in untreated TNT solution, supporting our hypothesis that reduction of nitro constituents in TNT enhanced the extent of degradation in the Fenton oxidation process. Fig. 2 also shows that H_2O_2 and Fe^{2+} ratios of 5:1 to 10:1 were optimal for the maximum TOC removal during Fenton oxidation of TNT and Fe(0)-treated TNT in the CSTR. We chose 5:1 ratio to conduct subsequent studies because differences of TOC removal between 5:1 and 10:1 were minimal. However, with 2 mM of Fe^{2+}, the maximum TOC removal in the CSTR was only 70.5%. In order to achieve complete TOC removal in Fe(0)-treated TNT solution, H_2O_2 and Fe^{2+} concentrations were increased, while maintaining the optimal ratio.
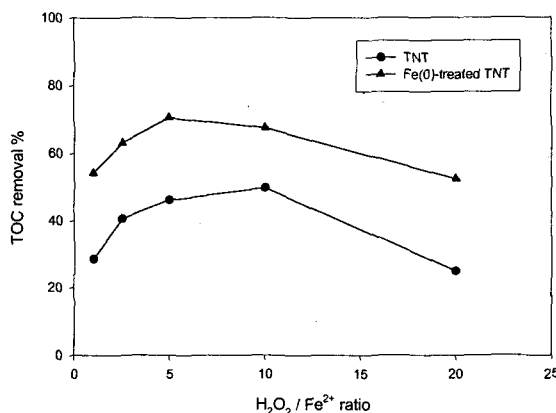

Fig. 2. The extent of TOC removal with various H_2O_2/Fe^{2+} molar concentration ratios in oxidation of TNT and Fe(0)-treated TNT with Fenton's reagent. Fe^{2+} concentration is 2 mM and initial concentration of TNT and Fe(0)-treated TNT is 20.0-20.8 mg/L TOC.

Fig. 3 shows the effect of increasing H_2O_2 and Fe^{2+} concentrations on TOC removal for TNT and iron-treated TNT. Iron pretreatment enhanced the TOC removal by 20-40%. For iron-treated TNT, the TOC removal increased with increasing H_2O_2 and Fe^{2+} dosages and complete mineralization was achieved with 5 mM Fe^{2+} and 25 mM H_2O_2. In comparison, Fenton oxidation of TNT was less efficient as indicated by the smaller increase in TOC removal with increasing Fe^{2+} and H_2O_2 dosages and incomplete TOC removal (81.4 ± 1.5%) even with 50 mM H_2O_2 and 10 mM Fe^{2+}.
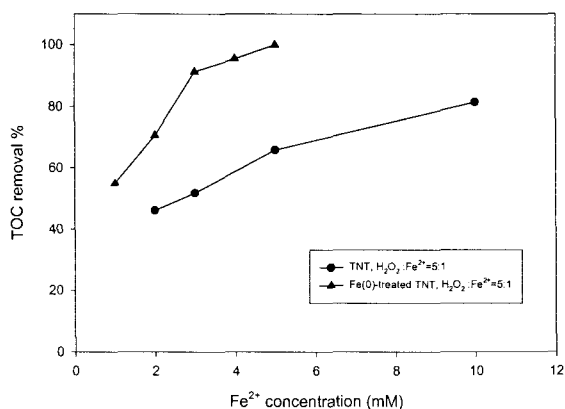
Fig. 3. The extent of TOC removal with various H_2O_2 and Fe^{2+} concentrations in oxidation of TNT and Fe(0)-treated TNT with Fenton's reagent. Initial concentration of TNT and Fe(0)-treated TNT is 20.2-22.0 mg/L TOC.

Fig. 4 shows the optimal ratio of H_2O_2 and Fe^{2+} for Fenton oxidation of RDX and Fe(0)-treated RDX in the CSTR. Under the same H_2O_2/Fe^{2+} dose ratio, iron pretreatment enhanced the mineralization of RDX by 50-60%. This significant enhancement of TOC removal also demonstrates that iron pretreatment makes explosives more favorable in the Fenton oxidation process. In addition, the extent of enhancement in Fe(0)-treated RDX is much more significant than Fe(0)-treated TNT. This difference may be due to Fe(0)-treated RDX being much more oxidizable than Fe(0)-treated TNT. It has been reported that the zero-valent iron pretreatment results in the cleavage of triazine ring in RDX and formation of NH_4^+ and a linear structure of C-N compounds (e.g. methylenedinitramine (MDNA)) as products (Oh et al., 2002b). This ring cleavage may make oxidation of Fe(0)-treated RDX much easier. Similar to TNT, optimum ratio of H_2O_2 and Fe^{2+} was found to be 5:1 for Fenton oxidation of RDX and Fe(0)-treated RDX. However, only 2 mM of Fe^{2+} was enough to obtain complete removal of TOC in Fe(0)-treated RDX solution at the optimal condition.

Degradation of Fe(0)-treated TNT and RDX solutions in a bench-scale integrated system

TNT was completely reduced to TAT in the iron column as 93.5% of initial TNT concentration (0.187 ± 0.017 mM) was accounted for in the column effluent. Reduction with iron did not reduce TOC concentration in TNT solution, indicating that sorption loss of TNT and its products in the column was minimal. After Fenton oxidation in the CSTR, $96.1 \pm 1.2\%$ of TOC was removed and 87.5% of initial nitrogen was recovered as 0.235 ± 0.007 mM of NH_4^+ and 0.257 ± 0.014 mM of NO_3^-. Similarly, RDX was also completely removed through reductive transformation in the iron column. After reduction in the iron column, 0.250 ± 0.004 mM of NH_4^+ was detected as a product, accounting for 23.8% of initial nitrogen. Subsequent Fenton oxidation in the CSTR showed $95.4 \pm 1.5\%$ TOC removal and 74.8% of nitrogen recovery (0.385 ± 0.038 mM of NH_4^+ and 0.400 ± 0.008 mM of NO_3^-).

Degradation of pink water in a bench-scale integrated system

Pink water was slightly acidic (pH 6.62 ± 0.01) and contained 17.4 ± 2.2 mg/L of inorganic carbon. Concentrations of TNT, RDX, and HMX were 108.2 ± 1.7 mg/L, 65.1 ± 7.8 mg/L, and 9.2 ± 0.4 mg/L, respectively. Concentrations of these explosives accounted for 82.9% (52.1 mg/L) of TOC in pink water (62.8 ± 0.6 mg/L). It appears that the unexplained 17.1% of TOC (10.7 mg/L) may be unidentified explosives in pink water or other organic compounds coming form loading, assembling, packing or demilitarization activities in the plant.

Fig. 5 shows the concentrations of TNT, RDX, and HMX during reduction of pink water with zero-valent iron at pH 7.4. TNT and RDX were completely removed from the pink water within 30 min. After 1 hour, HMX was completely removed, indicating that HMX removal with zero-valent iron was slower than TNT and RDX. After 30 min, TAT was increasingly formed as a product of TNT reduction. TAT showed 88.3% of initial TNT concentration after 2 hours. HPLC analysis of the column effluents indicated that TNT, RDX, and HMX were completely transformed in the iron column. TNT was fully reduced to TAT and no intermediates were detected. Concentrations of TAT and NH_4^+ were 58.9 mg/L (0.433 mM) and 12.2 mg/L (0.679 mM), respectively. The steady-state

concentration of Fe^{2+} in the effluent was below 0.1 mg/L. With 0.1 M HEPES buffer, the column effluent contained 115.5 ± 3.0 mg/L of Fe^{2+}, suggesting that the iron column may be used for generating Fe^{2+} for subsequent Fenton oxidation.
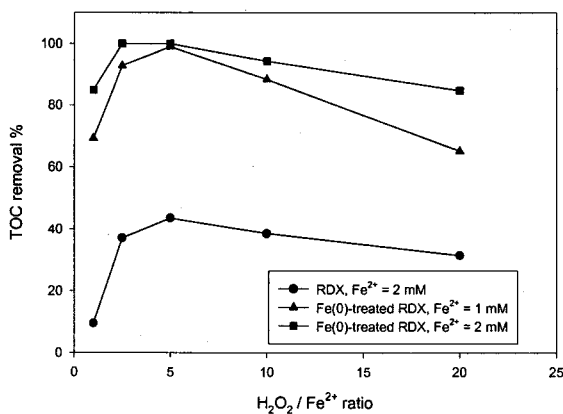

Fig. 4. The extent of TOC removal with various H_2O_2/Fe^{2+} molar concentration ratios in oxidation of RDX and Fe(0)-treated RDX with Fenton's reagent. Initial concentration of RDX and Fe(0)-treated RDX is 8.8-9.4 mg/L TOC.
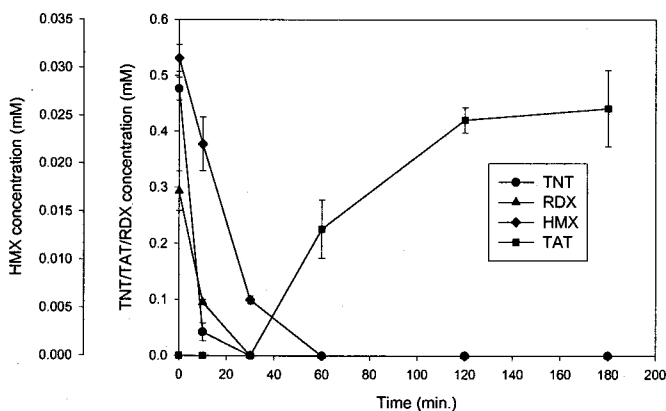

Fig. 5. Concentrations of TNT, RDX, and HMX during reduction of pink water with zero-valent iron at pH 7.4. The error bars are based on replicate reactors.

Fig. 6 shows the TOC removal in the bench-scale integrated system. With 0.5 mM of Fe^{2+} and 2.5 mM of H_2O_2, $52.9 \pm 4.0\%$ of TOC was removed in a CSTR. As concentrations of Fe^{2+} and H_2O_2 were increased, TOC removal in a CSTR was correspondingly increased. With 5 mM of Fe^{2+} and 25 mM of H_2O_2, $72.2 \pm 5.5\%$ of TOC was removed in Fenton oxidation. However, even with higher concentrations of Fe^{2+} and H_2O_2 under optimal condition, complete TOC removal was not achieved. With 10 mM of Fe^{2+} and 50 mM of H_2O_2, $83.3 \pm 4.2\%$ of TOC was removed. This incomplete TOC removal with large amounts of Fenton's reagent may be due to high concentration of TNT in the pink water. TNT concentration in the pink water was approximately 2.5 times higher than that in the TNT and RDX solutions used for the integrated system. The TOC content (10.7 mg/L) unexplained by the three major explosives may also be responsible for incomplete TOC removal in Fenton oxidation.

In summary, this study clearly showed that iron pretreatment enhanced TNT and RDX removal by Fenton oxidation process. Enhancement of mineralization in Fe(0)-treated RDX was much more significant than the mineralization of Fe(0)-treated TNT. TNT, RDX, and HMX were rapidly removed from pink water and that TAT and NH_4^+ were produced as products with zero-valent iron. Using the integrated system, $83.3 \pm 4.2\%$ of TOC was removed

from pink water with 10 mM Fe^{2+} and 50 mM of H_2O_2. This suggested that RDX-rich pink water may be more favorable for the application of iron pretreatment technology. Follow-up study on cost-effective design of Fenton process may be needed to generate sufficient amount of dissolved Fe^{2+} and minimize the amount of iron sludge in field application.
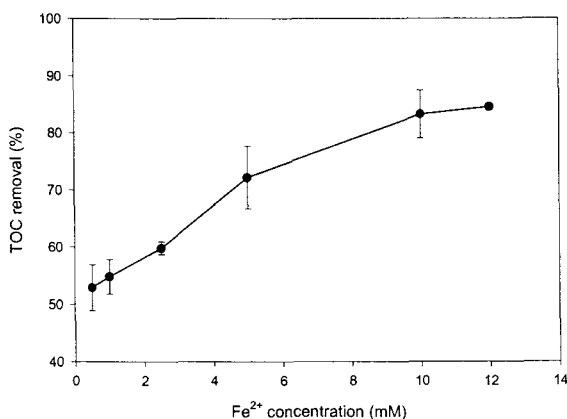

Fig. 6. The extent of TOC removal with various H_2O_2 and Fe^{2+} concentrations in Fenton oxidation of pink water. Molar ratio of H_2O_2 to Fe^{2+} is 5.

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