

Conceptual comparison of pink water treatment technologies: granular activated carbon, anaerobic fluidized bed, and zero-valent iron-Fenton process

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Abstract Pink water, explosive-laden wastewater produced in army ammunition plants is often treated using expensive and non-destructive granular activated carbon (GAC) adsorption. This paper compares GAC adsorption and two alternative treatment technologies, anaerobic GAC fluidized bed reactor and zero-valent iron-Fenton process. The bench-scale demonstration of the zero-valent iron-Fenton process with real pink water is reported. The features of three technologies are compared and their advantages and drawbacks are discussed.

Keywords Pink water; zero-valent iron; Fenton oxidation; fluidized bed reactor; granular activated carbon

Introduction

Pink water is explosive-laden wastewater originating from loading, assembling, and packing (LAP), as well as from demilitarization of munitions in army ammunition plants. Processing operation and housekeeping activities, such as flushing of explosives and laundering of workers' clothing also contribute to pink water generation (Concurrent Technologies Corporation, 1995). Composition of pink water can vary widely depending on the munitions-manufacturing processes and demilitarization facilities. Major constituents in pink water are known to be 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4-dinitrotoluene (DNT), 1,3,5-trinitrobenzene (TNB), and dinitrobenzene (DNB). Besides these compounds, more than 30 nitroaromatics and related compounds were identified in wastewater from a TNT-manufacturing plant (Spangord *et al.*, 1982). Jenkins *et al.* (1986) reported that the concentrations of TNT, RDX, and HMX in wastewater from several ammunition plants were as high as 51.3, 19.7, and 4.6 mg/L, respectively. The total concentration of explosives and other nitro compounds in pink water was found to be up to 206 mg/L (Concurrent Technologies Corporation, 1995). Because of the toxicity and possible carcinogenicity of TNT and RDX (McLellan *et al.*, 1988; USEPA, 1990), these explosives need to be removed before pink water is discharged to the environment. So far, no federal uniform limitations have been established to regulate the discharge of the explosives and related compounds from munitions-manufacturing plants. Instead, different discharge limits are used for different plants.

Adsorption with granular activated carbon (GAC) is commonly used for pink water treatment in munitions-manufacturing plants. The GAC treatment can be costly because it needs to be combined with additional treatment to regenerate spent GAC and to degrade adsorbed energetic compounds. Many chemical and biological oxidation processes have been investigated as potential treatment alternatives for pink water. However, biological oxidation processes (e.g., activated sludge) are not effective for treating pink water because

the electron-withdrawing nitro functions may inhibit electrophilic attack by enzymes (Knackmuss, 1996). Chemical oxidation methods (e.g., advanced oxidation processes) are also ineffective because of the hindrance to oxidation by nitro functions (Schmelling *et al.*, 1996). Therefore, many studies have focused on processes that can transform the nitro groups in explosive molecules in order to eliminate the hindrance to oxidation. U.S. Army Environmental Center performed a screening test for 27 destructive technologies to determine the most feasible pink water treatment technology. The criteria include total life cycle cost, effluent cost, process operability, flexibility, safety, and commercial availability (Concurrent Technologies Corporation, 1997). Based on the screening result and the pilot-scale tests, anaerobic GAC fluidized bed reactor, GAC thermophilic process, and treatment with large aquatic plants were suggested as promising alternative technologies for pink water treatment. Anaerobic GAC fluidized bed reactor appears particularly promising and has been shown to treat pink water successfully in field-scale operations (Maloney *et al.*, 2002).

For the last decade, zero-valent iron has been used to degrade oxidized pollutants through reductive transformation. Cast iron is often the material of choice for environmental applications because it is inexpensive and readily available commercially. Reductive iron treatment generally has low maintenance cost because of the passive nature of the process. In addition, iron corrosion in water does not generate toxic products. Several studies have shown that zero-valent iron is capable of removing TNT and RDX from solution (Agrawal and Tratnyek, 1996; Devlin *et al.*, 1998; Singh *et al.*, 1998). Hundal *et al.* (1997) suggested that the iron treatment process in combination with H₂O₂ oxidation or biooxidation might be effective to treat explosives-laden wastewaters. We recently demonstrated that rapid and complete reduction of TNT and RDX can be achieved with zero-valent iron, suggesting iron may be used for pink water treatment (Oh *et al.*, 2002). We further showed that Fenton oxidation can effectively remove TOC in iron-treated pink water and that mineralization of TNT and RDX can be greatly enhanced through iron pretreatment (Oh *et al.*, 2003).

In this paper, we review three pink water treatment technologies: GAC adsorption, anaerobic GAC fluidized bed reactor, and zero-valent iron treatment followed by Fenton oxidation. We also report bench-scale performance of the zero-valent iron-Fenton process with real pink water. The advantages and drawbacks of three technologies will be compared with respect to their potential for large-scale pink water treatment operations.

GAC adsorption

Granular activated carbon has highly porous structures and large internal surface area, in the range 500–1,500 m²/g (Perrich, 1981). Pink water is first filtered using 10- μ m filter paper in order to remove particles prior to the GAC treatment. The filtered solution is then passed through a column packed with GAC, to which the energetic compounds in pink water are removed via adsorption. The concentration of energetic compounds in the column effluent has been reported to be less than 1 ppm (Concurrent Technologies Corporation, 1995). Hinshaw *et al.* (1987) demonstrated that the GAC adsorption process could effectively remove explosives, such as TNT, DNT, RDX and HMX, from pink water. Ho and Daw (1988) found that DNT was effectively removed from solution by commercial activated carbon. They also suggested that acetone might be the most effective solvent to remove adsorbed DNT from spent activated carbon. Wujcik *et al.* (1992) reported that adsorption with GAC was capable of removing TNT, DNT, RDX, HMX, and TNB from explosive-laden groundwater. Fluidized bed furnace, rotary calciner, and multiple hearth furnace are common thermal processes used to degrade adsorbed explosives as well as to regenerate spent GAC. After thermal treatment, the regenerated GAC is mixed with fresh

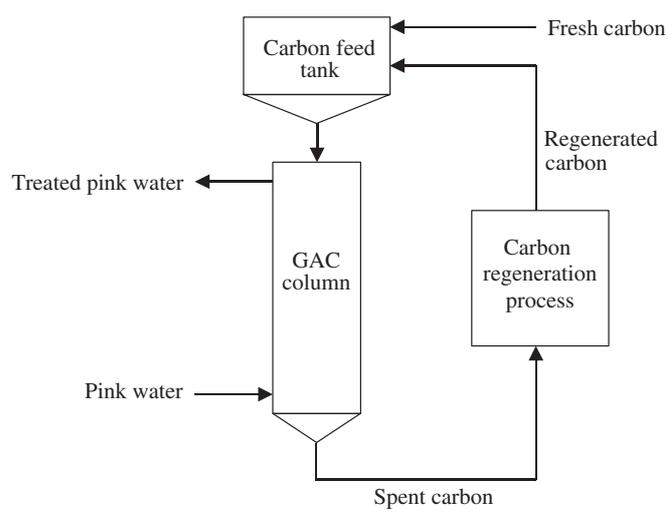


Figure 1 GAC adsorption process (Concurrent Technologies Corporation (1995))

activated carbon and used for further pink water treatment (Figure 1). The addition of fresh GAC is necessary to maintain the treatment efficiency because GAC regenerated thermally is known to lose 15–50% of its original sorption capacity (Concurrent Technologies Corporation, 1995).

Anaerobic GAC fluidized bed

An anaerobic GAC fluidized bed was suggested as a pretreatment process for pink water prior to its discharge to an aerobic wastewater treatment system (Maloney *et al.*, 2002). GAC in the fluidized bed reactor serves as a support medium for anaerobic bacteria to attach and form biofilms and as an adsorbent for explosive molecules. The high adsorption capacity of GAC provides the buffering capacity the reactor needs against high loadings of explosives in pink water (VanderLoop *et al.*, 1998). The biotransformation of explosives in the reactor is a cometabolic process which requires addition of ethanol, NH_4^+ , and nutrients (Figure 2). Berchtold *et al.* (1995) have shown that DNT was reductively transformed through amino intermediates to 2,4-diaminotoluene (DAT) in the fluidized-bed reactor

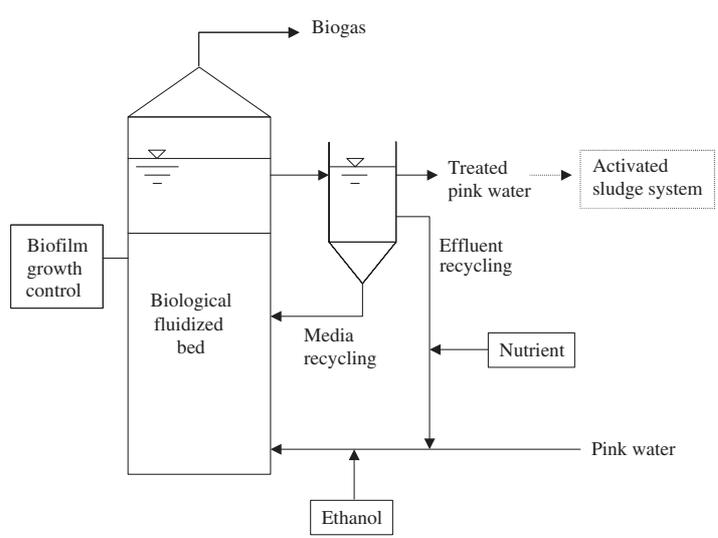


Figure 2 Anaerobic GAC fluidized-bed reactor (Maloney *et al.* (2002))

under methanogenic conditions. The DAT in the effluent accounted for more than 90% of the influent DNT and was stoichiometrically degraded to nitrate and biomass in the subsequent activated sludge reactor. VanderLoop *et al.* (1998) showed that TNT was completely biotransformed to unknown products by a mixed anaerobic culture in a GAC fluidized bed reactor. In the succeeding activated sludge reactor, the reduction products in the fluidized bed effluent were further oxidized, resulting in 73% carbon mineralization and 82% nitrogen recovery. Anaerobic treatment of pink water in a GAC fluidized-bed reactor was evaluated in a pilot-scale (EFX System Inc., 2000; Maloney *et al.*, 2002). After solids were removed by sand filtration, the explosives in pink water were transformed by a methanogenic mixed culture in a fluidized bed GAC reactor. Various hydraulic retention times (18.8–375 min) and temperature (90–106.5 °F) were tested. The field-scale operation demonstrated that energetic compounds were completely removed from the pink water and that TNT was reductively transformed to 2,4,6-triaminotoluene (TAT) with a short retention time of 37.5 min (EFX System Inc., 2000).

Zero-valent iron-Fenton process

We recently evaluated a two-stage process involving reductive iron treatment and Fenton oxidation (Figure 3) to mineralize TNT and RDX in water (Oh *et al.*, 2003). We hypothesized that reductive treatment with zero-valent iron can enhance the rate and extent of TOC removal by Fenton oxidation. Fenton oxidation; i.e., oxidation by hydroxyl radical generated through reaction of H_2O_2 and ferrous ion, is a common advanced oxidation process for treating organic pollutants. It was proposed because of its simplicity, effectiveness, and non-selectivity (Huang *et al.*, 1993). In addition, the ferrous ion produced in the iron column may enhance the subsequent Fenton oxidation.

The proposed zero-valent iron-Fenton technology was evaluated using a pink water from Iowa army ammunition plant. The pink water contains 108.2 ± 1.7 mg/L of TNT, 65.1 ± 7.8 mg/L of RDX, and 9.2 ± 0.4 mg/L of HMX, respectively. Concentrations of these explosives accounted for 82.9% (or 52.1 mg/L) of the TOC in the pink water (62.8 ± 0.6 mg/L). The remaining 17.1% of the TOC may be unidentified explosives or other organic compounds derived from loading, assembling, and packing activities in the plant.

We first demonstrated the effectiveness of zero-valent iron to completely remove TNT, RDX and HMX from pink water in batch reactors. Five millilitres of pink water (pH 7.4) was added to an 8-mL glass vial containing 1 gram of cast iron. The vials were sealed and shaken at 100 rpm in an anaerobic glove box. Replicate vials were set up and were sacrificed at different elapsed times for analysis of TNT, RDX, HMX, and TAT by HPLC. As shown in Figure 4, TNT and RDX were completely removed from the pink water within 30 min and HMX was removed within an hour. TAT appeared in the aqueous phase after 30 min and its concentration increased continuously up to approximately 88% of the initial TNT concentration in 2 hours. The remaining TAT was reversibly adsorbed on the cast iron surface, as we previously showed (Oh *et al.*, 2002). Results of this batch experiment are consistent with our previous findings that TNT was completely reduced to TAT within an hour with Masters Builder iron, and that RDX was removed within 30 min and a large fraction of the RDX-nitrogen was recovered as ammonia (Oh *et al.*, 2002). These results show that iron is capable of rapidly removing TNT and RDX through reduction. In an iron column experiment we performed recently, TNT was fully reduced to TAT within 9.7 min of residence time, regardless of the buffering capacity of the TNT solution (Oh *et al.*, 2003).

We further investigated the effect of reductive treatment with zero-valent iron on the efficiency of the subsequent Fenton oxidation. A bench-scale iron-Fenton system was constructed, similar to that shown in Figure 3, to evaluate the effectiveness of the integrated

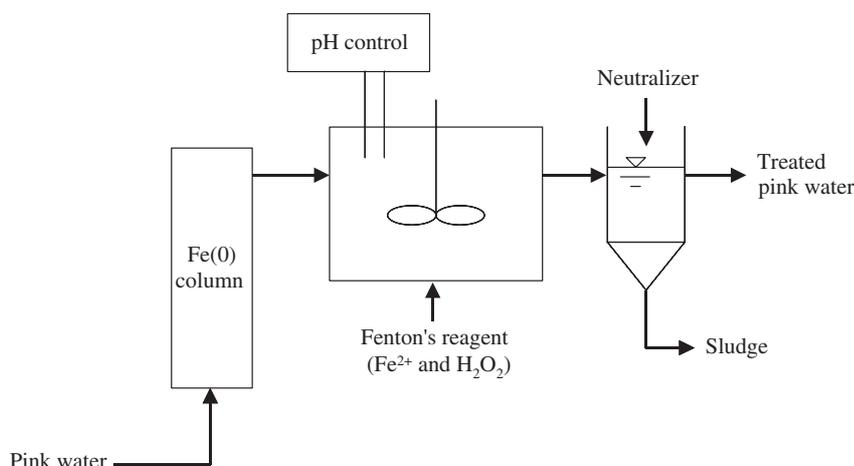


Figure 3 Proposed zero-valent iron-Fenton reactor (Oh et al. (2003))

process to remove the TOC in pink water. The system consisted of a glass column (2.5 cm i.d. \times 30 cm L) packed with Master Builders iron followed by a completely stirred tank reactor (CSTR, 8.8 cm dia. \times 3.5 cm H) in which Fenton oxidation took place. The iron column and the CSTR were connected with silicone tubing and a glass fiber filter. Column effluent and solutions of FeSO_4 and H_2O_2 were pumped into the CSTR using peristaltic pumps. The flow rate of the column effluent was 3.5 mL/min and that of Fe^{2+} and H_2O_2 solutions were 0.04 mL/min. A H_2O_2 -to- Fe^{2+} mole ratio of 5:1 was used, which was found to be the optimal ratio for iron-treated TNT and RDX (Oh et al., 2003). The pH in the CSTR was maintained at 3.0 ± 0.1 using an automatic pH controller with a 0.1-N NaOH solution (as the pH decreased slightly during Fenton oxidation). The hydraulic retention time in the CSTR was 1 h. After steady-state conditions were established, the column and CSTR effluents were collected for HPLC and TOC analysis, respectively.

HPLC analysis of the column effluent indicated that TNT, RDX, and HMX were completely removed from the pink water. Approximately 91% of the initial TNT was recovered as TAT (58.9 mg/L, or 0.433 mM) and no aminonitrotoluene intermediates were found. In addition, 12.2 mg/L (0.679 mM) of NH_4^+ was detected, which was formed during reduction of RDX (and possibly HMX) with cast iron (Oh et al., 2003). With unbuffered pink water,

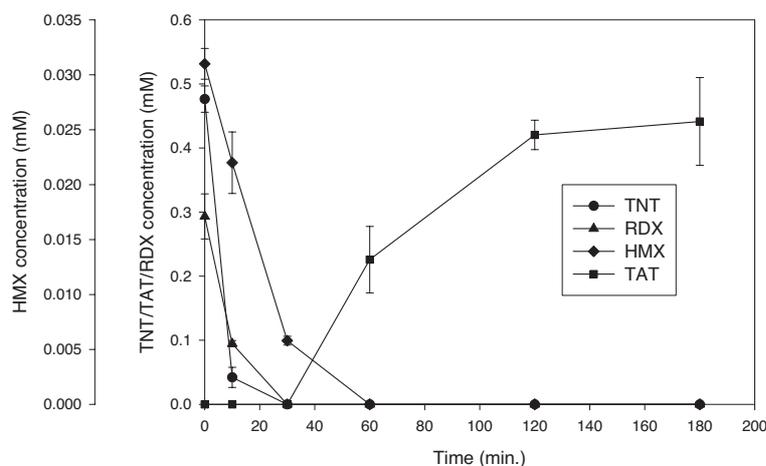


Figure 4 Concentration of TNT, RDX, and HMX during reduction of pink water with zero-valent iron at pH 7.4. The error bars are based on replicate reactors

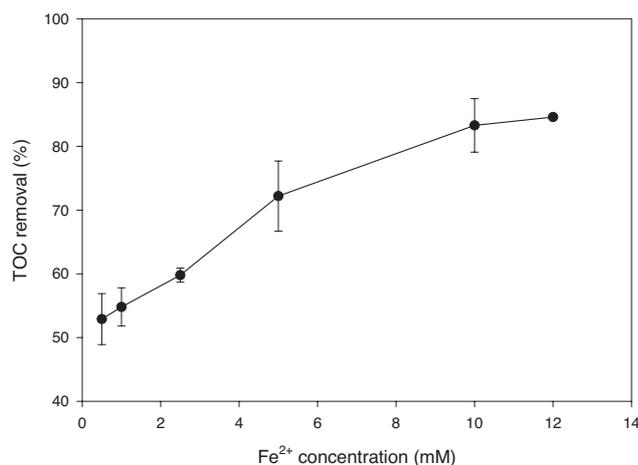


Figure 5 The extent of TOC removal with various H_2O_2 and Fe^{2+} concentrations in Fenton oxidation of pink water. Mole ratio of H_2O_2 to Fe^{2+} is 5

the steady-state concentration of Fe^{2+} in the column effluent was less than 0.1 mg/L. However, with 0.1 M HEPES buffer, the column effluent contained 115.5 ± 3.0 mg/L of Fe^{2+} , suggesting that an iron column may be used as a source of Fe^{2+} for the Fenton oxidation.

Figure 5 shows the TOC removal as a function of Fe^{2+} concentration in the integrated system. Higher TOC removal was observed with increasing Fe^{2+} concentration, and an $83.3 \pm 4.2\%$ TOC removal was achieved with 10 mM of Fe^{2+} (and 25 mM of H_2O_2). We previously found that 5 mM Fe^{2+} was sufficient to completely oxidize iron-treated TNT and RDX for lower concentrations of TNT and RDX (Oh *et al.*, 2003), the residual TOC may be due to the relatively high concentrations of TNT and RDX or the unidentified TOC (17.1%) in the pink water.

Discussion

Several observations can be made by comparing the three pink water treatment technologies. First, although GAC can be regenerated and reused whereas zero-valent iron is consumed continuously through oxidation (by oxygen, water, and the explosives), zero-valent iron is actually longer-lasting and requires less maintenance than GAC. A long-term study performed in our laboratory showed that a packed iron column with a residence time of 15 min remained active for over a year without breakthrough of TNT or RDX. In contrast, GAC needs to be regenerated and partially replaced with fresh GAC periodically in order to maintain removal efficiency (Construction Technologies Corporation, 1995).

Second, unlike the other two technologies, GAC adsorption is a non-destructive process and thus requires subsequent treatment, such as alkaline hydrolysis or incineration, to transform the adsorbed explosive molecules. And for both GAC adsorption and anaerobic fluidized bed reactor, the treated effluent containing incineration, hydrolysis or reduction products of explosives requires subsequent biological oxidation (Construction Technologies Corporation, 1995; EFX System Inc., 2000), in contrast to the iron-Fenton process which chemically oxidizes the reduction products. Both anaerobic fluidized bed (Maloney *et al.*, 2002) and the iron-Fenton process (Oh *et al.*, 2003) use reductive transformation to enhance the subsequent oxidation reactions, and both oxidation processes also generate biological or chemical sludge that needs to be disposed of.

Third, GAC adsorption consumes caustic chemicals for hydrolysis, whereas an anaerobic GAC fluidized bed reactor requires a constant supply of substrates and nutrients

(VanderLoop *et al.*, 1998). Unlike GAC adsorption and the iron-Fenton process, a fluidized bed reactor needs to be maintained continuously through substrate in order to sustain an active microbial population and ensure high removal efficiency. The Fenton oxidation also requires the addition of chemical reagents such as H_2O_2 ; however, it is more rapid than biological oxidation and therefore requires a shorter residence time in the reactor. Fenton oxidation is also insensitive to the toxicity of the reduction products of TNT (e.g., TAT, Sunahara *et al.*, 1998) and RDX (e.g., hydrazine and dimethylhydrazine isomers, McCormick *et al.*, 1981) and can mineralize these products on site.

While GAC adsorption is a proven technology and has been used to treat pink water at army ammunition plants for many years, anaerobic GAC fluidized bed reactor and zero-valent iron-Fenton process appear to have many advantages and may be potentially superior treatment options. Because the iron-Fenton process is relatively new, large-scale and long-term evaluation of this technology will be needed to allow better cost comparison of the three technologies.

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