

Zero-valent iron treatment of RDX-containing and perchlorate-containing wastewaters from an ammunition-manufacturing plant at elevated temperatures

S.-Y. Oh*, D.K. Cha*, P.C. Chiu* and B.J. Kim**

*Department of Civil and Environmental Engineering, University of Delaware, DE 19716, USA
(E-mail: quartzoh@ce.udel.edu; cha@ce.udel.edu; pei@ce.udel.edu)

**US Army Engineering Research and Development Center, Champaign, IL 61826-9005, USA
(E-mail: b-kim@cecer.army.mil)

Abstract The use of zero-valent iron for treating wastewaters containing RDX and perchlorate from an army ammunition plant (AAP) in the USA at elevated temperatures and moderately elevated temperature with chemical addition was evaluated through batch and column experiments. RDX in the wastewater was completely removed in an iron column after 6.4 minutes. Increasing the temperature to 75 °C decreased the required retention time to 2.1 minutes for complete RDX removal. Perchlorate in the wastewater was completely removed by iron at an elevated temperature of 150 °C in batch reactors in 6 hours without pH control. Significant reduction of perchlorate by zero-valent iron was also achieved at a more moderate temperature (75 °C) through use of a 0.2 M acetate buffer. Based on the evaluation results, we propose two innovative processes for treating RDX-containing and perchlorate-containing wastewaters: a temperature and pressure-controlled batch iron reactor and subsequent oxidation by existing industrial wastewater treatment plant; and reduction by consecutive iron columns with heating and acid addition capabilities and subsequent oxidation.

Keywords Ammunition wastewater; perchlorate; RDX; reduction; zero-valent iron

Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine ($C_3H_6N_3(NO_2)_3$, Royal Demolition Explosive or RDX) and perchlorate (ClO_4^-) are major constituents in wastewaters from an army ammunition plant (AAP) in USA. The production rates of RDX- and perchlorate/RDX-containing wastewaters at the plant were 9000 and 2000 gallons/day, respectively (personal communication). RDX is toxic to organisms including algae, fish, rat, and humans (Yinon, 1990). Perchlorate is also known to interfere with human iodine uptake, which is necessary for the production of thyroid hormones (Renner, 1999). Due to their adverse effect on human health and environment, RDX and perchlorate need to be removed from the wastewaters before they are discharged.

In recent years, zero-valent iron (Fe(0)) has been increasingly used in site cleanup, specifically in permeable reactive barriers (PRBs) for the remediation of contaminated groundwater (Gillham and O'Hannesin, 1994). Fe(0) is a strong reducing agent and can reductively degrade relatively oxidized pollutants including chlorinated solvents, metals, nitrate, explosives and radionuclides. Studies have also been conducted to investigate the reduction of RDX and other nitramines by Fe(0) (Singh *et al.*, 1998; Oh *et al.*, 2001; 2002). Oh *et al.* (2001) reported that RDX was readily transformed by Fe(0) and they identified three nitroso intermediates, methylenedinitramine (MDNA), and N_2O as RDX reduction products. Pretreatment with Fe(0) may be useful for treating RDX-containing

wastewater because iron can reductively transform electron-withdrawing moieties and thus make recalcitrant compounds more amenable to subsequent oxidation processes. We recently showed that pretreatment with Fe(0) markedly increased the rate and extent of RDX mineralization by Fenton reagent and by a mixed culture in activated sludge (Oh *et al.*, 2003; 2005a).

In contrast, use of Fe(0) to reduce aqueous perchlorate has had limited success due to the slow kinetics of this reaction under ambient conditions (Gurol and Kim, 2000; Moore *et al.*, 2003). Gurol and Kim (2000) showed that, through surface complexation and adsorption, about 80% of perchlorate (approximately 1 mg/L) in phosphate buffer solution was removed by elemental iron (100 g/L) in 5 hours. Moore *et al.* (2003) showed that 66% of perchlorate could be reductively removed from solution with elemental iron (1.25 g/mL) at neutral pH in two weeks. They proposed that the removal mechanisms might include reduction by hydrogen atoms or surface-bound Fe²⁺ and sorption to iron surface. They also concluded that due to the slow reaction elemental iron might not be useful as a remediation technology for perchlorate removal. Recently, Gu *et al.* (2003) observed a complete decomposition of perchlorate in 60 minutes at 195 °C with ferrous ion as the reducing agent. The rate of perchlorate reduction by ferrous ion, a weak reductant relative to Fe(0), increased by three orders of magnitude when the temperature was raised from 110 to 195 °C (Gu *et al.*, 2003). Horányi and co-workers (Ujvári *et al.*, 2002; Láng *et al.*, 2003; Láng and Horányi, 2003; Horányi, 2004) also found that perchlorate reduction to chloride by Fe(0) in acidic solution was enhanced by increasing proton concentration and temperature. They showed that elemental iron could reduce 18% of perchlorate to chloride at 25 °C in 1 M HClO₄ solution in 5 hours, and the extent of reduction was enhanced by about 15% with increasing temperature from 25–45 °C (Ujvári *et al.*, 2002; Láng *et al.*, 2003). Láng and Horányi (2003) concluded that reduction of perchlorate to chlorate was the rate-limiting step based on the result that reduction of chlorate by Al and Zn was one order of magnitude faster than that of perchlorate. Recently, our group showed that 98% of aqueous perchlorate was removed by Fe(0) in 1 hour at 200 °C (Oh *et al.*, 2006). We suggested that iron treatment at elevated temperatures might be an alternative for complete reduction of perchlorate in industrial wastewater.

In this study, the feasibility of zero-valent iron for the reductive degradation of RDX and perchlorate in wastewaters from an AAP was evaluated. The properties of the wastewaters were measured and the effectiveness of iron treatment was demonstrated through laboratory-scale batch and column experiments. We also evaluated the effect of temperature on the reduction kinetics of RDX and perchlorate in these wastewaters.

Materials and methods

Wastewaters containing RDX and perchlorate were provided by an active AAP. Sodium acetate (CH₃COONa·3H₂O, >99%) and hydrochloric acid (>99.9%) were purchased from Aldrich (Milwaukee, WI). Cast iron filings used in this study were obtained from Peerless Metal Powders and Abrasive (Detroit, MI). The iron was used as received without pretreatment. Specific surface area of the Peerless iron was 1.67 m²/g, as determined by the BET method with N₂.

The procedures and conditions for the batch reduction experiments were described in detail in a previous paper (Oh *et al.*, 2005b). Replicate Pyrex® vials (12 mL) each containing 10 g of iron and 3 mL of perchlorate wastewater were placed in a block heater (HACH, Loveland, CO, USA) at 150 °C. The heater was pre-heated to 150 °C before vials were introduced. At selected times, replicate vials were sacrificed and solution was immediately passed through a 0.20 μm cellulose membrane filter (Millipore, MA, USA) for perchlorate measurement.

Column experiments were conducted using glass columns (2.5 cm ID \times 30 cm L for the perchlorate wastewater and 1.1 cm ID \times 30 cm L for the RDX wastewater; Ace Glass, Vineland, NJ, USA) with Teflon end fittings in a water bath (Lab-Line Instruments, Melrose Park, IL, USA). The columns were packed with Peerless iron (porosity = 0.72) and column temperature was maintained at $75 \pm 3^\circ\text{C}$ using a water bath. Control experiments were conducted at room temperature ($21 \pm 1^\circ\text{C}$). To ensure anaerobic conditions, the wastewaters were purged with N_2 for at least 20 minutes prior to introduction into the columns. The perchlorate wastewater was pumped at a flow rate of 0.6–2.4 mL/minute, corresponding to 30–120 minute of hydraulic retention time (HRT) in the column. For the RDX wastewater, the flow rate ranged from 2.4–27.8 mL/minute (HRT = 1.1–13.1 minute). Before the experiment, the wastewaters were pre-heated to the desired temperature by using an additional water bath (Precision Scientific, Winchester, VA, USA) to maintain a constant temperature throughout each experiment. After at least one column retention time, effluent was sampled, filtered through a $0.20\ \mu\text{m}$ cellulose filter (Millipore), and analyzed for perchlorate and RDX by ion chromatography (ICS1000, Dionex, Sunnyvale, CA, USA) and high performance liquid chromatography (HPLC; Varian, Walnut Creek, CA, USA), respectively.

Results and discussion

Table 1 summarizes the characteristics of the RDX and perchlorate wastewaters from the AAP. The RDX wastewater was acidic (pH 4.71 ± 0.03) and contained a large amount of organic carbon (TOC = $452 \pm 7.8\ \text{mg/L}$). The low pH and high TOC might be attributed to acetate and nitric acid, which were used in RDX manufacturing in the plant. The concentration of RDX in the wastewater was $90.7 \pm 4.4\ \text{mg/L}$ ($0.406 \pm 0.02\ \text{mM}$), which was markedly higher than the solubility of RDX in water at room temperature ($\sim 60\ \text{mg/L}$). This high RDX concentration might be due to colloidal RDX ($< 0.20\ \mu\text{m}$) formation during cooling of the process wastewater. Nitrate was present at $114.3\ \text{mg/L}$. Perchlorate wastewater was approximately neutral (pH 7.25 ± 0.03) and had a relatively low TOC concentration ($87.5 \pm 1.7\ \text{mg/L}$). According to the AAP, in addition to perchlorate, the perchlorate wastewater contained 2,4-dinitroanisole, *N*-methyl-*p*-nitroaniline, and RDX, which might account for the TOC in the wastewater. The perchlorate concentration in the wastewater was $189.7 \pm 1.3\ \text{mg/L}$.

RDX was rapidly and completely removed from the AAP wastewater in the iron column at 20°C . With a 4.3 minutes HRT, 93% of RDX was removed with concurrent production of formaldehyde and NH_4^+ (Figure 1). At an HRT of 6.4 minutes, RDX was completely reduced and 1.15 mM of formaldehyde and 1.77 mM of NH_4^+ were formed. Further increase in HRT did not alter the yields of formaldehyde and NH_4^+ , suggesting that no intermediates existed in significant amounts that were precursors of formaldehyde and NH_4^+ , and that these products did not react with iron. The amounts of formaldehyde

Table 1 Characteristics of RDX and perchlorate wastewaters from an AAP in USA

	RDX wastewater	Perchlorate wastewater
pH	4.71 ± 0.03	7.25 ± 0.03
TOC	452.7 ± 7.8	87.5 ± 1.7
IC	3.6 ± 0.8	20.9 ± 2.0
RDX/ ClO_4^-	$90.7 \pm 4.4\ \text{mg/L}$	$189.7 \pm 1.3\ \text{mg/L}$
Conductivity	$520\ \mu\text{S/cm}$	$580\ \mu\text{S/cm}$
NO_3^-	$114.3\ \text{mg/L}$	$2.4\ \text{mg/L}$
$\text{NH}_4^+ - \text{N}$	$14.0\ \text{mg/L}$	$18.7\ \text{mg/L}$
SO_4^{2-}	$67.0\ \text{mg/L}$	$82.2\ \text{mg/L}$

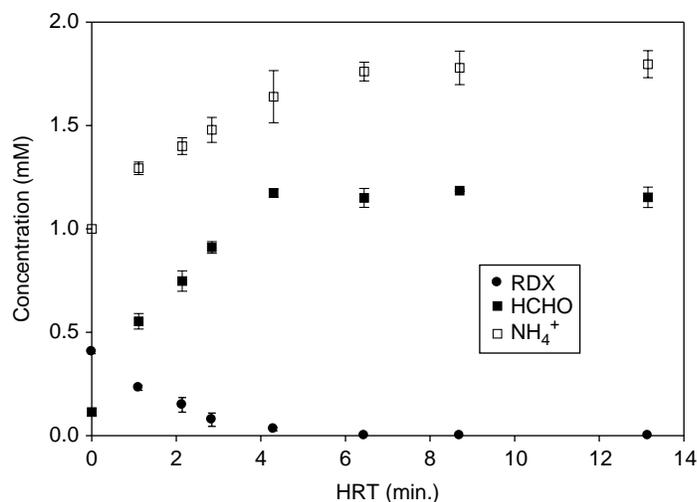


Figure 1 Concentrations of RDX, HCHO, and NH_4^+ in the RDX wastewater from an AAP before and after passing through an iron column at different HRTs at 20 °C

and NH_4^+ formed accounted for 85% of the carbon and 30% of the nitrogen of RDX in the wastewater. We recently showed that formaldehyde and NH_4^+ accounted for about 70% of the carbon and 40% of the nitrogen during RDX reduction with iron, respectively (Oh *et al.*, 2005b). The slightly different yields might be due to a different pathway involved in RDX reduction in this wastewater. In addition, other constituents (other nitramines) in the wastewater might exist that would react with iron to produce formaldehyde.

At 75 °C, reduction of RDX in the iron column was much faster. After 2.1 minutes, RDX was completely reduced by iron (Figure 2). The yields of formaldehyde and NH_4^+ were similar to those at 20 °C, indicating that the higher temperature did not change the reduction pathway of RDX in the iron column. The result suggests that increasing the temperature of the iron column and wastewater is an option to decrease the column retention time, which would reduce the size and/or increase the treatment capacity of the system.

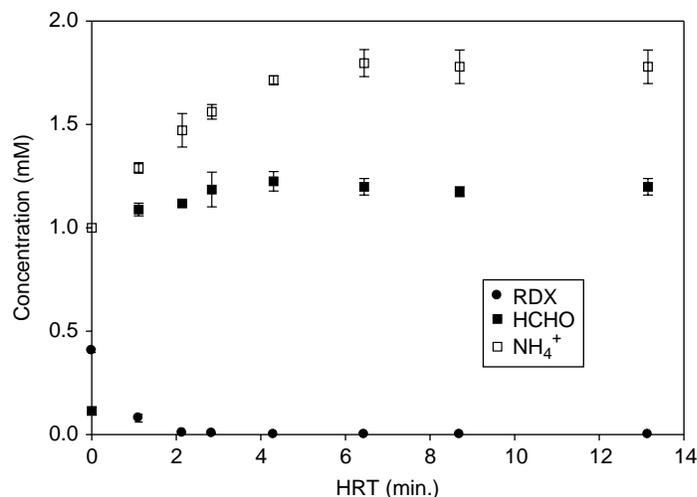


Figure 2 Concentrations of RDX, HCHO, and NH_4^+ in the RDX wastewater from an AAP before and after passing through an iron column at different HRTs at 75 °C

Results of batch experiments on perchlorate reduction showed that perchlorate in the wastewater were significantly removed with elemental iron at 150 °C. After 3 hours, about 96% of perchlorate was removed from the wastewater. Complete reduction of perchlorate was achieved in 6 hours. The pseudo first-order reduction rate constant was 1.08 hr^{-1} , similar to the reduction rate constant (0.90 hr^{-1}) of perchlorate at pH 7.4 in 0.1 M HEPES solution at 150 °C (Oh *et al.*, 2006). These results indicate that at elevated temperatures pH control may be less important in perchlorate reduction with iron. The results also suggest that iron treatment at high temperature without pH adjustment is a potential approach to manage perchlorate-laden wastewaters from munitions-manufacturing plants.

To apply the iron process for treating perchlorate wastewater in a continuous-flow system, column experiments were conducted at a moderately elevated temperature of 75 °C under pH-buffered conditions. Control experiments at room temperature showed that removal of perchlorate was less than 5% after 120 minutes in the iron column (Figure 3). Increasing the temperature to 75 °C without pH control did not increase perchlorate reduction in the iron column significantly. Only 10% of perchlorate was reduced in the iron column after 120 minutes without pH control. In contrast, with an added pH buffer (acetate), reduction of perchlorate by iron was markedly improved. Approximately 30% of the initial perchlorate was removed in 30 minutes. However, further reduction of perchlorate was negligible as the column retention time was prolonged to 60 minutes. At an HRT of 120 minutes, the additional reduction of perchlorate was only 5%.

We further evaluated the feasibility of combining high temperature and pH adjustment to increase the rate and efficiency of perchlorate reduction in an iron column. We hypothesized that, by repeatedly recirculating the perchlorate wastewater through the iron column and via pH adjustment of the wastewater after each passage, the efficiency of perchlorate reduction can be improved relative to that with only initial pH control. Based on the result with 0.2 M acetate at 75 °C, a 30 minute HRT was chosen for the experiment with recirculation and pH re-adjustment, because preliminary data showed that retention times shorter than 30 minutes under the same conditions gave lower removal efficiencies,

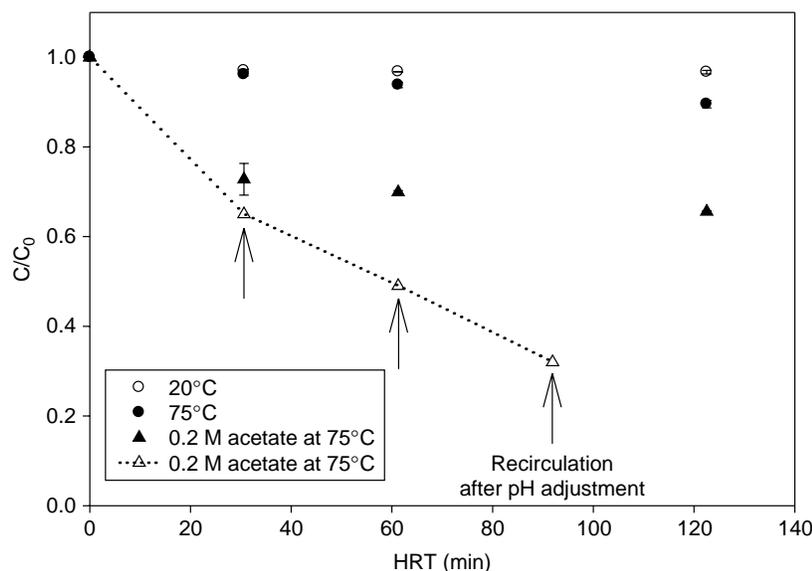


Figure 3 Reduction of perchlorate in an AAP wastewater using an iron column under different temperature and pH conditions

i.e. less than 30% (data not shown). After each 30 minutes cycle, the effluent was pH-adjusted to 4.7 by adding drops of concentrated HCl to restore the buffering capacity before the next cycle. The perchlorate in 0.2 M acetate was reduced by roughly 30% at 75 °C for each passage through the iron column. After three cycles, about 65% of perchlorate was removed from the wastewater (Figure 3). These results indicated that, in contrast to the results at 150 °C, buffering capacity (or total acidity) was a critical factor in improving the efficiency of perchlorate reduction by iron at moderately elevated temperatures.

Based on these results, we propose a new process for removing perchlorate in wastewater. The proposed perchlorate treatment process involves a series of iron columns equipped with a heating unit to maintain a desired temperature. Prior to introducing perchlorate-laden wastewater to the iron columns, a pH buffer or weak acid is added to the wastewater and, in between two iron columns, a strong acid is added to restore the pH and acidity and hence maintain perchlorate reduction efficiency. The proposed process, which combines both pH and temperature control, may be able to achieve acceptable perchlorate reduction rates (in a few hours) under relatively mild treatment conditions (<100 °C) and may have advantages over alternative options for the treatment and/or disposal of perchlorate-laden wastewaters.

Conclusions

In summary, our results show that RDX in the wastewater from the AAP can be rapidly and effectively degraded by zero-valent iron. Perchlorate could also be completely removed by iron at 150 °C in batch reactors. The combination of a pH buffer and moderately elevated temperature (75 °C) could enhance perchlorate reduction by zero-valent iron significantly in reasonable retention times. We propose two potential options to treat the perchlorate wastewater from the AAP: a temperature/pressure-controlled batch iron reactor; and a series of iron columns equipped with heating and acid addition capabilities.

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