Development of a physico-chemical and biological process for the treatment of pink water and perchlorate

*M. Sidhoum[1], P. Wanaratna[1], S. Nah[1], C. Christodoulatos[1], T. L. Su[1],
K. Jasinkiewicz[2], S. Faluotico[2], K. Hogrelius[2], and P. L. Sheehan[3]*

*[1]Center for Environmental Systems,
Stevens Institute of Technology, Hoboken, NJ, 07030
E-Mail: msidhoum@stevens.edu
[2]US Army RDECOM-ARDEC, Energetics, Warheads and Environmental Technology Division, Picatinny, NJ, 07806
[3]North Forty Environmental, Kingston, NJ, 08528*

ABSTRACT

Military ordnance production facilities generate explosive and perchlorate-laden wastewater streams which must be treated prior to their discharge off the plant facility limits. Wastewater containing energetic materials such as TNT, RDX, HMX, etc. is often referred to as pink water. As part of the development, construction and installation of a bench scale pink water treatment demonstration unit at Picatinny Arsenal (New Jersey), applied research is being conducted to establish design criteria and operational parameters. The treatment unit consists of two unit operations installed in series: (i) reduction of the energetic compounds with zero-valent iron (ZVI), followed by (ii) a biological reactor for the destruction of perchlorate. Fundamental research was conducted to assess the efficiency of ZVI for the reduction of TNT, RDX, and HMX; and the biological destruction of perchlorate. The reduction of RDX, HMX and TNT in pink water by ZVI was investigated and found to follow pseudo-first order kinetics. The effect of ZVI loadings and the nature of the acid used (sulfuric acid and acetic acid) on the destruction efficiency of the energetic compounds was assessed. It was found that the utilization of acetic acid results in higher reduction rates. Experiments were conducted to isolate and harvest perchlorate degraders from activated sludge where acetic acid was used as the carbon and energy source. The harvested perchlorate degraders were used to inoculate a bioreactor packed with plastic flakes onto which the perchlorate degraders are attached. The bioreactor performance was assessed under laboratory conditions and is currently being demonstrated by the bench scale unit at Picatinny Arsenal.

Key words: pink water, zero-valent iron (ZVI), kinetics, perchlorate

1. INTRODUCTION

Past practices in ordnance production generated explosive-laden wastewater, which was often discharged legally into drainage ditches, local streams, and settling lagoons decades ago due to unregulated waste effluents. Among the discharged energetic compounds, TNT, RDX, and HMX are of environmental concern since they are known to be toxic to aquatic and terrestrial organisms and are probable/possible human carcinogens. Past disposal practices have resulted in serious environmental problems, establishing a need to develop cost effective and environmentally friendly technologies for the destruction of these energetic compounds in contaminated waters. In addition to TNT, RDX, and TNT, ammonium perchlorate is now a contaminant of concern. Perchlorate poses a significant health threat to humans because even at low concentrations, it affects the function of thyroid glands [1]. The toxicity of perchlorate is an active area of research, primarily focused on the potential of perchlorate to hinder the synthesis of thyroid hormones and/or subsequent consequences resulting from decreases in thyroid hormones [2]. The thyroid gland may absorb perchlorate instead of inorganic iodide, thereby decreasing the human body's ability to produce hormones [3]. Activated carbon is often used as the "state-of-the-art technology" for treating the energetic compounds in pink water. In recent years, zero-valent iron (ZVI) has been extensively studied for its ability to reduce organic pollutants including nitroaromatic compounds [4,5], explosive-contaminated soil [6], and nitrate [7]. It is highly attractive since it is a passive method that rapidly reduces the targeted compounds. For perchlorate, traditional physico-chemical methods used in water treatment systems have thus far proved ineffective or too expensive [3]. Perchlorate adsorbs poorly onto activated carbon which results in very short breakthrough times. However, biological treatment, where perchlorate is the terminal electron acceptor for anaerobic respiration, is believed to be a practical remediation technology [8]. The efficient treatment of these waste streams will contribute to the Department of Defense (DoD) sustainability and stewardship by minimizing their effect on the environment. To this effect, we are evaluating a treatment system which consists of two unit operations installed in series: (i) reduction of the energetic compounds with ZVI, followed by (ii) a biological reactor for the destruction of perchlorate.

2. Reduction of the energetic compounds with zero valent iron

2.1 Materials

The zero-valent iron (ZVI) in a powder form with a surface area of 2.2 m^2/g [determined by Brunauer, Emmitt, and Teller (BET) analysis] was obtained from ARS Technologies, Inc. (New Brunswick, NJ). Reagent grade sulfuric acid and acetic acid were purchased from Fischer Scientific (Springfield, NJ). The pink water composition for this study was TNT (73 mg/L), RDX (85 mg/L), HMX (13 mg/L) and ammonium perchlorate (150 mg/L) with a pH of 7.2.

2.2 Methods of analysis

All energetic compounds (TNT, HMX, and RDX) were quantified by HPLC using an Adsorbosphere C-18 10-pm reversed-phase column (Alltech, Deerfield, IL) equipped with a prefilter element and a guard column (C-18, 5-pm, Alltech). The HPLC (Varian®, Inc., Palo Alto, CA) is equipped with a ProStar 410-Auto sampler, 230-Solvent delivery system, and ProStar-330 PDA Detector with a Chromatography Workstation version 6.0 software. A gradient mobile phase (water, methanol and acetonitrile) for the separation of the energetic compounds was prepared.

2.3 Experimental Procedure

The effect of zero-valent iron (ZVI) concentrations on the reduction of TNT, RDX, and HMX in pink water was studied by conducting batch experiments at room temperature in glass beakers. The pH of the pink water was adjusted to around 3 with sulfuric acid (1N) or acetic acid and the reaction was initiated by adding the desired amount of ZVI. Experiments were conducted in the dark to prevent the photolytic degradation of the energetic compounds. Samples (3 ml) were withdrawn periodically and filtered through a 0.2 μm filter (Whatman® Puradisc, Whatman International Ltd) to remove suspended iron particles. To overcome potential adsorption losses of the energetic compounds during filtration, it was necessary to discard the first mL of the filtered samples prior to HPLC analyses. All samples were analyzed in duplicate. A three-blade propeller rotated by an overhead lab stirrer (Stirpak model 4554-10, Cole Parmer) was used to stir the mixture at 600 rpm to overcome external mass transfer limitations.

2.4. Results and Discussion

2.4.1 Reduction of energetic compounds with ZVI

Preliminary experiments indicated that pink water energetic constituents are labile in the presence of ZVI and disappears rapidly from solution. In addition, these experiments indicated that HMX is reduced at a slow rate as compared to RDX and TNT. Therefore, the reduction of HMX by ZVI is the rate-limiting step. After the complete disappearance of the energetic compounds in the aqueous phase, ZVI was recovered and subjected to extraction with methanol. HPLC analyses of the methanol extract indicated that there was no energetic compound. Next, degradation experiments carried out with dissolved ZVI did not result in the disappearance of the energetic compounds from the bulk solution. These findings indicate that (i) the observed disappearances from the bulk aqueous phase could not be attributed to physical adsorption onto ZVI, and (ii) the degradation of the energetic compounds can be attributed to chemical reaction(s) mediated by the iron surface.

2.4.2 Effect of acid on the reduction of the energetic compounds

Experiments were conducted to determine the effect of the acid used for the initial pH adjustment on the reduction of energetic compounds with ZVI. Two acids were evaluated, acetic and sulfuric acid. For all three energetic compounds, it was found that the utilization of acetic acid to adjust the initial pH of the reaction medium yields faster degradation rates. This is clearly illustrated in Figure 1, which shows that the degradation of HMX is greatly influenced by the nature of the acid used to adjust the initial pH.

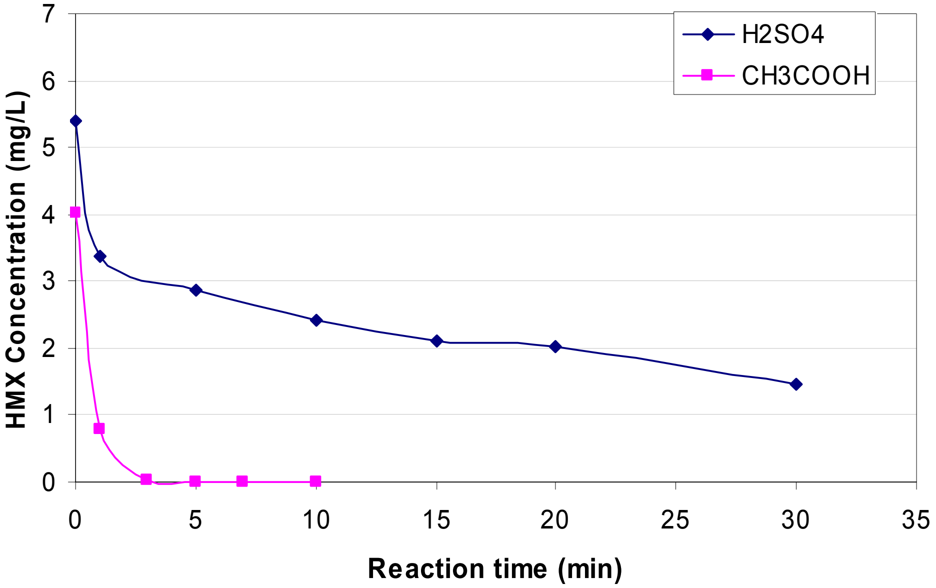

Figure 1: Effect of acid on the reduction of HMX by ZVI (1% w/v)

2.4.3 Effect of ZVI loading on the reduction of energetic compound in pink water

First, the assumption that the reduction follows a second-order rate law with respect to the energetic compound and iron concentrations was made:

$$\frac{dC}{dt} = -k_2\ C\ C_{Fe}^{0} \tag{1}$$

Where, C is the energetic compound concentration, C_{Fe}^{0} is the iron concentration, and k_2 is the second-order rate constant. By maintaining the iron concentration sufficiently in excess, Equation (1) is reduced to the following pseudo first-order rate equation:

$$\frac{dC}{dt} = -k_1\ C \tag{2}$$

where

$$k_1 = k_2\ C_{Fe}^{0} \tag{3}$$

By using the integrated form of Equation (2), the pseudo first-order rate constant, k_1, is obtained using regression analysis as the slope of the semi-logarithmic plots of concentration-time profiles for each elemental iron concentration.

Pink water reduction experiments were carried out with ZVI loadings ranging from 1 to 5% (wt/v) using acetic acid to adjust the initial pH to 3. The time-concentration profiles for the reduction of TNT, RDX, and HMX by ZVI at a loading of 5% w/v are shown in Figure 2. Similar trends were obtained with ZVI loadings of 1, 2, 3, and 4% w/v. The pseudo first-order kinetic constants (k_1) obtained by linear regression using Equation (2) are summarized in Table 1. These results show that for the ZVI loadings studied the reduction of the energetic compounds in pink water follow pseudo first-order kinetics. In addition, the results indicate that the HMX reduction is the rate-limiting step for pink water treatment using ZVI.

The second-order kinetic constants (k_2) were determined using Equation (3) by determining the slope of the plot k_1 versus ZVI loading (expressed in molar concentration). The obtained k_2 values for TNT, RDX, and HMX are 2.83, 1.09, and 0.77 M^{-1} min^{-1}, respectively.

Table 1: Pseudo first-order kinetic rate constant for the reduction of TNT, RDX, and HMX in pink water at various ZVI loadings

ZVI	Molar Ratio			Pseudo first order rate constant* (k_1)		
(%w/v)	ZVI:TNT	ZVI:RDX	ZVI:HM	TNT	RDX	HMX
1.00	491	423	2354	0.4507 (0.9986)	0.1455 (0.9881)	0.0573 (0.9534)
2.00	933	757	7476	0.8549 (0.9979)	0.3806 (0.9992)	0.1951 (0.9779)
3.00	1614	1365	11761	1.4204 (0.9908)	0.6551 (0.9921)	0.3053 (0.9349)
4.00	2210	1751	14545	1.8242 (0.9850)	0.7185 (0.9687)	0.5410 (0.9919)
5.00	2844	2335	17957	2.8352 (0.9940)	0.9995 (0.9856)	0.8264 (0.9831)

* Values in parenthesis are the R^2

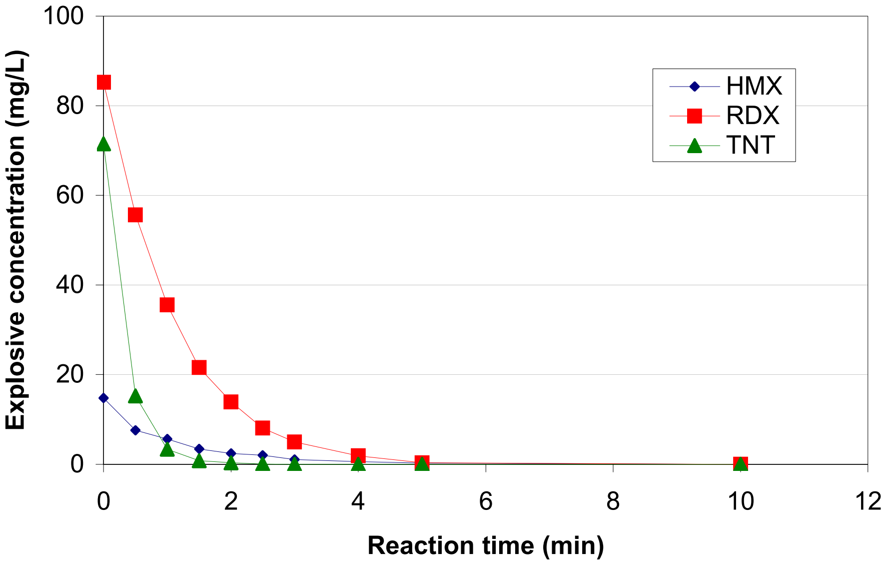

Figure 2: Time-concentration profile for pink water treatment with ZVI at a loading of 5.0% (w/v)

3 Perchlorate Biodegradation

Traditional physico/chemical methods used in water treatment systems have thus far proved ineffective or too expensive in removing perchlorate from drinking water sources [3]. However, biological treatment, where perchlorate is the terminal electron acceptor for anaerobic respiration, is believed to be most practical remediation technology [8].

This section deals with the biological treatment of perchlorate present in the pink water. Experiments have been conducted to isolate and harvest perchlorate degraders from activated sludge, where acetic acid is used as the electron donor and carbon source. The harvested perchlorate degraders were used to inoculate a bioreactor packed with either plastic flakes or sintered glass beads onto which the perchlorate degraders are attached. The performance of the bioreactors has been assessed under laboratory and field conditions.

The biological reduction of perchlorate is mediated by microorganisms which are able to use perchlorate as a terminal electron acceptor. Acetic acid was used as the source for the carbon and energy required by the perchlorate degrader microorganisms. Perchlorate is biologically reduced to chloride and oxygen according to the following pathway [9]:

$$ClO_4^- \xrightarrow[\substack{\text{Perchlorate} \\ \text{reductase}}]{} ClO_3^- \xrightarrow[\substack{\text{Chlorate} \\ \text{reductase}}]{} ClO_2^- \xrightarrow[\substack{\text{Chlorite} \\ \text{reductase}}]{} Cl^- + O_2 \tag{4}$$

3.1 Harvesting of perchlorate degraders from activated sludge

Perchlorate degraders were harvested from activated sludge obtained from a nearby wastewater treatment plant (Bergen County Utility Authority, Little Ferry, NJ). Essential nutrients for the microorganisms were provided using a growth medium (VG medium) whose composition was adapted from van Ginkel et al. [10]. Experiments were carried out in serum bottles. The batch perchlorate reducing enrichment experiments were conducted at room temperature in 125 mL Wheaton serum bottles. The reaction medium consists of 25 mL of growth medium, 75 mL of DI water, activated sludge, ammonium perchlorate, and acetic acid. The final pH of the solution ranged from 7.0 to 7.5. In a typical experiment, perchlorate concentration dropped from 21 ppm to less than 1 ppm within 6 days. Subsequently, initial perchlorate concentration adjusted to 50 ppm dropped to less than 1 ppm within 24 hours.

3.2 Perchlorate biodegradation studies in a bioreactor packed with plastic flakes

A bioreactor packed with plastic chips, was constructed and operated with a synthetic ammonia perchlorate feed stream to study the perchlorate biodegradation kinetics. The bioreactor consists of a 1 inch inner diameter (2.54 cm) plastic column, and 2 foot (60 cm) height filled with plastic flakes. The empty column volume is 325 cm^3 and the void volume is 180 cm^3 corresponding to a reactor void volume ratio of 0.55. A photograph of the plastic flakes is shown in Figure 3.

Figure 3: Plastic flakes used as packing media in the bioreactor

The bioreactor is equipped with 7 sampling ports installed at 3 inch (7.62 cm) intervals. The experimental set-up consists of a feed tank, a feed pump (FMI pump; Fluid Metering, NY) and the bioreactor. A schematic and photograph of the experimental set-up are shown in Figures 4 and 5, respectively.

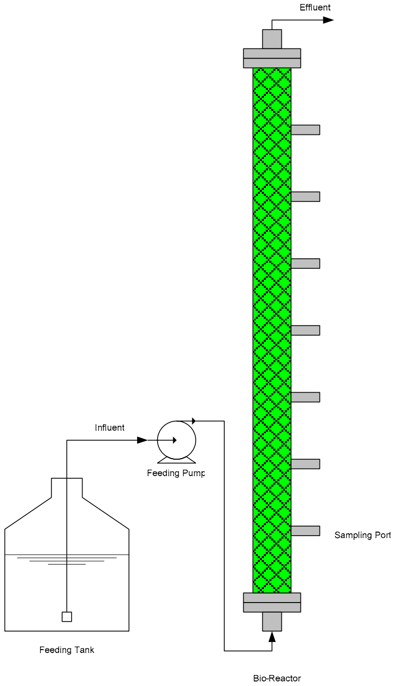

Figure 4: Schematic diagram of the bioreactor packed with plastic flakes

Figure 5: Photograph of the bioreactor packed with plastic flakes

3.2.1 Experimental Methodology

The bioreactor was operated using synthetic water containing ammonium perchlorate, VG medium, and acetic acid. A 1 L feed solution consists of ammonium perchlorate, 0.9 L distilled water, 0.1 L of VG medium, and 0.2 mL of acetic acid. The pH of the feed water was 6.5. The bioreactor was inoculated for two weeks with the perchlorate degraders harvested from activated sludge. During the inoculation period, the bioreactor was operated in total recycle mode for biofilm build-up. Once the biofilm was established, flow-through biodegradation experiments were conducted at different flow rates and influent perchlorate concentrations. The bioreactor performance was assessed by measuring the influent and effluent perchlorate concentrations and collecting samples from the sampling ports located along the column for perchlorate analyses. High perchlorate concentrations (> 1 mg/L) were measured using an ion chromatography system (IC; Dionex Corporation) equipped with an AS-16 analytical column (IonPac® AS-16, 4 x 250 mm, Dionex Corporation). Lower perchlorate concentrations (< 1 ppm) were measured using an Ion Chromatography-Mass Spectrometry (IC-MS) (4 ppb detection limit) system equipped with an AS-16 analytical column (IonPac® AS-16, 2 x 250 mm., Dionex Corporation).

3.2.2 Bioreactor Performance

The performance of the bioreactor operating in flow through mode following the inoculation/biofilm build-up period is shown in Table 2. After 4 days of operation, the effluent perchlorate concentration was consistently below detection limit (4 ppb) which corresponds to a perchlorate biodegradation rate greater than 99.99 %. The pH of the effluent is higher than the pH of the influent which indicates that acetic acid is consumed by the perchlorate degraders. These results show that the pack-bed bioreactor can effectively remove ammonium perchlorate from aqueous feed streams.

Table 2: Packed bed bioreactor performance

Time (day)	Flow rate (mL/min)	Time (day)	pH		Perchlorate	
			Influent	Effluent	Influent (ppm)	Effluent (ppb)
0	3.5	0	6.25	6.34	25.2	9.99
1	3.5	1	6.27	6.34	25.9	7.46
2	3.5	2	6.51	6.66	25.6	ND
4	3.5	4	6.54	6.75	25.5	ND
6	3.5	6	6.62	6.79	23.9	ND
7	3.5	7	6.65	6.80	26.3	ND
9	2.0	9	6.75	7.01	24.7	ND
13	2.0	13	6.82	7.03	24.2	ND
15	2.0	15	7.05	7.08	24.5	ND
20	5.0	20	6.73	7.14	24.5	ND

3.2.3 Bioreactor Kinetic Studies

Experiments were conducted at five different flow rates (2, 2.5, 3, 4.5 and 5 mL/min), which correspond to hydraulic loadings of 5.18, 7.10, 8.53, 9.95, and 14.3 $m^3/(m^2$-day). The bioreactor performance was assessed by measuring the influent and effluent perchlorate concentrations and collecting samples from the sampling ports located along the column for perchlorate analyses. The steady-state perchlorate concentration profiles along the bioreactor for various flow rates and an influent concentration of 50 ppm are shown in Table 3.

Table 3: Concentration profile along the bioreactor packed with plastic flakes.

Flow Rate	pH		Perchlorate Concentration Along the Bioreactor								
	In	Out	ppm	ppb							
(cc/min)			In	Port 1	Port 2	Port 3	Port 4	Port 5	Port 6	Port 7	Out
2.0	6.45	6.70	50.0	1615	12.34	2.12	1.36	ND	ND	ND	ND
2.5	6.45	6.70	50.0	4505	43.7	4.50	3.44	ND	ND	ND	ND
3.0	6.50	6.71	50.0	6591	3013	2018	41.73	ND	ND	ND	ND
3.5	6.45	6.70	50.0	8297	4694	2895	1822	787	84	ND	ND
5.0	6.45	6.70	50.0	21506	17684	15513	13108	11073	8679	4444	3081

In situations where external mass transfer is the rate limiting step (that is when the biological reaction is very fast), the concentration profile of the degrading substrate (perchlorate) can be predicted using the following equation (also known as the Eckenfelder Equation):

$$\frac{S_e}{S_i} = \exp\left(-\frac{KZ}{Q_a^n}\right) \qquad (5)$$

where,

S_i = Influent perchlorate concentration (ppm)
S_e = Perchlorate concentration at position z along the reactor (ppm)
K = Model constant
Q_a = Hydraulic loading rate (gpm/ft^2)
N = Hydrodynamic constant
Z = Distance along the reactor from inlet (ft)

The constants, K and n, are determined by operating a bioreactor at different hydraulic loading rates and monitoring the perchlorate concentration at different reactor heights. If the model is valid, a plot of ln S_e/S_i versus Z should yield a straight line for each hydraulic loading rate. Because the slopes of such lines are given by K/Q_a^n, then a plot of ln K/Q_a^n versus ln Q_a should also yield a straight line whose slope yields n and the intercept corresponds to K. By applying the above procedure to the packed bed bioreactor, the perchlorate concentration profile in the bioreactor packed with plastic flakes can be predicted using the following equation:

$$\frac{S_e}{S_i} = \exp\left(-\frac{0.02Z}{Q_a^{2.95}}\right) \qquad (6)$$

4. CONCLUSIONS

The study shows that zero-valent iron is highly effective in degrading the energetic components of pink water in aqueous solution. The degradation could be attributed to chemical reaction(s) mediated by the ZVI surface. TNT, RDX, and HMX degradation rates increase with ZVI concentration. At the ZVI concentration studied, TNT, RDX, and HMX reductions follow pseudo-first order kinetics.

Perchlorate degraders harvested from activated sludge have been shown to effectively degrade perchlorate. Experiments are currently underway at Picatinny Arsenal to assess the efficacy of bioreactor for the destruction of perchlorate present in the pinkwater waste stream.

ACKNOWLEDGEMENTS

This research was supported by the DOD US ARMY RDECOM-ARDEC contract number. DAAE30-00-D-1011 #23.

REFERENCES

[1] Song Y. and Logan, B.E. (2004). ‘Effect of O2 exposure on perchlorate reduction by Dechlorosoma sp. KJ.’ *Water Resource*, **38**(6):1626-1632.

[2] Urbansky E.T,2002, Perchlorate as an Environmental Contaminant, *Environ Sci & Pollution Res.*, 9(3):187-192.

[3] Miller J. (1999), ‘Bioreduction of perchlorate under hydrogen-oxidizing conditions “MS Thesis, The Pennsylvania State University, 1999.

[4] Agrawal, A., Tratnyek, P.G. (1996), ‘Reductions of nitroaromatic compounds by zero-valent iron metal’, Environ. Sci. Technol. **30**, 153–160.

[5] Devlin, J.F., Klausen, J., Schwarzenbach, R.P. (1998), ‘Kinetics of nitroaromatic reduction on granular iron in recirculating bath experiments’, Environ. Sci. Technol. **32**, 1941–1947.

[6] Singh, J., Comfort, S.D., Shea, P.J. (1998), ‘Remediating RDX contaminated water and soil using zero-valent iron’, J. Environ. Qual. **27**, 1240–1247.

[7] Huang, C.P., Wang, H.W., Chiu, P.C. (1998), ‘Nitrate reduction by metallic iron’, Wat. Res. **32**, 2257–2264.

[8] Urbansky E.T. (1998), ‘Perchlorate chemistry: implications for analysis and remediation’, *Bioremediation Journal* **2**, 81-95.

[9] Rikken GB, Kroon AGM, and Van Ginkel C.G. (1996), ‘Transformation of perchlorate into chloride by a newly isolated bacterium: reduction and dismutation’, Appll Microbial Biotechnol. **45**:420-426.

[10] van Ginkel C.G, Plugge, C.M., and Stroo, C.M., (1995), ‘Reduction of chlorate with various energy substrates and innocula under anaerobic conditions‘, Chemosphere, 31:4057-4066