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Hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX)

Reduction by Granular Zero-Valent Iron

in Continuous Flow Reactor

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### Keywords

RDX, GZVI, Oxic, Anoxic, Column Tests, Acid Wash, BOD

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## Abstract

Wastewater streams containing hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) are subject to regulatory discharge regulations that require processing through industrial waste treatment. Thus, the development of easy-to-apply technologies for the treatment of RDX-laden wastewater streams is imperative. In the present study, the reduction of RDX by granular zero valent iron (GZVI) in batch and column experiments was investigated. Preliminary batch tests conducted under both oxic and anoxic conditions showed that after 3.0 hours of reaction with GZVI, RDX was mainly converted to formaldehyde ( $\text{CH}_2\text{O}$ ), nitrate ( $\text{NO}_3^-$ ), and ammonium ( $\text{NH}_4^+$ ). Column filtration tests showed that pre-treatment of the GZVI media with acid wash and low influent pH ( $4.0 \pm 0.1$ ) achieved 99% removal of RDX up to 5000 bed volume. BOD tests carried out on the post-treatment streams showed increased biodegradability of the treated wastewater, leading to a lower environmental impact for the final waste.

## Introduction

Industrial munitions facilities generate large quantities of regulated wastewater contaminated with hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine ( $\text{C}_3\text{H}_6\text{N}_3(\text{NO}_2)_3$ ) (RDX) (Fig.1), which requires processing through industrial waste treatment systems. Removal of RDX from wastewater and soil is not a simple task because of its low volatility ( $K_H = 2 \cdot 10^{-11}$ ), high solubility ( $35 \text{ mg L}^{-1}$ ), and high mobility in aquifers ( $\log K_{ow} = 0.8$ ) (Wildman and Alvarez 2001; Sheremata et al. 2001). Several technologies have been used to remove RDX from wastewater streams, such as biological and physical/chemical treatments.

Biological treatments are not effective as RDX is resistant to aerobic biodegradation due to the presence of electron-withdrawing nitro-constituents which makes the degradation slow

1 and limited in loading (Bruhn et al. 1987; Knackmuss 1996). Degradation in anaerobic  
2 fluidized bed reactors (AFBR) is a treatment technology commonly applied for  
3 biotransformation of explosives (Atikovic et al. 2008), however this cometabolic process  
4 requires addition of supplements such as ethanol, ammonia and nutrients which lead to  
5 additional costs (Oh et al. 2004).

6 Adsorption-based technologies, such as activated carbon (AC), for RDX wastewater are  
7 widely used but expensive because of the disposal of the spent media; moreover, additional  
8 treatments such as alkaline hydrolysis or incineration are often required in order to transform  
9 the adsorbed contaminants (Rajagopal and Kapoor 2001; Oh et al. 2004). Regeneration has  
10 been proved to be expensive and inefficient (Wujcik et al 1992; Chen et al 2011) as AC loses  
11 up to 50% of its original sorption capacity after thermal regeneration, which requires the  
12 addition of fresh adsorbent to maintain the treatment efficiency (Oh et al. 2004).

13 Biochar, is another emerging carbon enriched adsorbent that has attracted considerable  
14 attention in recent years for removal of heavy metals and organic contaminants including RDX  
15 (Roh et al. 2015; Lingamdinne et al. 2015). However, because it is generated from pyrolysis of  
16 diverse biomass sources, its physicochemical characteristics and efficiency highly depend on  
17 the quality of raw material and preparation process employed, making it difficult to ensure a  
18 stable and durable performance.

19 Among most treatment techniques, zero-valent iron (ZVI) has showed promising  
20 application for the removal of energetic compounds such as trinitoluene (TNT), 2,6  
21 dinitrotoluene (DNT) and RDX in both soil and wastewater (Hundal et al. 1997; Singh et al.  
22 1998; Oh et al. 2001; Comfort et al. 2003; Wanaratna et al. 2006; Naja et al. 2008; Oh et al.

2010). ZVI column packed filters have shown to obtain effluent concentrations of the energetic compounds less than  $1.0 \text{ mg L}^{-1}$  without any further treatment on the spent media (Oh et al. 2004).

ZVI is a reactive material that has been widely used in the last decades to degrade chlorinated organic compounds, nitroaromatic pollutants, phenol and nitrobenzene (Doong et al. 2003; Liu et al. 2005; Li et al. 2006; Ma and Zhang 2008). The cast iron from which the ZVI is made is a suitable choice for environmental applications because it is inexpensive and readily available commercially (Zhang 2003). The successful implementation of ZVI in permeable reactive barrier (PRB) for ground water treatment since 1990s, it is an example of the high efficiency, versatility of this material (Gu et al. 1999; Elliott and Zhang 2001).

The degradation of organic contaminants by ZVI takes place through reductive transformation induced by spontaneous corrosion of the metal (Li et al. 2006). The corrosion mechanism occurs primarily through electrochemical reactions, with anodic and cathodic components (Crane and Scott 2011). In particular the ZVI and dissolved ferrous ions ( $\text{Fe}^{2+}$ ) form a redox couple (Cheng and Wu 2000) which reacts with the contaminants in proximity (electronic range) of the iron surface, physically destroying the target organic pollutant (Noubactep 2008; Ghauch et al. 2001).

The aim of the presented study was to determine the optimal operating conditions for the treatment of RDX wastewater using granular zero valent iron (GZVI) packed into column filters. Although GZVI is characterized by a smaller surface area compared to the parent nano version, it is cheaper as it requires less processing and purity (Gavaskar et al 2005; Crane and Scott 2011). In addition, its coarser particle size distribution makes it easier to handle and avoid

cementation which often occurs after corrosion. Laboratory-scale batch and column experiments were performed to assess the feasibility of RDX reduction by GZVI and to characterize the post-reduction products. The application of acid wash as pretreatment or regeneration for the GZVI in the column filtration was also tested. Moreover, BOD tests were carried out in order to assess the biodegradability of the post-column filtered wastewater.

## Materials and Methods

### Materials

All chemicals implemented in this study were reagent grade. The GZVI was obtained from ARS technologies Inc. (New Brunswick, NJ) and sieved to reach a mesh size of 16-40. Synthetic solutions of RDX ( $30 \text{ mg L}^{-1}$ ;  $0.135 \text{ mmol m}^{-3}$ ) were prepared by dissolving 0.190 g of RDX crystalline powder in 6.0 L of deionized (DI) water (Nanopure Infinity System, Barnstead, Dubuque, IA, at  $>18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ), mixing for three days to ensure complete dissolution. In addition, two RDX wastewater streams (Table 1) from different production lines were obtained from an industrial munitions facility. Hydrochloric acid (HCl), sodium hydroxide (NaOH) and acetic acid ( $\text{CH}_3\text{COOH}$ ) solutions (1 N) were prepared using reagent grade liquid chemicals (Fisher Scientific, Pittsburg, PA) and DI water.

**Table 1.** Chemical characteristics of RDX industrial wastewater steams.

	RDX ( $\text{mg L}^{-1}$ )	RDX ( $\text{mmol m}^{-3}$ )	pH	$\text{NO}_3\text{-N}$ ( $\text{mg L}^{-1}$ )	$\text{NH}_4\text{-N}$ ( $\text{mg L}^{-1}$ )	TN ( $\text{mg L}^{-1}$ )
stream $\text{W}_1$	$75 \pm 2.0$	0.338	$3.95 \pm 0.1$	$25.9 \pm 0.5$	$14.0 \pm 1.0$	$294 \pm 5.0$
stream $\text{W}_2$	$10 \pm 0.5$	0.045	$6.90 \pm 0.1$	$5.46 \pm 0.05$	$0.534 \pm 0.05$	$33.7 \pm 1.0$

### RDX and byproducts analyses

RDX and its byproducts were analyzed by high-performance liquid chromatography

(HPLC) (Agilent, 1200 Infinity series) equipped with a DAD Detector. For separation, an Adsorbosphere C-18 10- $\mu$ m reversed-phase column (Alitech, Deerfield, IL) with prefilter element and guard column (C-18, 5- $\mu$ m, Alitech, Deerfield, IL) was employed. RDX as well as its nitroso-derivatives, hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) were quantified with an isocratic mobile phase consisting of DI water and methanol (50:50 by volume) at a flow rate of 1.0 mL min<sup>-1</sup> and a detection wavelength at 254 nm (M.D.L. 0.05 mg L<sup>-1</sup>). Formaldehyde (CH<sub>2</sub>O) was analyzed by HPLC following derivatization with Nash's reagent [0.02 M of 2, 4 pentanedione and 2.0 M of ammonium acetate, at pH 6.0, (Summers, 1990)]. One milliliter of sample was derivatized with one ml of Nash's reagent for one hour at 60 °C in a water bath. After samples cooled at room temperature, derivative CH<sub>2</sub>O was analyzed with HPLC using a mobile phase mixture of acetonitrile and DI water (40:60 by volume) at a flow rate of 1.0 mL min<sup>-1</sup> and a detection wavelength at 410 nm.

#### **Nitrogen byproduct analyses**

Nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>) and total nitrogen (TN) concentrations were quantified with dedicated kits for nitrogen compounds analysis (HACH Company, Loveland, CO) (D.L. TN=5.0 mg L<sup>-1</sup>; NO<sub>2</sub><sup>-</sup>=0.005 mg L<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>=0.006; NH<sub>4</sub><sup>+</sup>= 0.1 mg L<sup>-1</sup>) using a UV-Vis spectrophotometer (DR 6000, HACH Company, Loveland, CO). The total nitrogen concentrations obtained analytically are indicated as "analytical total nitrogen" while the "calculated total nitrogen" refers to the sum of nitrogen from all identified species in solution.

#### **TOC analyses**



1 Total organic carbon (TOC) concentrations were analyzed using a Phoenix 8000 UV-  
2 Persulfate TOC analyzer (Teledyne Tekmar Company, Mason, OH), equipped with a TOC boat  
3 sampler (Rosemount Dohrmann Model 183, Teledyne Tekmar Company, Mason, OH), and a  
4 TOC talk software (Teledyne Tekmar Company, Mason, OH) (M.D.L.  $0.5 \text{ mg L}^{-1}$ ). The  
5 instrument was calibrated each time with a set of TOC standards prepared by dilution of 1000  
6  $\text{mg-C L}^{-1}$  stock solution (SCP Science, Champlain, NY) with DI water (Nanopure infinity  
7 system, Barnstead, Dubuque, IA, at  $>18.2 \text{ M}\Omega \text{ cm}$  at  $25^{\circ}\text{C}$ ).

#### 8 **BOD and COD analyses**

9 Biochemical Oxygen Demand (BOD) analyses were performed on samples collected from  
10 effluent of the column tests for treatment of the lab-prepared RDX solution as well as untreated  
11 RDX solution. A standard 5-day BOD test was performed according to the standard procedure  
12 5210B (Standard Methods for the Examination of Water and Wastewater, 22nd Ed). The seeded  
13 dilution water used in the procedure was prepared with POLYSEED capsule purchased from  
14 InterLab® (Texas, USA). COD of the samples before and after treatment, was quantified with  
15 dedicated kits for COD analysis (HACH, Loveland, CO) (D.L. COD= $1.0 \text{ mg L}^{-1}$ ) using a UV-  
16 Vis spectrophotometer (DR 6000, HACH, Loveland, CO).

#### 17 **Batch experiments**

18 All batch experiments were performed using 1-liter plastic bottles (Nalgene, LDPE Wide-  
19 Mouth Bottles, Fisher Scientific, Pittsburgh, PA) in oxic or anoxic conditions. Anoxic  
20 conditions were ensured by purging the RDX solution before and during the test with nitrogen  
21 gas ( $\text{N}_2$ ) (oxygen free) until the dissolved oxygen concentration (DO) (Orion Star™ A123  
22 Dissolved Oxygen Portable Meter, Thermo Scientific) reached values  $\leq 0.5 \text{ mg L}^{-1}$ . The initial

pH (accumet® glass Ag/AgCl electrode) of the synthetic RDX solution ( $6.5 \pm 0.1$ ) was adjusted to  $6.0 \pm 0.1$  by addition of acetic acid ( $0.05 \text{ ml L}^{-1}$ ) ( $\geq 97.8 \%$  w/w chemical grade, Fisher Scientific, Pittsburgh, PA) and the reaction was started upon adding of the GZVI ( $10 \text{ g L}^{-1}$ ). The bottles with the prepared RDX solution were placed in a shaker with a rotating plate at 80 rpm, to keep the suspension well mixed, for 3.0 hours at room temperature. A 10 mL sample was periodically collected with a 15 ml syringe and filtered through  $0.45 \mu\text{m}$  filters (Whatman® Puradisc, Whatman International Ltd). To avoid potential RDX adsorption losses during filtration, the first 1.0 mL of the filtered samples was discarded prior to HPLC analyses. At the end of the experiments, 1.0 g of GZVI was collected from each bottle and mixed with 10 ml of acetonitrile for one hour; subsequently, the solvent was analyzed with HPLC in order to check for potential adsorption of RDX on the GZVI.

## Column experiments

Column experiments were conducted using acrylic glass columns (2.5 cm i.d. X 30 cm length, 100 ml, Ace Glass, Vineland, NJ) with teflon end fittings; the tests were performed both on lab-prepared and industrial RDX wastewater. The mass of GZVI to pack into the columns was calculated based on a residence time ( $\tau$ ) of 3.0 hours and flow rate of  $0.018 \text{ L hr}^{-1}$ . Since the dimensions of the column are fixed, the hydraulic loading rate (HLR) was calculated as  $3.66 \text{ cm}^3 \text{ hr}^{-1} \text{ cm}^{-2}$  and in order to maintain a contact time of at least 3.0 hours per liter of influent solution, the iron volume was calculated to be at least  $53.8 \text{ cm}^3$  or 67.2 g of GZVI ( $d_{\text{GZVI}} = 1.26 \text{ g/cm}^3$ ) which is equivalent to about 60 ml of media per column.

The RDX solution/wastewater was introduced in the columns with peristaltic pumps (masterflex series, Cole Palmer) in a downward flow configuration. The collected samples

were filtered through 0.45  $\mu\text{m}$  filters and acidified prior to HPLC analysis, to prevent iron precipitation in the column.

Two filtration tests ( $S_1$  and  $S_2$ ) were carried out for the synthetic RDX solution ( $30\text{ mg L}^{-1}$ ) and two for industrial wastewater streams ( $W_1$  and  $W_2$ ). The operating conditions applied to the column tests for both synthetic and industrial RDX wastewater are summarized in Table 2. The column tests for the synthetic RDX solution were designed in order to assess the efficiency of the treatment under different conditions by variation of several parameters [influent pH, Empty Bed Contact Time (EBCT), media pretreatment]. For the tests performed with the industrial RDX wastewater, the EBCT (min) was the only parameter varied, when necessary, in order to maintain the 99% removal of RDX.

**Table 2.** Working conditions for column filtration tests for synthetic ( $S_1$ ;  $S_2$ ) and industrial ( $W_1$ ;  $W_2$ ) RDX wastewater.

	Column $S_1$	Column $S_2$	Column $W_1$	Column $W_2$
Flow rate, $\text{ml min}^{-1}$	0.3	1.5	1.5, 0.5	3, 1
EBCT, min	180	40	40, 60	20, 60
Influent pH	$6.0\pm0.1$	$6.5\pm0.1$	$4.0\pm0.1$	$7.0\pm0.1$
Media pre-treatment	/	acid wash	acid wash	acid wash

## Results and Discussion

### Kinetics of RDX degradation with GZVI

Degradation kinetic studies of  $30\text{ mg L}^{-1}$  of synthetic RDX solution by  $10\text{ g L}^{-1}$  of GZVI under oxic or anoxic conditions were first carried out. Based on the results shown in Fig. 2, the target compound was removed up to 99% of the initial concentration within three hours of treatment. The pH of the RDX solutions ( $6.0\pm0.1$ ) increased by about two units at the completion of the treatment, in both systems (Fig. 3). The final value of DO in the oxic system

was  $4.5 \pm 0.5 \text{ mg L}^{-1}$  while for the anoxic system, the DO remained below  $0.5 \text{ mg L}^{-1}$  ( $0.32 \pm 0.5 \text{ mg L}^{-1}$ ) confirming the persistence of the anoxic environment.

The degradation rate of RDX can be described by a second-order rate law as it is a function of both RDX and the active sites concentrations of the GZVI (Wanaratna et al., 2005; Kitcher et al. 2017):

$$-\frac{dC_{RDX}}{dt} = k_2 C_{RDX} C_{S(GZVI)} \quad (1)$$

Thus,  $C_{RDX}$  represents the RDX concentration ( $\text{mmol m}^{-3}$ ) while  $C_{S(GZVI)}$  is the concentration of active sites of the iron ( $\text{mmol m}^{-3}$ ) and  $k_2$  is the second-order rate constant ( $\text{m}^3 \text{ mmol}^{-1} \text{ min}^{-1}$ ).

In particular, the concentration of active sites,  $C_{S(GZVI)}$ , can be expressed as a function of the specific surface area ( $\alpha_s$ ) ( $\text{m}^2 \text{ g}^{-1}$ ) and the number of active sites per unit area ( $k$ ) ( $\text{mmol m}^{-2}$ ) of GZVI, (Kitcher et al. 2017):

$$C_{S(GZVI)} = k \alpha_s C_{GZVI} \quad (2)$$

with  $C_{GZVI}$  representing the mass concentration of GZVI ( $\text{g m}^{-3}$ ) in solution. Combining the two constants ( $k$ ,  $k_2$ ) through Eq. 2 and 1, the following equation is obtained:

$$-\frac{dC_{RDX}}{dt} = k_{SA} \alpha_s C_{GZVI} C_{RDX} \quad (3)$$

which accounts for the surface area of the media through the normalized rate constant ( $k_{SA}$ ) ( $\text{min}^{-1}$ ) (Kitcher et al. 2017). Since the concentration of GZVI can be considered constant under the experimental conditions adopted (the difference in weight of the iron by the end of the experiment was  $\leq 10\%$  of the initial), the Eq. 3 can be simplified to pseudo-first order respect to the RDX concentration:

$$-\frac{dC_{RDX}}{dt} = k_1 C_{RDX} \quad (4)$$

Thus, the apparent rate constants  $k_1$  ( $\text{min}^{-1}$ ) (Table 3) were calculated using linear regression fit as slope of the semi-logarithmic plots of concentrations vs time according to Eq. 4.

**Table 3.** Pseudo-first order rate constants and regression coefficients for RDX degradation with GZVI under oxic and anoxic conditions.

	RDX ( $\text{mg L}^{-1}$ )	RDX ( $\text{mmol m}^{-3}$ )	$k_1$ ( $\text{min}^{-1}$ )	Standard Error	$R^2$
Oxic condition	30	0.135	$1.48 \cdot 10^{-2}$	$\pm 3.53 \cdot 10^{-3}$	0.966
Anoxic condition	30	0.135	$1.84 \cdot 10^{-2}$	$\pm 4.11 \cdot 10^{-3}$	0.985

The degradation of RDX was slightly faster under anoxic conditions as indicated by the pseudo-first order rate constants (Table 3) with rapid formation and disruption of the intermediate byproducts (Fig. 4a). The slower reaction under oxic conditions can be attributed to the corrosion of the iron surface due to its reaction with oxygen (Lavine et al. 2001; Keenan et al. 2008), reducing the availability of active sites. Moreover, the dissolved oxygen in solution can also compete as an electron acceptor with the target contaminant (Lavine et al. 2001). No presence of RDX was detected in the solvent used to wash the iron utilized in the batch tests; thus, the removal of RDX can be solely attributed to chemical reaction mediated through the iron surface.

### Degradation mechanism of RDX and byproducts

In both oxic and anoxic conditions, the disruption of RDX was followed by immediate formation of the nitroso-derivative intermediates identified as MNX, DNX and TNX (Fig. 4a,b) and ring cleavage products such as formaldehyde ( $\text{CH}_2\text{O}$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) ions (Fig. 5, 7). The production and subsequent disappearance of the mono-,

1 di-, and trinitroso derivatives (MNX, DNX, and TNX) indicates that the reduction of nitro- to  
2 nitroso-groups is the first degradation step of RDX (Wanaratna et al. 2005). The detection of  
3 the three nitroso derivative products is consistent with the transformation pathways reported  
4 by other studies (Naja et al. 2008; Koutsospyros et al. 2012).

5 The organic carbon mass balance was calculated based on the concentrations of the organic  
6 compounds for the conditions tested (Fig. 5a, b). The recovered total carbon percentages were  
7 98% and 87% for the oxic and anoxic systems, respectively. The  $\text{CH}_2\text{O}$ , as expected, accounted  
8 for most of the carbon from RDX degradation (85% in oxic and 83 % in anoxic conditions),  
9 while the intermediates MNX, DNX, and TNX accounted for  $\leq 10\%$  of the total carbon mass  
10 (Fig. 6). Oh et al. (2006) also found that  $\text{CH}_2\text{O}$  accounted for 80% of the total carbon mass  
11 from the degradation of RDX with elemental iron.

12 The unaccounted carbon under oxic conditions was within the range of analytical errors  
13 ( $\leq 2\%$ ). The significantly higher level of unaccounted carbon under anoxic conditions (13%),  
14 can be attributed to unidentified intermediate(s) in solution, such as methylenedinitramine  
15 (MEDINA,  $\text{CH}_4\text{N}_4\text{O}_4$ ). The formation of MEDINA has been observed in the degradation  
16 pathway of RDX by elemental iron in other studies (Oh et al. 2005; Naja et al. 2008), but its  
17 conversion to  $\text{CH}_2\text{O}$  upon reaction completion has been postulated (Naja et al. 2008). Thus,  
18 the reactive anoxic system may not be favorable for the completion of this last step of the  
19 transformation pathway. Based on the obtained results, closure of the carbon balance for both  
20 systems can be safely assumed.

21 More notable differences between the oxic and anoxic conditions were found through  
22 characterization of the nitrogen byproducts and total nitrogen balance calculations. Under

1 anoxic conditions, at least 22% of the total nitrogen accounted for the formation of gaseous  
2 products, as indicated by the difference between the initial and final value of the analytical total  
3 nitrogen (TN) (Fig. 8). Reportedly, the main nitrogen gaseous products found under anoxic  
4 conditions from degradation of RDX by ZVI nanoparticles are nitrogen gas ( $N_2$ ) and nitrous  
5 oxide ( $N_2O$ ) (Singh et al. 1999; Naja et al. 2008). Nitrous oxide ( $N_2O$ ) has also been identified  
6 as one of the major nitrogen gas products of RDX degradation by anoxic cultures and ZVI  
7 filings (Hawari et al. 2000; Oh et al. 2001). Naja et al. (2008) attributed the formation of  $N_2O$   
8 to the decomposition of MEDINA while  $N_2$  derived mostly from the reduction and degradation  
9 of  $NO_2^-$  and  $NH_4^+$ , groups. The latter finding is consistent with this study where, under anoxic  
10 conditions, the lower concentrations of ionic nitrogen species (IN) ( $NO_2^-$ ,  $NO_3^-$ ,  $NH_4^+$ ) (Fig  
11 7a) and their subsequent transformation into  $N_2$  align with the observed higher amount of  
12 gaseous nitrogen products. On the other hand, under oxic conditions, the formation of gaseous  
13 nitrogen was not significant ( $\leq 2\%$ ) and most of the nitrogen (76%) was reclaimed in the form  
14 of ionic nitrogen species (Fig. 8).

15 Moreover, the difference between the analytical and calculated total nitrogen indicates the  
16 presence of unidentified nitrogen containing byproducts in the liquid phase; this fraction was  
17 higher in the anoxic system (39%) rather than in the oxic system (7%) (Fig.8). Such portion of  
18 unidentified compounds is most probably represented by C-N or N containing (nonionic)  
19 intermediates such as MEDINA and hydrazine ( $NH_2NH_2$ ) (Singh et al 1998; Naja et al. 2008)  
20 and is also supported by the carbon balance calculations (Fig.6). Hydrazine ( $NH_2NH_2$ ) has  
21 been noted as a reduction byproduct of RDX with ZVIs nanoparticle (Naja et al. 2008) that is  
22 ultimately oxidized to  $NH_4^+$ ; however, the lower  $NH_4^+$  concentrations in the anoxic system

1 suggest incomplete reduction and transformation of the hydrazine in solution (Fig. 7a).

2 The unaccounted nitrogen missing from the nitrogen balance was  $\leq 5\%$  for both anoxic  
3 and oxic systems which can be safely attributed to analytical errors from the characterization  
4 of the nitrogen byproducts.

## 5 **Column filtration for synthetic RDX wastewater**

6 The column filtration tests were carried out in order to assess the RDX removal efficiency  
7 by GZVI in a continuous flow reactor, scalable for field applications.

8 First, two column tests ( $S_1$ ,  $S_2$ ) were performed using as influent synthetic RDX solution  
9 ( $30 \text{ mg L}^{-1}$ ;  $\text{pH}=6.5\pm0.1$ ). Varying operational conditions were applied to identify the optimal  
10 settings for RDX removal; thus, the EBCT for column- $S_1$  and column- $S_2$  were set to 180  
11 minutes ( $0.3 \text{ ml min}^{-1}$ ) and 40 minutes ( $1.5 \text{ ml min}^{-1}$ ), respectively (Fig. 9). In addition,  
12 different approaches were experimented for passivation prevention of the iron media. For  
13 column- $S_2$  (Fig. 9b), the GZVI was pretreated with an acid wash (300 ml tap water with 5%  
14 acetic acid (97.8% assay;  $\text{EBCT}=25 \text{ min}$ ) before pumping the RDX solution through the iron  
15 bed. The pretreatment of elemental iron with acid wash is a practice that has proved to enhance  
16 reduction of nitroaromatics and chlorinated methanes (Agrawal and Tratnyek 1996; Matheson  
17 and Tratnyek 1994). It is known that water and oxygen naturally lead to corrosion of iron, with  
18 consequent formation of a coating made of iron hydroxides/oxides at the surface (Lavine et al.  
19 2001). This layer of corrosion products limits the direct interactions of the GZVI particles with  
20  $\text{H}_2\text{O}/\text{O}_2$  as well as with the contaminant inhibiting its reduction (Crane and Scott 2011) Hence,  
21 the acid wash pretreatment is used to prevent/dissolve the surface passivating-oxide layer,  
22 increase the density of reactive sites, and further facilitate the destruction of the target



1 compound.

2 In column-S<sub>1</sub>, instead of the acid wash pretreatment of the GZVI, the influent of the  
3 column was continuously spiked with a constant amount of acid. Thus, the initial pH of the  
4 RDX solution ( $6.5 \pm 0.1$ ) was adjusted to  $6.0 \pm 0.1$  by adding 0.1 ml of acetic acid (97.8 % assay)  
5 per liter of influent solution.

6 After nearly 400 bed volumes (40 days filtration), the RDX concentration in the effluent  
7 from column-S<sub>1</sub> increased up to  $\sim 20 \text{ mg L}^{-1}$  ( $0.1 \text{ mmol L}^{-1}$ ) (Fig. 9a); thus, the pH adjustment  
8 on the influent proved to be insufficient in preventing the oxidation of the iron media. Hence,  
9 to dissolve the passivating layer on the iron surface (i. e. regenerate the iron), the acid solution  
10 used for pretreatment in column-S<sub>2</sub> (300 ml tap water with 5% acetic acid, 98.7% assay) was  
11 pumped directly through the column for 2 hours. After the regeneration, the removal efficiency  
12 of the column was re-established at 99% up to 1200 bed volumes (160 days filtration) when a  
13 new spike of RDX concentrations in the effluent was detected; at that time, the washing  
14 procedure was reapplied (Fig. 9a). The acid wash of the media allowed overcoming up to three  
15 breakthroughs of RDX concentrations for the column-S<sub>1</sub>. However, multiple applications of  
16 this procedure caused a visible loss of the iron bed in the column. In fact, the acid solution led  
17 to significant dissolution of the iron, with increasing iron concentrations in the effluent up to  
18  $150 \text{ mg L}^{-1}$ .

19 On the other hand, column-S<sub>2</sub> maintained a 90% removal of RDX up to  $\sim 5000$  bed volumes  
20 (160 days of filtration), although the EBCT was  $\sim 5$  times lower than the one applied to column-  
21 S<sub>1</sub> (Fig. 9b). The different performance of the two column tests can be attributed to the  
22 application of the acid wash as pretreatment of the media (column-S<sub>2</sub>) which proved to be an

effective strategy against passivation of the GZVI media.

## BOD assessment for water post-treatment from column tests

The efficiency of the treatment technique using GZVI column filters was also quantified in terms of the biodegradability of the reduction byproducts. For this purpose, the BOD/COD ratios for the post-treated RDX solution were obtained. The BOD and COD values of the treated and untreated RDX were first determined through analytical measurements and the resulting BOD/COD ratios were calculated (Table 4). The initial BOD of the influent RDX solution ( $\text{TOC} = 4.88 \text{ mgC L}^{-1}$ ,  $\text{RDX} = 30 \text{ mg L}^{-1}$ ) was  $\leq 1.0 \text{ mg L}^{-1}$  (B.D.L), which indicates that the organic carbon in RDX is not readily biodegradable (Table 4).

**Table 4.** BOD and COD values of untreated and treated synthetic RDX solution.

	<b>BOD (<math>\text{mg L}^{-1}</math>)</b>	<b>COD (<math>\text{mg L}^{-1}</math>)</b>	<b>BOD/COD</b>
Untreated RDX	/	$12.4 \pm 0.5$	/
Treated RDX-Column-S <sub>1</sub>	$2.99 \pm 1.0$	$14.7 \pm 0.5$	0.206
Treated RDX-Column-S <sub>2</sub>	$4.33 \pm 1.0$	$16.1 \pm 0.5$	0.268

The BOD level of the treated effluent was  $2.99 \pm 1.0 \text{ mg L}^{-1}$  for column-S<sub>1</sub> and  $4.33 \pm 1.0 \text{ mg L}^{-1}$  for column-S<sub>2</sub>, respectively (Table 4). The BOD/COD ratio increased to about  $0.25 \pm 0.05$  after treatment with GZVI which implies that the byproducts from RDX reduction are more biodegradable than the original compound. Since each molecule of RDX contains 3 carbon atoms, it is possible to assume that 3 oxygen molecules ( $\text{O}_2$ ) are necessary to oxidize all the organic carbon to inorganic ( $\text{CO}_2$ ) (Oh et al. 2005). Hence, the theoretical oxygen demand (Th-OD) to oxidize all the carbon in  $30 \text{ mg L}^{-1}$  of RDX was calculated to be  $15 \text{ mg L}^{-1}$ . However, in both systems (oxic, anoxic), the BOD values determined were lower than the Th-OD, which could be attributed to the presence of non-biodegradable and/or toxic

1 byproducts. This condition, more prominent under anoxic conditions, is attributed to  
2 incomplete mineralization of the intermediate products; in fact, as shown from the results  
3 obtained from the batch tests, anoxic conditions led to lower levels of biodegradable carbon  
4 (lower  $\text{CH}_2\text{O}$ ) and ionic nitrogen species (Fig. 7, 8) that serve as essential nutrients for  
5 microbial populations.

6 The results obtained from the BOD measurements and BOD/COD ratio calculations  
7 suggest that the byproducts of the reductive degradation RDX by the GZVI are less toxic and  
8 more biodegradable than the original parent compound.

### 9 **Column filtration for industrial RDX wastewater**

10 Additional column tests were performed using two different RDX wastewater streams ( $W_1$ ,  
11  $W_2$ ) from an industrial munitions facility. The treatment was carried out without any pH  
12 adjustment of the influents.

13 As shown in Fig. 9, the highest performance in the treatment of the lab-prepared RDX  
14 wastewater was achieved when the media was pre-treated with acid wash (column- $S_2$ ); hence,  
15 the GZVI used for treatment of the industrial RDX wastewater was pre-treated following the  
16 same procedure. Column- $W_1$  was employed for treatment of the wastewater stream at high  
17 RDX concentration ( $75 \text{ mg L}^{-1}$ ) and low pH ( $4.0 \pm 0.1$ ). Since the low pH of the wastewater  
18 provides a favorable condition for the prevention of the iron passivation, the EBCT of the  
19 column was set at 40 minutes ( $1.5 \text{ ml min}^{-1}$ ). After 20 days of continuous filtration ( $\sim 900$  bed  
20 volumes), the EBCT was increased to 60 minutes ( $1.0 \text{ ml min}^{-1}$ ) as the RDX concentrations in  
21 the effluent reached a first breakthrough ( $\geq 1.0 \text{ mg L}^{-1}$ ) (Fig. 10a). At these conditions, the GZVI  
22 was capable of attaining 99% removal of RDX up to 162 days of continuous filtration ( $\sim 2600$

bed volume).

Column-W<sub>2</sub> was dedicated to the treatment of a second wastewater stream with low RDX concentration (10 mg L<sup>-1</sup>); thus, the EBCT was set to 20 minutes (3.0 ml min<sup>-1</sup>) (Fig. 10b). The EBCT was increased to 1 hour (1.0 ml min<sup>-1</sup>) when a breakthrough in the RDX concentrations ( $\geq 1.0$  mg L<sup>-1</sup>) was reached after 10 days of filtration (~ 1000 bed volumes), (Fig. 10b). The breakthrough was caused by a rapid passivation of the iron surface due to the high flow rate and high pH of the influent wastewater ( $\geq 7.0 \pm 0.1$ ). After increase of the EBCT, the column operated at 95% RDX removal up to 90 days of filtration (bed volume ~4400).

Although the two columns filtered approximately the same volume of wastewater (~120 L), the column-W<sub>1</sub> obtained a better performance, even though the initial RDX concentration of the influent was 8 times higher than the one treated by the column-W<sub>2</sub>. Overall, the results from the treatment of industrial RDX wastewater indicate that the combination of acid wash pre-treatment and low influent pH ( $4.0 \pm 0.1$ ) represent the optimal conditions in order to achieve a higher performance from the GZVI in continuous flow systems.

## Conclusions

The results obtained from our work show that GZVI column filters represent a promising, simple, and efficient technique to treat RDX-laden wastewater streams. Preliminary batch tests conducted on 30 mg L<sup>-1</sup> lab prepared RDX solution showed that the reduction of the target contaminant by the GZVI was faster in anoxic conditions due to lower corrosion of the iron surface. However, the oxic conditions led to higher percentage of carbon (84%) converted to CH<sub>2</sub>O and nitrogen (76%) mineralized to NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. The formation of gaseous nitrogen products was more significant under anoxic condition (22%) than oxic (3%).

1       The outcomes of the column tests performed on both synthetic and industrial RDX  
2 wastewater showed that the optimal condition maximizing the volume of treated wastewater  
3 involves an acid wash pre-treatment of the media combined with low influent pH ( $4.0\pm0.1$ -  
4  $5.0\pm0.1$ ); the application of these conditions is an effective preventive strategy against the  
5 formation of the passivating-oxide layer on the iron surface, which impairs the surface-  
6 mediated reactions for the reduction of RDX.

7       BOD/COD ratio calculations showed that the treated RDX solution had higher  
8 biodegradability than the original solution because of formation of non-toxic carbon  
9 byproducts, thus lowering the overall environmental impact of the final waste.

## References

- Agrawal A and Tratnyek PG (1996) Reduction of Nitro Aromatic Compounds by Zero-Valent Iron Metal. *Environ Sci Technol* 30(1): 153-160
- Atikovic E, Suidan MT, Maloney SW (2008) Anaerobic treatment of army ammunition production wastewater containing perchlorate and RDX. *Chemosphere* 72(11):1643-1648
- Bruhn C, Lenke H, Knackmuss HJ (1987) Nitrosubstituted aromatic compounds as nitrogen source for bacteria. *Appl Environ Microbiol* 53(1): 208-210
- Chen Y, Hong L, Han W, Wang L, Sun X, Li J (2011) Treatment of high explosive production wastewater containing RDX by combined electrocatalytic reaction and anoxic-oxic biodegradation. *Chem Eng J* 168(3): 1256-1262
- Cheng SF, Wu SC (2000) The enhancement methods for the degradation of TCE by zero-valent metals. *Chemosphere* 41:1263–1270
- Comfort SD, Shea PJ, Machacek TA, Satapanajaru T (2003) Pilot-scale treatment of RDX-contaminated soil with zerovalent iron. *J Environ Qual* 32: 1717–1725
- Crane RA and Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *J hazard mater* 211:112-125
- Doong RA, Chen KT, Tsai HC (2003) Reductive dechlorination of carbon tetrachloride and tetrachloroethylene by zerovalent silicon-iron reductants. *Environ Sci Technol* 37(11): 2575–2581
- Elliott DW and Zhang WX (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. *Crit. Rev. Solid State Mater. Sci.* 31:111–122
- Gavaskar A, Tatar L, Condit W (2005) Cost and performance report nanoscale zero-valent iron technologies for source remediation (No. CR-05-007-ENV), Naval facilities engineering service center port, Hueneme, Ca.
- Ghauch A (2001) Degradation of benomyl, picloram, and dicamba in a conical apparatus by zero-valent iron powder. *Chemosphere* 43:1109–1117
- Gu B, Phelps TJ, Liang L, Dickey MJ, Roh Y, Kinsall BL, Palumbo AV, Jacobs GK (1999) Biogeochemical dynamics in zero-valent iron columns: Implications for permeable reactive barriers. *Environ Sci Technol* 33:2170–2177
- Hawari J, Halasz A, Sheremata T, Beaudet S, Groom C, Paquet L, Thiboutot S (2000) Characterization of metabolites during biodegradation of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) with municipal anoxic sludge. *Appl Environ Microbiol* 66(6): 2652-2657
- Hundal LS, Singh J, Bier EL, Shea PJ, Comfort SD, Powers WL (1997) Removal of TNT and RDX from water and soil using iron metal. *Environ Pollut* 97(1-2): 55–64
- Lavine BK, Auslander G, Ritter J (2001) Polarographic studies of zero valent iron as a reductant for remediation of nitroaromatics in the environment. *Microchem J* 70(2): 69-83
- Li XQ, Elliott DW, Zhang WX (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Crit Rev Solid State Mater Sci*

31(4): 111–122

Lingamdinne LP, Roh H, Choi YL, Koduru JR, Yang JK, Chang YY (2015) Influencing factors on sorption of TNT and RDX using rice husk biochar. *J Ind Eng Chem* 32:178-186

Liu YQ, Majetich SA, Tilton RD; Sholl DS, Lowry GV (2005) TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. *Environ Sci Technol* 39(5): 1338–1345

Ma L and Zhang WX (2008) Enhanced Biological Treatment of Industrial Wastewater With Bimetallic Zero-Valent Iron. *Environ Sci Technol* 42(15): 5384-5389

Matheson LJ and Tratnyek PG (1994) Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. *Environ Sci Technol* 28(12): 2045-2053

Naja, G, Halasz A, Thiboutot S, Ampleman G, Hawari J (2008) Degradation of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) using zero valent iron nanoparticles. *Environ Sci Technol* 42(12): 4364-4370

Noubactep C (2008) A critical review on the process of contaminant removal in  $\text{Fe}^0\text{-H}_2\text{O}$  systems. *Environ Technol* 29(8): 909–920

Keenan CR and Sedlak DL (2008) Factors affecting the yield of oxidants from the reaction of monoparticulate zero-valent iron and oxygen. *Environ Sci Technol* 42(4): 1262-1267

Kitcher E, Braida W, Koutsospyros A, Pavlov J, Su TL (2017) Characteristics and products of the reductive degradation of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) in a Fe-Cu bimetal system. *Environ Sci Pollut Res* 24: 2744-2753

Knackmuss HJ (1996) Basic knowledge and perspectives of bioelimination of xenobiotic compounds. *J Biotech* 51: 287-295

Koutsospyros A, Pavlov J, Fawcett J, Strickland D, Smolinski B, Braida W (2012) Degradation of high energetic and insensitive munitions compounds by Fe/Cu bimetal reduction. *J Hazard Mater* 219-220:75-81

Oh BT, Just CL, Alvarez PJ (2001) Hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine mineralization by zero valent iron and mixed anoxic cultures. *Environ Sci Technol* 35(21): 4341-4346

Oh SY, Cha DK, Chiu PC, Kim BJ (2004) Conceptual comparison of pink water treatment technologies: granular activated carbon, anaerobic fluidized bed, and zero-valent iron-Fenton process. *Water Sci Technol* 49(5-6): 129-136

Oh SY, Cha DK, Chiu PC, Kim BJ (2006) Zero-valent iron treatment of RDX-containing and perchlorate-containing wastewaters from an ammunition-manufacturing plant at elevated temperatures. *Water Sci Technol* 54(10): 47-53

Oh SY, Chiu PC, Kim BJ, Cha DK (2005) Zero-valent iron pretreatment for enhancing the biodegradability of RDX. *Water Res* 39(20): 5027-5032

Oh SY, Kang SG, Chiu, PC (2010) Degradation of 2, 4-dinitrotoluene by persulfate activated with zero-valent iron. *Sci Total Environ* 408(16):3464-3468

Rajagopal C, Kapoor JC (2001) Development of adsorptive removal process for treatment of explosives contaminated wastewater using activated carbon. *J hazard mater*, 87(1-3):73-98.

Roh H, Yu M R, Yakkala K, Koduru JR, Yang JK, Chang YY (2015) Removal studies of Cd (II) and explosive compounds using buffalo weed biochar-alginate beads. *J Ind Eng Chem* 26: 226-233

Ronen Z, Brenner A, Abeliovich A (1998) Biodegradation of RDX-contaminated wastes in a nitrogen-deficient environment. *Water Sci Technol* 38(4-5): 219-224

1 Rosenblatt DH, Burrows EP, Mitchell WR, Parmer DL (1991) Organic explosives and related  
 2 compounds. In *Anthropogenic Compounds*, Springer Berlin Heidelberg 195-234  
 3 Sheremata TW, Halasz A, Paquet L, Thiboutot, S, Ampleman G, Jalal H (2001) The Fate of the  
 4 Cyclic Nitramine Explosive RDX in Natural Soil. *Environ Sci Technol* 35(6): 1037-1040  
 5 Singh J, Comfort SD, Shea PJ (1998) Remediating RDX-contaminated water and soil using  
 6 zero-valent iron. *J Environ Qual* 27(5): 1240-1245  
 7 Summers WR (1990) Characterization of formaldehyde and formaldehyde-releasing  
 8 preservatives by combined reversed phase cation-exchange high-performance liquid  
 9 chromatography with postcolumn derivatization using Nash's reagent. *Anal Chem* 62: 1397-  
 10 1402  
 11 Tratnyek PG (1996) Putting corrosion to use: remediating contaminated groundwater with  
 12 zero-valent metals. *Chem. Ind.* 13: 499-503  
 13 US EPA, (2014) Technical Fact Sheet—Hexahydro-1, 3, 5-Trinitro-1, 3, 5-Triazine (RDX).  
 14 Office of Solid Waste and Emergency Response, EPA 505-f-11-010  
 15 US EPA, (2002) Drinking Water Standards and Health Advisories, Office of Water, EPA 822-  
 16 R-02-038  
 17 Zhang WX (2003) Nanoscale iron particles for environmental remediation: an overview. *J*  
 18 *Nanopart Res* 5:323–332  
 19 Wanaratna P, Christodoulatos C, Sidhoum M (2006) Kinetics of RDX degradation by zero-  
 20 valent iron (ZVI). *J Hazard Mater* 136(1): 68-74  
 21 Wildman MJ, Alvarez PJJ (2001) RDX degradation using an integrated Fe(0)-microbial  
 22 treatment approach. *Water Sci Technol* 43(2): 25-33  
 23 Wujcik WJ, Lowe WL, Marks PJ, Sisk WE (1992). Granular activated carbon pilot treatment  
 24 studies for explosives removal from contaminated groundwater. *Environ Prog* 11(3): 178-189  
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## Figure Captions

**Fig. 1** Chemical structure of RDX.

**Fig. 2** Kinetic reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI, in oxic and anoxic conditions, pH 6.0±0.1. Solid curves represent the pseudo-first order kinetic fit. Error bars represent standard deviation from two replicates.

**Fig. 3** Solution pH for reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI, in oxic and anoxic conditions, pH 6.0±0.1. Error bars represent standard deviation from two replicates.

**Fig. 4** Kinetic reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI and by products (MNX, DNX, TNX and HCHO) (a) anoxic and (b) oxic conditions, pH 6.0±0.1. Error bars represent standard deviation from two replicates.

**Fig. 5** Carbon byproducts (MNX, DNX, TNX and HCHO) and carbon balance (solid curves) for reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI in (a) anoxic and (b) oxic conditions; pH 6.0±0.1. Error bars represent standard deviation from two replicates.

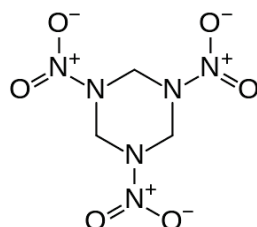
**Fig. 6** Carbon percentages distribution in oxic and anoxic systems based on data in Fig.5.

**Fig. 7** Nitrogen byproducts (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and nitrogen balance (solid curves) for reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI in (a) anoxic and (b) oxic conditions; pH 6.0±0.1. Error bars represent standard deviation from two replicates.

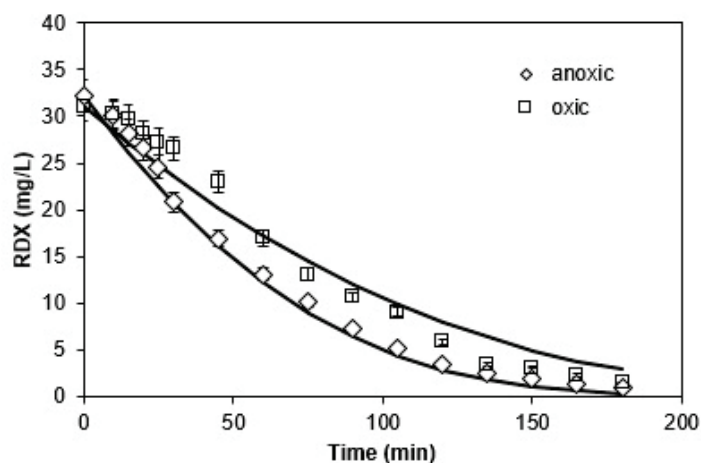
**Fig. 8** Nitrogen percentages distribution in oxic and anoxic systems based on data in Fig.7.

**Fig. 9** RDX concentrations and effluent pH vs bed volume for (a) column-S<sub>1</sub> and (b) column-S<sub>2</sub>; RDX (i) = 30 mg L<sup>-1</sup>, pH (i) (a) 6.0±0.1 (b) 6.5±0.1.

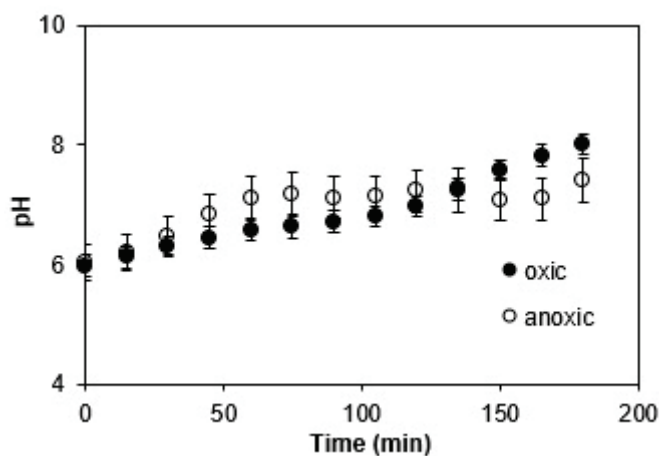
**Fig. 10** RDX concentrations and effluent pH vs bed volume for (a) column-W<sub>1</sub> and (b) column-W<sub>2</sub>; (a) RDX(i)=75 mg L<sup>-1</sup>, pH(i)=4.0±0.; (b) RDX(i)=10 mg L<sup>-1</sup>, pH(i)= 7.0±0.1.



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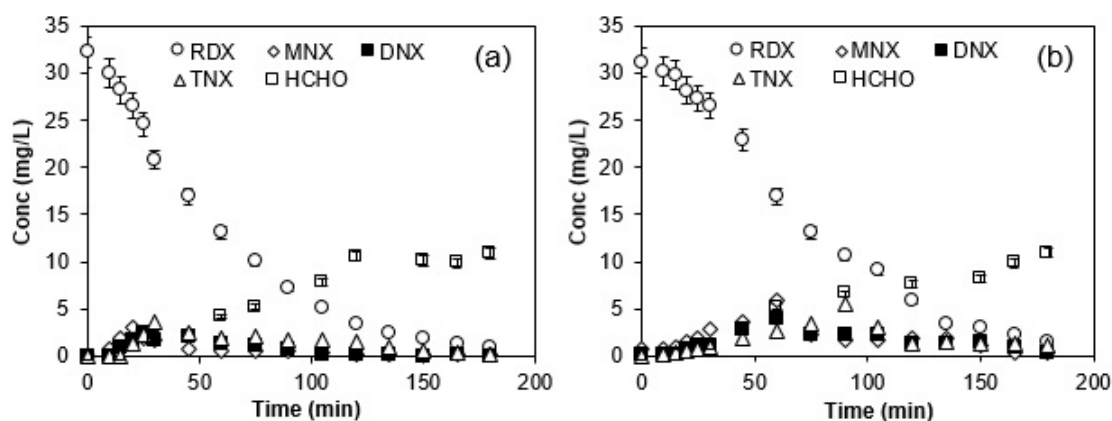


**Fig. 2** Kinetic reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI, in oxic and anoxic conditions, pH(i) 6.0±0.1. Solid curves represent the pseudo-first order kinetic fit. Error bars represent standard deviation from two replicates.

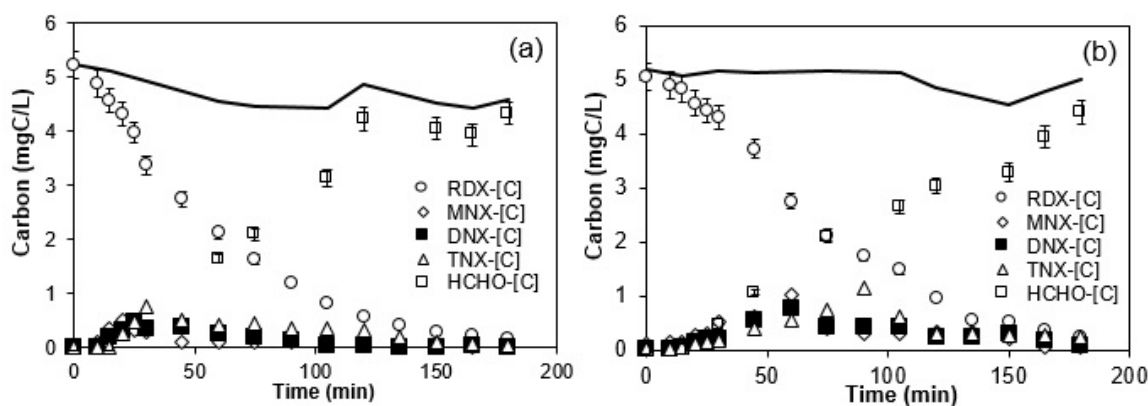


**Fig. 3** Solution pH for reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI, in oxic and anoxic

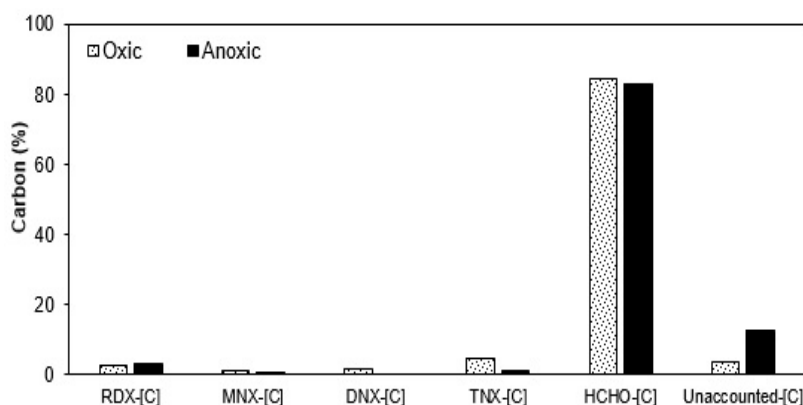
conditions, pH(i)  $6.0 \pm 0.1$ . Error bars represent standard deviation from two replicates.



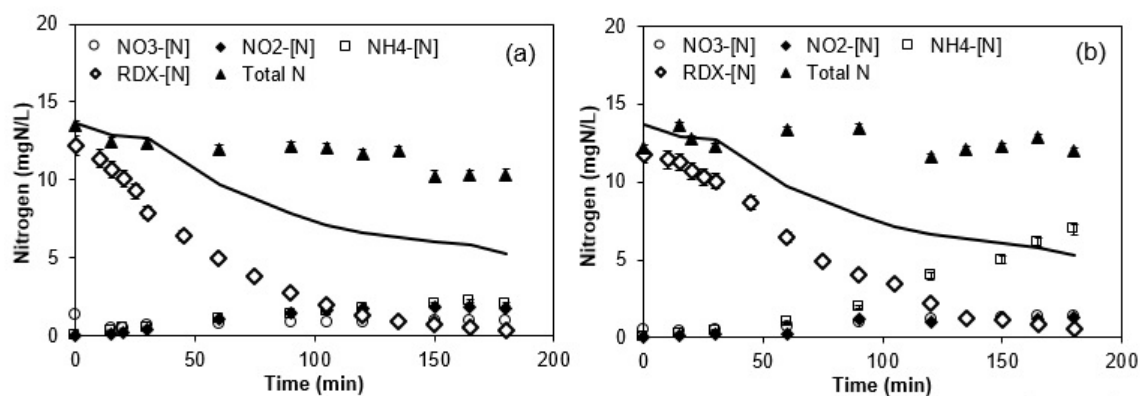
**Fig. 4** Kinetic reduction of  $30 \text{ mg L}^{-1}$  RDX with  $10 \text{ g L}^{-1}$  of GZVI and by products (MNX, DNX, TNX and HCHO) in (a) anoxic and (b) oxic conditions, pH(i)  $6.0 \pm 0.1$ . Error bars represent standard deviation from two replicates.



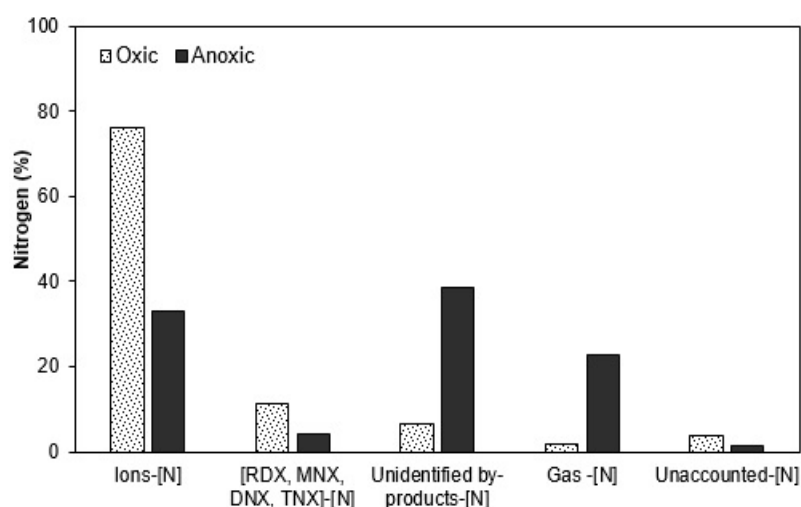
**Fig. 5** Carbon byproducts (MNX, DNX, TNX and HCHO) and carbon balance (solid curves) for reduction of  $30 \text{ mg L}^{-1}$  RDX with  $10 \text{ g L}^{-1}$  of GZVI in (a) anoxic and (b) oxic conditions; pH(i)  $6.0 \pm 0.1$ . Error bars represent standard deviation from two replicates.



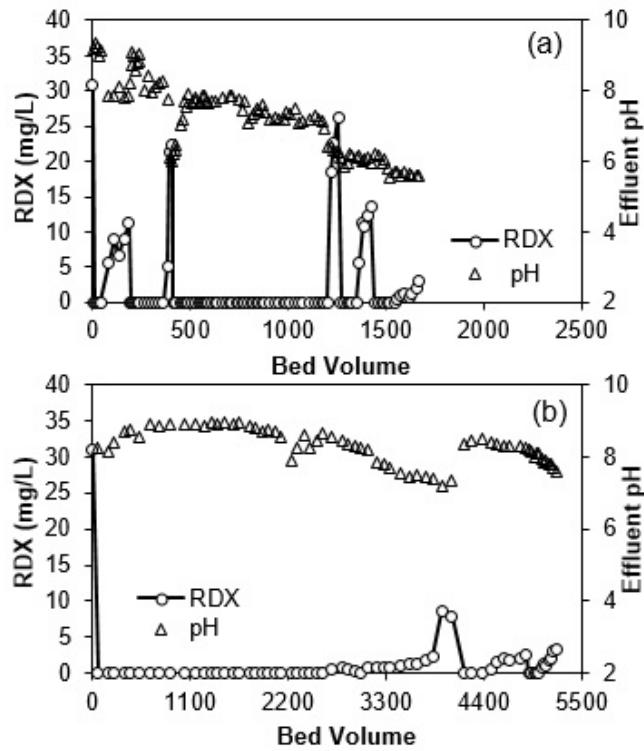
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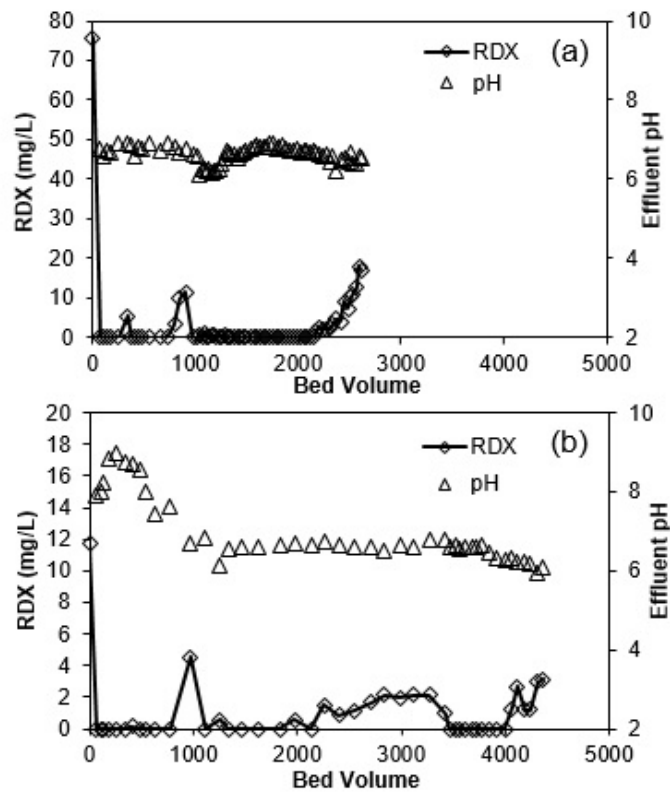
**Fig. 7** Nitrogen byproducts (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and nitrogen balance (solid curves) for reduction of 30 mg L<sup>-1</sup> RDX with 10 g L<sup>-1</sup> of GZVI in (a) anoxic and (b) oxic conditions; pH(i) 6.0±0.1. Error bars represent standard deviation from two replicates.



**Fig. 8** Nitrogen percentages distribution in oxic and anoxic systems based on data in Fig.7.



**Fig. 9** RDX concentrations and effluent pH vs bed volume for (a) column-S<sub>1</sub> and (b) column-S<sub>2</sub>; RDX (i) = 30 mg L<sup>-1</sup>, pH (i) (a) 6.0±0.1 (b) 6.5±0.1.



**Fig. 10** RDX concentrations and effluent pH vs bed volume for (a) column-W<sub>1</sub> and (b) column-W<sub>2</sub>; (a) RDX(i)=75 mg L<sup>-1</sup>, pH(i)=4.0±0.1; (b) RDX(i)=10 mg L<sup>-1</sup>, pH(i)= 7.0±0.1.