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Dynamic and equilibrium studies of the RDX removal from soil using CMC-coated zerovalent iron nanoparticles

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RDX chemical degradation in a contaminated soil was conducted using coated zerovalent iron nanoparticles in both batch and dynamic column studies.

ABSTRACT

Rapid chemical degradation of toxic RDX explosive in soil can be accomplished using zerovalent nanoiron suspension stabilized in dilute carboxymethyl cellulose solution (CMC-ZVINs). The effect of operating conditions (redox-potential, Fe/RDX molar ratio) was studied on batchwise removal of RDX in contaminated soil. While anaerobic conditions resulted in 98% RDX removal in 3 h, only slightly over 60% RDX removal could be attained under aerobic conditions. The molar ratio did not have any influence on the intermediate and final RDX degradation products (methylenedinitramine, nitroso derivative, N_2, N_2O, NO_2^-), however, their distribution changed. Dynamic studies were conducted using a flow-through short column packed with RDX-contaminated soil and fed with CMC-ZVINs. The column was operated at two interstitial velocities (2.2 and 1.6 cm min^{-1}), resulting in the 76.6% and 95% removal of the initial RDX soil contamination load (60 mg kg^{-1}), respectively. While the column operating conditions could be further optimized, 95% of the RDX initially present in the contaminated soil packed in the column was degraded when flushed with a CMC-ZVINs suspension in this work.

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1. Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine also known as RDX is generally and widely used in explosives (Hawari et al., 1996) resulting in severe environmental "soil" contamination. This pollutant could also migrate through the soil and contaminate the groundwater because of its high mobility (Selim et al., 1995). Indeed, the soil sorption coefficient values for RDX range from 63.1 to 270 indicating a medium to high mobility (Swann et al., 1983). RDX can thus be expected to easily leach into groundwater creating a major environmental problem (Sheremata et al., 2001). The toxicity of RDX has been well documented since many people involved with military activities suffered from generalized convulsions, muscular twitching, hyperactive reflexes, headaches, severe nausea and vomiting, hematuria, and loss of memory within several hours of ingesting 25–180 g C-4 explosive (containing 91%

of RDX) (Stone et al., 1969). The estimated fatal dose of RDX in humans ranges from 5 to 500 mg kg^{-1} (EPA, 1989). Thus, due to its high toxicity and mobility, it is primordial to decontaminate RDX polluted soil or groundwater.

Although several ex situ and physico-chemical processes have been developed for RDX removal (e.g., incineration), these methods are costly and not widely accepted (Gregory et al., 2004). Zerovalent iron (ZVI) has been used as a reducing agent to remediate many organic compounds such as halogenated aliphatics (Gillham and Ohannesin, 1994), azo dyes (Nam and Tratnyek, 2000), nitrobenzene (Mu et al., 2004), nitroaromatic pesticides (Keum and Li, 2004) as well as RDX (Oh et al., 2005a). While those studies mainly focused on RDX removal from water, in situ soil remediation applications mainly involve RDX from a solid phase. For example, Hundal et al. (1997) reported that Fe(0) could be efficiently used for treating RDX-contaminated soil slurries resulting in more than 90% of RDX removal within 48 h. However, batch studies using ZVI, even though important for establishing equilibrium and kinetics constants, could yield misleading determinations of RDX mobility and degradation. Mainly due to the RDX diminishing concentration

gradient that normally provides an important driving force for effective RDX degradation. These problems are, to a large degree, eliminated by conducting dynamic flow-through column studies. The column system can be operated with a variety of column sizes accommodating a wide spectrum of flow rates resulting in establishing more reliably the actual process performance. The system behavior under continuous-flow conditions can only be assessed in flow-through column experiments. The column experiments determine the "transfer zone" extent that, in turn, affects the overall column utilization efficiency and the column service time – these are the key operating parameters important for scaled-up applications of the RDX removal process optimally operated in the column configuration.

Understanding the transport mechanism of the ZVI nano-particles (ZVINs) through different types of soil is important for the eventual implementation of an effective RDX remediation process. The major problem rarely addressed in the column studies is the aggregation of iron nanoparticles making their transport through soil ineffective and their chemical reactivity slower (He et al., 2007; Kanel et al., 2008). Extensive studies have been devoted to the stabilization of the ZVINs in batch studies. While Schrick et al. (2004) used hydrophilic carbon and poly-acrylic acid as delivery vehicles to support ZVI nanoparticles, Sun et al. (2007) reported a new strategy for synthesizing fully dispersed and reactive nano-scale particles of zerovalent iron using polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A), a nontoxic and biodegradable surfactant. Furthermore, our previous work (Naja et al., 2008) showed that the use of carboxymethyl cellulose (CMC) as a surfac-tant to stabilize the ZVINs in water led to significantly enhanced nanoparticle surface reactivity, stability and mobility. Among several stabilizers compared (Naja et al., 2008), CMC-coated ZVINs featured the highest RDX (water contamination) removal efficiency in batches. Indeed, 6 min were sufficient to degrade 100% of RDX (82 μmol L^{-1}) using 0.3 g L^{-1} of CMC-ZVINs under anoxic conditions.

In the present work, the chemical degradation of RDX in contaminated soil was investigated using zerovalent iron nano-particles (ZVINs) coated with carboxymethyl cellulose (CMC) in both batch (equilibrium) and dynamic column studies under aerobic and anaerobic conditions. The transformation intermediate and final products as well as the yields and the kinetic constants have been determined based on the Fe/RDX ratio used. The opti-mization of this ratio is required to enhance the column perfor-mance in order to attain the highest and fastest RDX removal performance in the system. Ultimately, a flow-through fixed-bed column with RDX-contaminated soil was used to examine the CMC-ZVINs mediated RDX removal. This is most relevant to the envi-ronmental case where the RDX-contaminated soil is in close proximity to groundwater.

2. Experimental methods

2.1. Chemicals

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, >99%), hexahydro-1,3,5-trini-troso-1,3,5-triazine (TNX) (99%) were obtained from Defence Research and Devel-opment Canada (Valcartier, QC). Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX) (98%), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX) (56%), methyl-enedinitramine (MEDINA) and 4-nitro-2,4-diazabutanal (NDAB) were provided by Dr. R. J. Spanggord from SRI International (Menlo Park, CA, USA). Hydrazine sulfate (99%) was obtained from Aldrich (Ontario, Canada). Sodium borohydride (≥98.5%) was purchased from Aldrich while sodium carboxymethyl cellulose, CMC, (M.W. 90,000) and nitrous oxide standard (1000 ppm) were procured from Sigma–Aldrich (ON, Canada). Ferrous sulfate (99%) and sodium hydroxide (99%) were bought from Anachemia (QC, Canada) and EMD (ON, Canada), respectively. Nitrite and ammo-nium standards (1000 ppm) were purchased from Alltech Associates Inc. (IL, USA). All other chemicals were reagent grade and all solutions were prepared using Milli-Q-UV Plus Ultrapure water system (>18 MΩ, Millipore, MA, USA).

2.2. Contaminated soil

Soil (Sassafras Sandy Loam; fine-loamy, siliceous, semiactive, mesic, Typic Hapludults) was sampled from an open grassland on the property of U.S. Army Aberdeen Proving Ground (Edgewood, MD). The soil was artificially contaminated with RDX and left for aging during one year before using. The soil was then ground to pass through 5 mm sieve and air dried before characterization (Table 1). The contaminated soil was then mixed with uncontaminated Ottawa sand (w/w = 1/9, respectively), homogenized by blending with acetone, air dried overnight and stored in light brown bottles away from light. The final RDX concentration in the soil mixed with sand (used in the present study) was about 60 mg kg^{-1}.

2.3. Preparation of the coated zerovalent iron nanoparticles

Carboxymethyl cellulose modified zerovalent iron nanoparticles (CMC-ZVINs) were prepared according to Naja et al. (2008). In brief, CMC-ZVINs were prepared by reducing Fe^{2+}-CMC complex using sodium borohydride solution. Once the reaction ended, the prepared solution was washed several times, freeze dried and stored under argon. The amount of iron Fe in our prepared CMC-ZVINs was analyzed by ICP-MS and was about 120 g kg^{-1}.

2.4. RDX chemical degradation in soil using batch experiments

To determine RDX removal using CMC-ZVINs, batch experiments were per-formed by mixing 2 g of contaminated soil with 2 mL of deionized water and 0–18 mg of CMC-ZVINs (0–38.57 μmol of iron). The serum bottles were crimp-sealed with Teflon coated septa. The mixture was either made anaerobic by purging the headspace for 10 min with argon or kept under a blanket of air for the aerobic experiments. Unless otherwise noted, the mixtures were mixed in a rotary shaker at a rate of 150 rpm for 23 h, followed by 1 h of acetonitrile extraction (2 mL). The temperature was controlled at 25 ± 1 °C. All experiments were made in triplicates, the results were averaged and their standard deviation was determined. Controls containing CMC-ZVINs in water without the contaminated soil and the contami-nated soil in deionized water without CMC-ZVINs were also performed and investigated.

RDX removal kinetics was studied using the same procedure as described above varying the contact time from 1 to 24 h (extraction included). The amounts of CMC-ZVINs used for these experiments were 18 mg (19.2 mM of Fe) mixed into 2 g of contaminated soil in 2 mL of deionized water. Kinetic studies were carried out under both anaerobic and aerobic conditions, Eh and pH were determined using pH-ORP meter (Accumet AB15, Fisher Scientific).

2.5. Extraction method

2 mL of acetonitrile were added to the mixture of 2 g of polluted soil and 2 mL of CMC-ZVINs solution using a glass syringe. The mixture was then shaken for 1 h in a rotary shaker at a rate of 150 rpm and analyzed as described above. The results showed that RDX concentration was 61.80 ± 3.48 mg kg^{-1} (278.2 ± 15.67 μmol kg^{-1}) for the soil admixed with sand. This value was similar to the one obtained after RDX extraction using the standard sonication technique described in Hundal et al. (1997) (61.96 ± 3.35 mg kg^{-1} after mixing with sand) indicating that the acetonitrile extraction technique is reliable and time saving for the determination of RDX in polluted soils.

Parallel extractions using 2 mL of deionized water instead of acetonitrile were performed when water soluble products were analyzed or when acetonitrile interfered in the analytical technique.

Table 1
Chemical characterization of the soil.

Parameters	Value ± SD
pH	4.9 ± 0
Organic Matter (%)	2.3 ± 0.03
Sand (%)	54.9 ± 0.63
Silt (%)	28.0 ± 1.13
Clay (%)	17.8 ± 0.67
CEC (μmol kg^{-1})	9.3 ± 0.45
Mg (mg kg^{-1})	87.0 ± 1.73
P (mg kg^{-1})	6.3 ± 0.33
K (mg kg^{-1})	74.0 ± 3.06
Ca (mg kg^{-1})	335.3 ± 6.64
Zn (mg kg^{-1})	11.3 ± 0.45
Cu (mg kg^{-1})	8.6 ± 0.48

2.6. RDX chemical degradation in soil using flow-through column experiments

These experiments were performed in small scale cylindrical fixed-bed columns of 9 mm internal diameter and 43 mm high. The columns were packed with 4 g of contaminated soil with a packing density of about 1600 g L^{-1}. The column headspace was purged for 10 min with argon to maintain an anaerobic condition. Parallel control columns were filled in the downflow mode two interstitial velocities v of 1.6 cm min^{-1} and 2.2 cm min^{-1} with deoxygenated deionized (DD) water to displace any air and to determine the column porosity. The porosity of each column was determined prior to initiating each column test. The RDX leaching amount was also followed to establish the mobility of RDX under the chosen conditions.

The dynamic study was conducted in short columns (43 mm) to distinguish between the RDX dissolution and degradation reactions. The operating conditions in these columns were chosen to maximize the RDX removal in the shortest time possible and minimize the required chemicals. Short columns also offer lower flow resistance (pressure drop) as demonstrated by Huang et al. (2004): the pressure drop for a short column (38 mm) was only 3.63 MPa at the flow rate of 7.0 mL min^{-1}, whereas it was 6.66 MPa for a long column (150 mm) at the flow rate of 2.5 mL min^{-1}. When nanoparticles are involved, they tend to often block the flow more as they aggregate due to their magnetic properties.

Due to the reaction between nanoparticles and RDX, retention time in the column is of a special importance. Low interstitial velocities (1.6 and 2.2 cm min^{-1}) were used to allow sufficient retention time for the reaction to occur while minimizing RDX leaching due to its water solubility (Dontsova et al., 2006) and increasing the contact time between RDX-contaminated soil and CMC-ZVINs. CMC-ZVINs solution (13 g L^{-1} containing 27.9 mM of Fe) was fed into the column at two interstitial velocities v of 1.6 cm min^{-1} and 2.2 cm min^{-1}. Lower interstitial velocities ($v < 1.6$ cm min^{-1}) would increase the iron nanoparticle aggregation and the pressure drop across the column as nanoparticles would pack into the interstices among sand soil particles and thus obstruct the column flow.

The effluent was then collected at different time intervals using a fraction collector (Model FRAC-100, Pharmacia, Ramsey, MN) and the collected solution fractions were analyzed to quantify the amounts of RDX and its products. At the end of the experiment, the contaminated soil in the column was carefully extracted and divided into 5 compartments. The soil was then dried overnight and the remaining RDX concentration was determined using the extraction method described above. The obtained RDX mass balance indicated that there is no binding of RDX to the column and tubing materials. The same column experiments were conducted by injecting different volumes (1, 2.2 and 24 pore volumes, PV) of CMC-ZVINs solution (13 g L^{-1} containing 27.9 mM of Fe) in the column at $v = 1.6$ cm min^{-1}.

2.7. Chemical analysis

The gas phase in the headspace of the chemical assays was sampled using a gas tight syringe (250 ìL) and then analyzed for nitrogen, nitrous oxide and hydrogen by a Gas Chromatograph (Hewlett-Packard 6890 GC, Mississauga, ON) with either a TCD or an ECD detector (Sheremata and Hawari, 2000). Aliquots of the aqueous phase of the reaction mixtures were filtered through 0.45 mm filters (Millipore) prior to analyzing RDX, intermediates and final products. The nitroso derivatives MNX, DNX, and TNX and the ring cleavage products methylenedinitramine (MEDINA) and 4-nitro-2,4-diazabutanal (NDAB) were analyzed as previously described (Hawari et al., 2002; Bhushan et al., 2003). Formaldehyde (HCHO), formic acid (HCOOH), ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-) were analyzed as described by Monteil-Rivera et al. (2005). Hydrazine (N_2H_4) formation was monitored by analyzing aliquots of the reaction mixture after derivatization using salicylaldehyde (98%, Aldrich) followed by LC/MS analysis (Monteil-Rivera et al., 2005). The iron concentration at the column outlet was determined by spectroscopic methods as described by Schrick et al. (2004).

3. Results and discussion

3.1. Batch RDX chemical degradation reaction

Rapid *in situ* chemical removal of RDX can be accomplished using reactive zerovalent iron nanoparticles. These nanoparticles act as a reducing agent and require an anaerobic environment for an optimized RDX degradation reaction. However, if this process were to be applied on a large scale, the anaerobic condition might be hard to establish making the process economically unfeasible. Fig. 1a shows that under aerobic conditions (Eh$_{initial}$ −250 mV, Eh$_{final}$ 150 mV) CMC-ZVINs degraded RDX after 3 h less efficiently (60%) than under anaerobic conditions (98% at Eh$_{initial}$ −400 mV, Eh$_{final}$ −350 mV). This was because Fe(0) was oxidized by O$_2$ to Fe(OH)$_{3(s)}$ and quickly precipitated from the system resulting in the
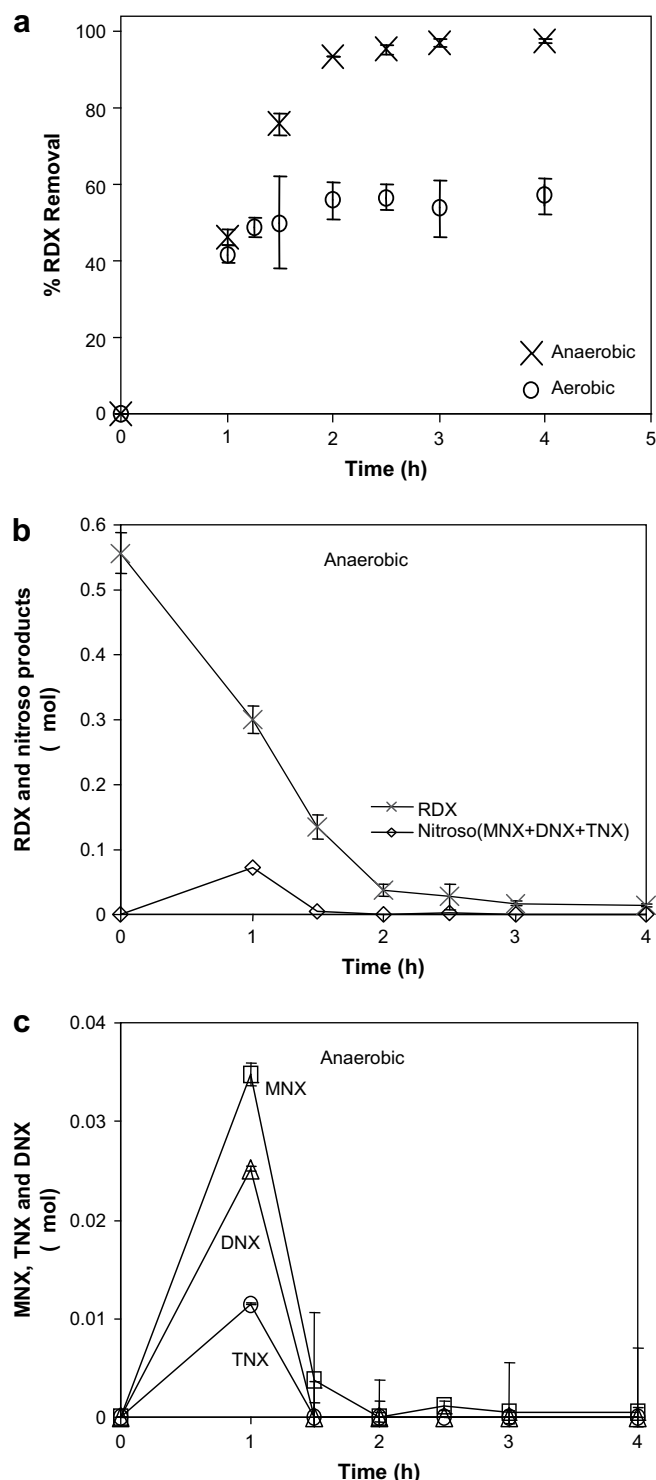

Fig. 1. Time course of RDX chemical degradation under aerobic (a) and anaerobic (a–c) conditions. The formation of the nitroso compounds (MNX, TNX and DNX) was followed in time (b and c). 18 mg of CMC-ZVINs (19.2 mM of Fe) was mixed with 2 g of soil contaminated with 0.5564 μmol of RDX in 2 mL of deionized water.

loss of the reducing agent for RDX removal (Singh et al., 1999; Keenan and Sedlak, 2008).

While Hundal et al. (1997) reported that Fe(0) could be efficiently used for treating RDX-contaminated soil slurries resulting in more than 90% of RDX transformation within 48 h, Singh et al. (1999) showed that batches of RDX polluted soil could be

decontaminated using Fe(0) with (75–99%) RDX removal in 24 h. In comparison, biodegradation of RDX in soil under aerobic conditions required 13 days (Crocker et al., 2005). In the present work, 0.557 μmol (98%) of RDX in 2 g soil were degraded using 9 g L^{-1} of CMC-ZVIN (Fe/RDX molar ratio ∼ 70) under anaerobic conditions in 3 h (Fig. 1b). The nitroso derivatives appearing during the first 2.5 h were also quickly degraded (Fig. 1c). The pseudo-first order rate constant (k_1) value (1.06 h^{-1} with a correlation coefficient of 0.9109) lies in the range of reported values (Naja et al., 2008) as summarized in Table 2. While these rates are lower in the presence of soil (Hundal et al., 1997; Oh et al., 2001), the kinetics observed in the present study was at least 5 times faster than reported in the literature. This might be due to the higher surface area of the nanoparticles compared to iron micro-particles. Furthermore the effect of the carboxymethyl cellulose coating the iron nanoparticles and decreasing their tendency to aggregate also facilitated a fuller utilization of their available surface area as well as their chemical reactivity (Phenrat et al., 2008).

Moreover, the effect of the molar ratio Fe/RDX on the chemical reactivity of the modified nanoiron was investigated by determining the removal reaction intermediate and final products and their distribution. With increasing Fe/RDX molar ratio, the amount of degraded RDX increased gradually and linearly (Fig. 2) reaching almost 100% for the Fe/RDX molar ratio of 70. Theoretically, the reduction of RDX represents a transfer of 6 electrons and requires several consecutive reactions, all of which are surface-mediated. However the applied higher Fe/RDX ratio indicates that during the chemical degradation reaction iron nanoparticles donate electrons to RDX and an oxide layer forms on the iron surface that can hinder the transfer of electrons with the resulting slow-down of the RDX removal process (Klausen et al., 2001). The degradation reaction stops when all the available Fe(0) is consumed. This finding also agrees with the results obtained by Pereira and Freire (2006) when using ZVI for azo dye removal in aqueous solution. The Fe/RDX molar ratio of 55 resulted in 90% RDX removal. The 4.91 mg kg^{-1} of RDX left over was lower than the USEPA remediation goals (5.8 mg kg^{-1}) for the Nebraska Ordnance Plant (NOP) site. At this Fe/RDX ratio, the nitroso derivative products (MNX, DNX, and TNX) were still detected. RDX was almost completely degraded with traces of nitroso derivative products at the Fe/RDX molar ratio of 70. This molar ratio value was lower than the one reported by Singh et al. (1999) who noted 75% RDX removal in 24 h for the Fe/RDX molar ratio of 780.

Analyses were performed at Fe/RDX molar ratios of 31 and 70 to determine the intermediate and final reaction products and to investigate the influence of the molar ratio on the RDX removal product distribution. Fig. 3 shows that the molar ratio did not have any influence on the final or intermediate product type but solely on their quantitative levels. Higher molar ratios led to increased amounts of some of the final products (N$_2$, N$_2$O, NO$_2^-$) with low intermediate product levels (MEDINA, MNX, TNX and DNX). The product distribution and type were in agreement with those
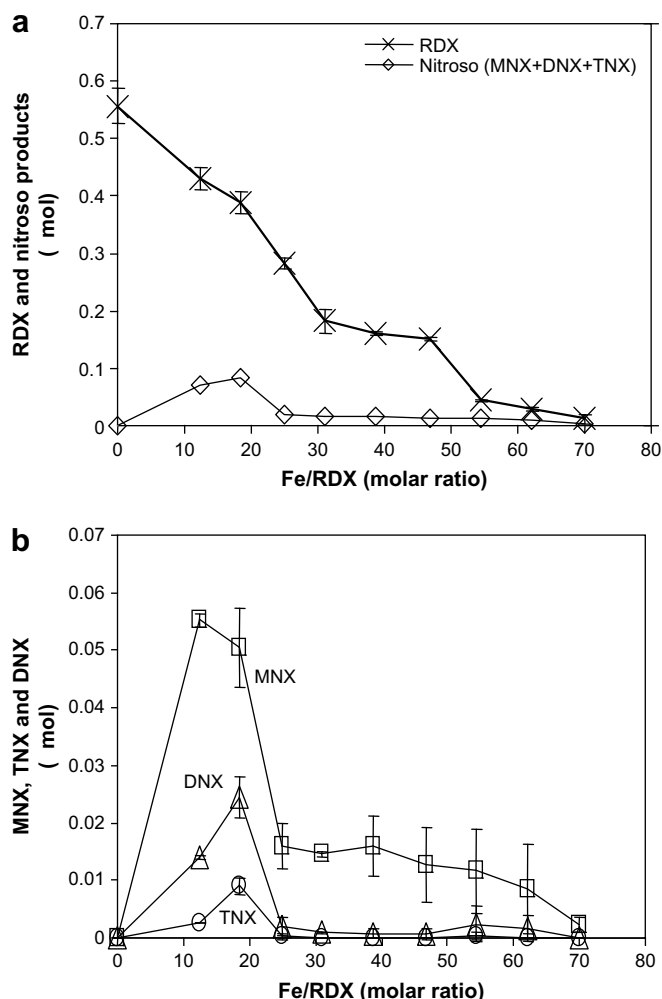

Fig. 2. Effect of Fe/RDX molar ratio on RDX chemical degradation under anaerobic conditions. 2 g of RDX (0.5564 μmol) contaminated soil in 2 mL of water was mixed with increasing amount of nanoiron (<39 μmol).

reported previously in Naja et al. (2008) (HCHO, N$_2$, N$_2$O, NO$_2^-$, NH$_4^+$ and N$_2$H$_4$ as final products and MEDINA and nitroso derivative compounds as intermediate products). The carbon and nitrogen recovery mass balances were about 104.6% and 91%, respectively at Fe/RDX molar ratio = 31. HCHO (52.5 and 55.2%) and MEDINA (16.7 and 14.1%) were the major products in the carbon mass balance after RDX removal for Fe/RDX molar ratios = 31 and 70, respectively (Fig. 3). MEDINA (33.4 and 28.3%) and N$_2$ (14.6 and 23.2%) were the major products based on nitrogen mass balance for both molar ratios = 31 and 70, respectively (Fig. 3). Table 3 reveals that one RDX molecule was cleaved to 2.447 and 1.700 HCHO molecules for the

Table 2
Comparison of the first order degradation rate constant of RDX.

| k_1 (h^{-1})	Fe/RDX	System	Reference
1.06	70	Degradation of RDX-contaminated soil using CMC-ZVINs	This study
0.00125	670.46	Degradation of RDX-contaminated water using micro elemental iron in the presence of soil	(Oh et al., 2001)
0.960	128.63	Degradation of RDX-contaminated water using micro elemental iron	(Oh et al., 2005a)
0.0641	31.07	Degradation of RDX-contaminated soil using micro elemental iron	(Hundal et al., 1997)
0.160	62.14	Degradation of RDX-contaminated soil using micro elemental iron	(Hundal et al., 1997)
0.225	93.21	Degradation of RDX-contaminated soil using micro elemental iron	(Hundal et al., 1997)
0.32	186.42	Degradation of RDX-contaminated water using Fe^{2+} on magnetite	(Gregory et al., 2004)
5.7	414	Degradation of RDX-contaminated water using micro elemental iron	(Wanaratna et al., 2006)
1.14	65.5	Degradation of RDX-contaminated water using nanoiron	(Naja et al., 2008)
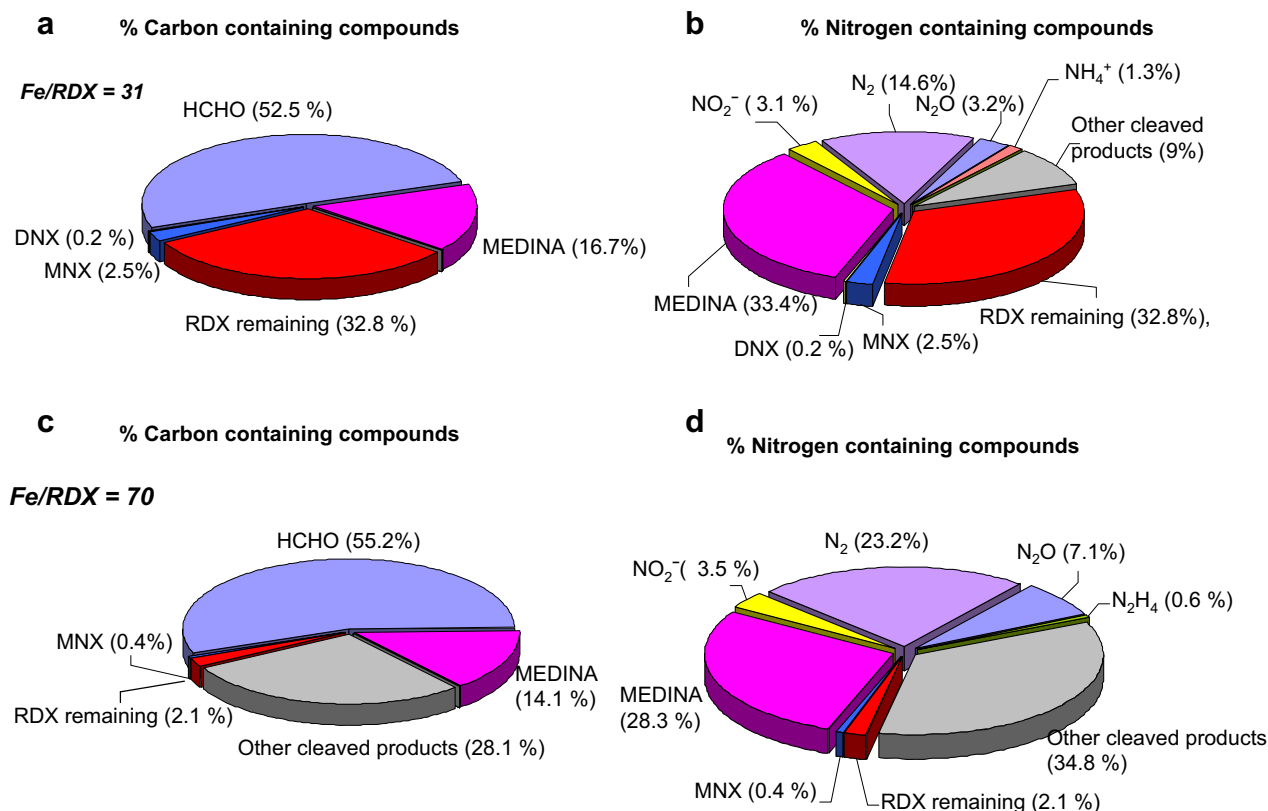
Fig. 3. RDX chemical degradation products using CMC-ZVINs under anaerobic conditions. The results are expressed in percentage of carbon or nitrogen containing compounds. The molar ratio Fe/RDX is 31 (a and b) or 70 (c and d).

Fe/RDX molar ratios = 31 and 70, respectively. Obviously, HCHO was getting reduced most probably to methanol (McKee, 1985; Idriss et al., 1992) and other carbon containing compounds were formed at a higher molar ratio of 70. In the case of nitrogen mass balance, MEDINA represented 25.8 and 14.5% of the total nitrogen of the cleaved products for Fe/RDX molar ratio = 31 and 70, respectively.

3.2. Dynamic study of the RDX chemical degradation reaction using CMC-ZVINs

When studying the removal of RDX in a flow-through fixed-bed column packed with RDX-contaminated soil, the flow rate of the feed suspension of nanoiron is an important parameter to optimize (Oh et al., 2005b). The leaching of RDX should be minimized and its degradation reaction maximized. In the control experiment, only water was fed into the column packed with RDX-contaminated soil.

Table 3
Molar yield of RDX ring cleaved product after 24 h of RDX (0.557 mmol) degradation using CMC-ZVINs (9 g L^{-1} or 4 g L^{-1}).

Products	Fe:RDX ~ 31	Fe:RDX ~ 70
HCHO	2.447 ± 0.193	1.700 ± 0.104
MEDINA	0.778 ± 0.116	0.433 ± 0.203
NO$_2^-$	0.286 ± 0.034	0.215 ± 0.045
N$_2$	0.676 ± 0.030	0.713 ± 0.049
N$_2$O	0.149 ± 0.043	0.220 ± 0.007
NH$_4^+$	0.120 ± 0.038	nd
N$_2$H$_4$	nd	0.019 ± 0.003

The values were calculated based on the moles of product observed for each mole of RDX ring cleaved. Values of triplicate measurements expressed as the mean ± standard deviation.

It was conducted in parallel in order to establish the portion of RDX solubilized and leached by the flow-through feed water. The RDX solubility in CMC solution (0.5%, at the same concentration as the prepared CMC-ZVINs) at $T = 27\,°C$ was of 50.15 mg L^{-1} in the same range as the RDX solubility in water (Lynch et al., 2001). Furthermore, when conducting the degradation reaction experiment in the column with CMC-ZVINs, the reaction was terminated at the outlet by separating the nanoiron from the solution.

The column used had an average overall porosity (void volume) of 20.7% and a packing density of 1600 g L^{-1}. Experimental data obtained from the controls indicated that RDX was not readily bound or retained in soil as demonstrated by its breakthrough leaching from the column. Indeed, at the interstitial velocity v of 5 cm min^{-1}, RDX leached continuously from the contaminated soil in the column. At the same flow rate and for the fed volume = 28 pore volumes (PV), 65% of the initial amount of RDX present in the column leached out. For the fed volume = 500 PV, almost 90% of the RDX initial amount leached from the contaminated soil. The remaining RDX was likely more firmly adsorbed on the clay content of the studied soil (17.8%) (Army, 1980).

Lower interstitial flow-through velocities (2.2 and 1.6 cm min^{-1}) were chosen to investigate the RDX degradation reaction and iron nanoparticle behavior in the column. The breakthrough of CMC-ZVINs in a control column containing noncontaminated soil ($v = 2.2$ cm min^{-1} and a nanoiron feed concentration of 13 g L^{-1}) was followed measuring the total iron at the outlet (Fig. S-1). Iron was detected at the control column outlet before 4 PV and the column became fully saturated at 15 PV. Visually, the iron nanoparticles were distributed quite homogeneously inside the column. When measuring the iron in the filtrate at the outlet of an RDX-contaminated soil packed column (Fig. S-1), Fe^{2+} was detected indicating that the RDX was degraded and iron oxidized. In this

case, the breakthrough occurred before 4 PV and reached a plateau indicating a slow-down in RDX removal.

Overall, the same intermediate and final products were observed during RDX soil contaminated removal in batch and column studies using ZVINs. Fig. 4a shows cumulative amounts of the different RDX breakdown products (HCHO, MNX, TNX and DNX) as well as that of RDX (leaching) monitored at the column outlet. Nitroso derivatives (products MNX, DNX, and TNX) as well as HCHO were detected during the CMC-ZVINs treatment confirming the batch experiment results. The cumulative amount of HCHO at the column exit rapidly increased (Fig. 4a) as its early peak concentration was leaving the column (Fig. 4b). The RDX exit level can be compared to the control run and its amount actually degraded in the column can be calculated from the difference between the amount of RDX at the outlet of the control column and that remaining in the treated column exit solution (Fig. 4b). When 24 PV ($v = 2.2$ cm min^{-1}) of CMC-ZVINs suspension passed through the column, the total amount of degraded RDX was 75% with 8.8% of residual RDX bound to the soil in the column that likely could not

be easily degraded. The remaining 16.2% leached out of the column due to the RDX mobility. Almost 61% of the initial amount of RDX present in the column leached out when conducting the control experiment without injecting the nanoiron under the same conditions. Fig. 4a shows that RDX amount at the column outlet was extremely low at PV > 5. Indeed, 90% of the RDX leaching occurred during the first PVs added to the flow-through process when the nanoiron was reacting only with the upper column layers and its reactivity was largely diminished when it progressed into the column bottom layers (Klausen et al., 2001) where it only contributed to important RDX leaching. The stabilization of the RDX leaching (Fig. 4b), while the HCHO amount in the exit stream was relatively steady, indicated that the degradation reaction was occurring inside the column. The concentration of RDX degraded during the experiments conducted in the present paper reached 10 mg kg^{-1} (of soil) by layer at PV = 4.5 and $v = 1.6$ cm min^{-1}. This compares quite favorably with similar results that removed only 90 µg kg^{-1} of RDX from RDX-contaminated soil mixed with mulch packed into a flow-through column (Ahmad et al., 2007). The presently observed overall RDX removal is an order of magnitude higher than that seen in the presence of organic mulch. Furthermore, from the results plotted in Fig. 4b, the overall amount of RDX degraded in the column could be calculated from the area (trapezoidal method) between the RDX-control and RDX-experiment curves (area $A_1 = 1.7$ µmol.PVnumber). The area under the HCHO breakthrough curve (area $A_2 = 5.04$ µmol.PVnumber) represents the overall amount of HCHO evolved due to the degradation reaction. The ratio of the two areas (A_2/A_1) = 3 indicates that one RDX molecule was cleaved into 3 HCHO molecules confirming the degradation pathway established in Naja et al. (2008).

The effect of the column flow rate on the column treatment process performance was examined at two different interstitial velocities ($v = 2.2$ and 1.6 cm min^{-1}). The results are shown in Fig. 5 presenting the percentage of RDX degraded, corrected through the control experiments, in the 5 layers of the column. The contaminated soil inside the column was divided into 5 layers and each layer was analyzed for RDX concentration (after treatment with CMC-ZVINs or water). Uniform RDX concentrations in all these layers were observed in the control column experiments (no CMC-ZVINs used). However, when corresponding experiments with CMC-ZVINs column feed were conducted at identical flow rates, at the end of the experiment (PV = 24), the soil layers at the entrance
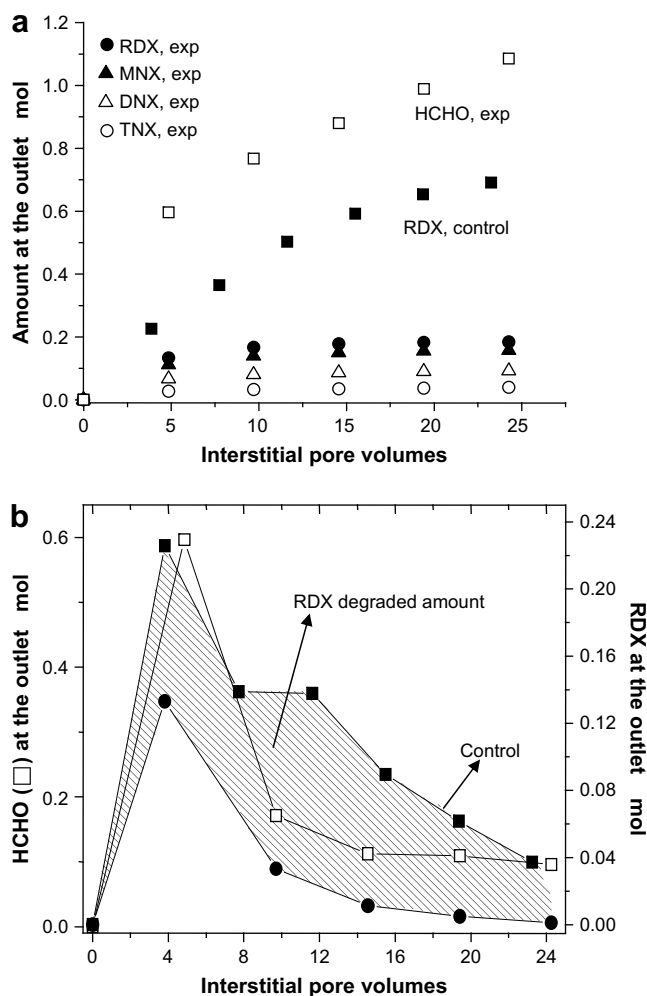

Fig. 4. a) Breakthrough of RDX, HCHO, MNX, TNX and DNX in an RDX-contaminated soil packed column (cumulative values). The CMC-ZVINs nanoiron feed concentration was 13 g L^{-1} and the interstitial velocity $v = 2.2$ cm min^{-1}. Breakthrough of RDX in the control experiment (column with RDX-contaminated soil fed with water at the same interstitial velocity). b) Breakthrough of HCHO and RDX in a contaminated soil packed column. The CMC-ZVINs feed concentration is 13 g L^{-1} and the interstitial velocity $v = 2.2$ cm min^{-1}. Breakthrough of RDX in the control experiment (column with RDX-contaminated soil fed with water at the same interstitial velocity). The hatched area represents the amount of RDX actually degraded.
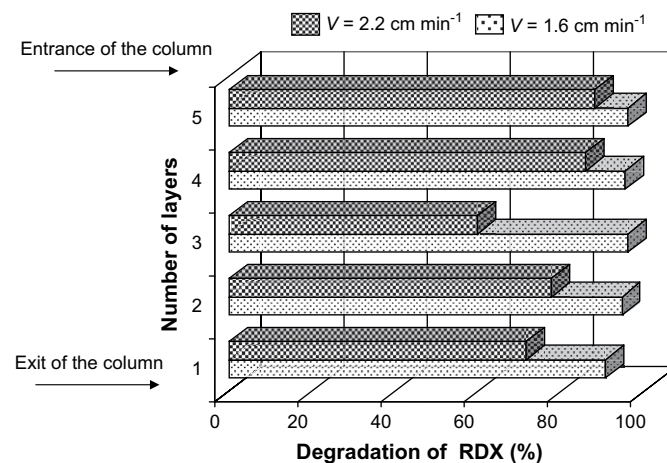

Fig. 5. Percentage of RDX degraded in the 5 layers constituting the column. The column is packed with RDX-contaminated soil and fed with CMC-ZVINs at a concentration of 13 g L^{-1}, pore volumes = 24, and the interstitial velocity $v = 2.2$ cm min^{-1} and 1.6 cm min^{-1}.

of the column contained lower concentrations of RDX than the layers closer to the column exit indicating that the amount of RDX degraded was higher at the top of the column than at its exit (for $v = 2.2$ cm min^{-1}, the layer at the entrance of the column contained 0.01 μmol compared to 0.024 μmol contained in the layer at the column exit). This observation is explained by the fact that a certain amount of iron nanometal reacted with the RDX at the entrance of the column and reached the exit layers with its reactivity already exhausted. The nanometal was less available for the degradation reaction at locations closer to the end of the column system. Correspondingly, as the capacity of the nanoiron to degrade RDX decreased as it moved through the column, the proportion of RDX degraded in these locations also decreased. For example at $v = 2.2$ and 1.6 cm min^{-1}, 88% and 96% of the RDX of the upper layer were degraded compared to 72% and 90.6% of the end layer, respectively. The RDX degradation decreased from the upper to the lower column layer, this was less pronounced for the lower flow rate because of the increase of the residence time in the column.

The degree of RDX removal, particularly in short columns, depends upon the flow rate (Oh et al., 2005b). For example, 96% and 88% of RDX was degraded at the column entrance layer with the nanoiron feed at $v = 1.6$ cm min^{-1} and $v = 2.2$ cm min^{-1}, respectively. Under the same respective feed velocity conditions, 90.6% and 72% of RDX was removed at the exit layer. Overall, 76.6% and 95% of the initial column RDX load were removed (degraded) with interstitial velocities of $v = 2.2$ cm min^{-1} and 1.6 cm min^{-1}, respectively. These results indicate that for the maximum column utilization and its longest service time, the flow rate should be the lowest possible resulting in increased retention time. However, very low interstitial velocities ($v < 1.6$ cm min^{-1}) would also have a side-effect of increased iron nanoparticle aggregation with corresponding pressure drop across the column. The optimum value should be established for each and every case. Similar results, consistent with the sorption/reaction column operational characteristics, have been reported by other researchers (Aksu and Tezer, 2005; Pamukoglu and Kargi, 2007) who studied the effect of flow rates on different types of reaction yields occurring in fixed-bed flow-through columns. At lower feed flow rates, reactions inside the column were not limited by contact time and the reagent (nanoiron in our case) had more time to react with the contaminant (RDX in the soil solid phase) resulting in a higher overall removal of RDX from the column fill (Naja and Volesky, 2007).

The effect of nanoiron amount fed into the column (specified in pore volumes) also had an important effect on the amount of RDX degraded as seen in Fig. 6 (CMC-ZVINs feed at $v = 1.6$ cm min^{-1}). While the entry column layer featured 88% and 74.2% of RDX

degraded after PV = 10.5 and 4.5 of the nanoiron solution was fed through, respectively, the RDX removals were higher in the column. 62% and 58% of RDX was degraded at the column exit layer for the same respective volumes fed through. The column overall RDX removals (at $v = 1.6$ cm min^{-1}) were 65%, 71% and 95% for 1.0, 2.5 and 24 pore volumes (PV) fed through, respectively. Similar results have been reported when studying different reactions in columns (Naja and Volesky, 2007).

In actual process applications, the concentration or the total amount of nanoiron fed into the column purification system should not be chosen arbitrarily because of costs and possible flow restrictions inside the column caused by excessive nanoiron feed concentrations. Similarly, the solubility of RDX would cause its excessive leaching and escape from the system if elevated amounts (pore volumes) of nanoparticle solution were to be pumped through the system. A careful optimization of the process operating parameters is required that must preferably be based on a reasonably sophisticated column performance modeling in order to attain the highest and fastest RDX removal in the system.

4. Conclusion

CMC-ZVINs solution could be applied to degrade RDX-contaminated soil in both batch and column operating modes. The degradation process using CMC-ZVINs transformed RDX to formaldehyde, MEDINA, nitrite ion, nitrous oxide, ammonium ion, hydrazine, and nitrogen. The flow-through dynamic column study demonstrated that the RDX removal reaction rate was faster (overall) than RDX leaching from the column. The best experimental study conditions led to the removal of 95% of the RDX initially present in RDX-contaminated soil packed in a flow-through column flushed with a CMC-ZVINs suspension.

The studied case is most relevant to the environmental case that could occur in the environment where the RDX-contaminated soil is in close proximity to groundwater.

Acknowledgements

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2009.03.019.
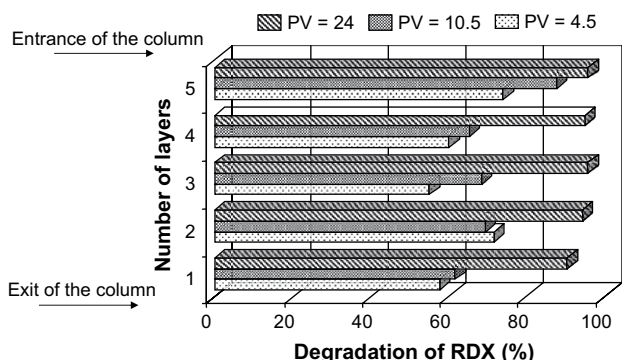

Fig. 6. Percentage of RDX degraded in the 5 layers constituting the column. The column is packed with RDX-contaminated soil and fed with CMC-ZVINs at a concentration of 13 g L^{-1}, the interstitial velocity $v = 1.6$ cm min^{-1} and the pore volumes = 4.5, 10.5 and 24.

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