Short communication

Reductive transformation of 2,4,6-trinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine, and nitroglycerin by pyrite and magnetite

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Abstract

Reductive transformation of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and nitroglycerin (NG) by pyrite (FeS_2) and magnetite (Fe_3O_4) was investigated to determine the role of Fe(II)-bearing minerals on the fate of toxic explosives in Fe/S-rich natural environment. Results from batch experiments showed that 65% of TNT and 45% of RDX were transformed from solution in the presence of pyrite under pH 7.4 buffered conditions within 32 days. Without a buffered solution, transformation of TNT and RDX decreased. NG was continuously and rapidly transformed by pyrite under both conditions. Complete removal of NG was achieved in 32 days under buffered conditions. NH_4^+ was identified as a reduction product for RDX and NG in the pyrite–water system. Reductive transformation of RDX and NG by magnetite was slower than that by pyrite. The results suggest that abiotic transformation of the explosives by pyrite and magnetite may be considered when determining the fate of explosives in Fe/S-rich subsurface environments.
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1. Introduction

2,4,6-Trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, RDX), and propane-1,2,3-triyl-trinitrate (nitroglycerine, NG) are the most widely used explosives in the world [1]. TNT is known to be carcinogenic and mutagenic and is acutely toxic to microbes, algae, fish, and other organisms [1]. RDX is a heterocyclic nitramine which, together with octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (high melting explosive, HMX), can be a persistent compound that is toxic to organisms including humans [2]. Soil and groundwater in the proximity of munitions-manufacturing plants are often contaminated with TNT and RDX [3,4]. NG is also known to be toxic at high levels to microorganisms, fish, rats, and humans [5]. Though the NG contamination of soil and aquifers was not reported, NG-manufacturing plants produce NG-containing wastewaters that need to be treated before being discharged to the natural environment.

Current studies have examined the fate and transformation of explosives in subsurface environments to determine relevant remediation technologies for cleaning up toxic explosives in soil and aquifers such as bioremediation, monitored natural attenuation, advanced oxidation processes or chemical reduction. However, most of these studies have focused on anaerobic biodegradation of explosives in subsurface environment. Limited studies examined abiotic transformations of explosives with minerals by themselves in soil and groundwater [6,7]. Recently, studies have investigated the role of Fe(II)-bearing minerals such as pyrite (FeS_2) and magnetite (Fe_3O_4) in the transformation of contaminants in natural environments. Kriegmen-King and Reinhard [8] showed that more than 90% of CCl_4 was reductively transformed by pyrite within 12–36 days and produces CO_2 and $CHCl_3$ as major transformation products under aerobic and anaerobic conditions, respectively. Weerasooriya and Dharmasena [9] showed that about 80% of trichloroethylene (TCE) was reduced by pyrite to C_2H_2, 1,1-dichloroethylene, and C_2H_4 in 240 h. Tetrachloroethylene (PCE), TCE, *cis*-dichloroethylene,

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and vinyl chloride were reported to be reductively transformed by pyrite [10]. Pyrite was also shown to reductively transform Cr^{6+} [11,12]. Abiotic transformation of contaminants by magnetite has been increasingly studied during the last decades. Transient metal ions such as Cu^{2+} and $Cr_2O_7{}^{2-}$ could be reduced in the presence of magnetite [13,14]. Radionuclides such as U and Pu were also reductively transformed by magnetite [15]. 1,1,1-Dichloroethylene and *cis*-dichloroethylene were reported to be reductively removed from groundwater in an aquifer containing magnetite [16].

Many studies have been conducted to examine the transformation of other toxic contaminants by pyrite and magnetite. However, to our knowledge, there are few studies investigating the transformation of explosives by pyrite and magnetite [7]. The current study explored reductive transformation of explosives in the presence of pyrite and magnetite. The objective of this study was to determine whether explosives could be reductively transformed by pyrite and magnetite, which are possibly present in Fe/S-rich subsurface environments, including abandoned mine lands, near shore or marine sediments. It was hypothesized that pyrite and magnetite may abiotically transform explosives under anaerobic conditions. TNT, RDX, and NG were chosen as nitroaromatic, nitramine, and nitro ester explosives for this study. Batch experiments were performed with pyrite and magnetite.

2. Materials and methods

2.1. Chemicals

TNT (>99%) and RDX (>99%) were provided by the Holston Army Ammunition Plant (Kingsport, TN). NG dissolved in deionized water (497.3 ± 0.7 mg/L) was provided by the Redford Army Ammunition Plant (Redford, VA). NG standard solution in ethanol (0.1 mg/mL) was purchased from Accustandard (New Haven, CT). *N*-(2-Hydroxyethyl)piperazine-*N'*-(ethanesulfonic acid) (HEPES, >99%) was purchased from Sigma (St. Louis, MO). All chemicals were used as received.

Pyrite and magnetite were acquired from Ward's Geology (Rochester, NY). Pyrite and magnetite chips were pulverized and sieved to obtain fine particles of diameters less than 150 μm. Quantitative analysis of mineralogy was not conducted in this study. However, previous analyses reported that the purity of the pyrite and magnetite obtained from Ward's geology is 95% and 65%, respectively [7]. The pyrite included 5% of calcite and the magnetite contained 10% of muscovite and 20% of other minerals including plagioclase feldspar, kaolinite, and vermiculite [7]. Previous analyses also showed that iron in these other minerals is a trace element and that most of ferrous iron is associated with the pyrite and magnetite [7]. Specific surface areas of the pyrite and magnetite powder were 0.53 ± 0.03 and 0.56 ± 0.02 m^2/g, respectively, as determined by the Brunauer–Emmett–Teller (BET) method with N_2.

2.2. Batch reduction experiments with pyrite and magnetite

All experiments involving sealed batch reactors were performed in a glove box ($I^2R^{\circledR}$, Cheltenham, PA) under Ar.

Duplicate 8-mL borosilicate amber vials were set up, each of which contained a 5-mL solution of the test compound and 0.1 g of either pyrite or magnetite powder, corresponding to approximately 10.6 or 11.2 m^2 of surface area per liter of solution, respectively. The solution was deoxygenated by purging with Ar for more than 30 min. No buffer solution was added to maintain the pH in the magnetite system. For pyrite, pH of the solution was either unbuffered or maintained at 7.4 using 0.1 M HEPES buffer to determine the effect of pH. Initial pH of the solutions ranged from 7.1 to 7.4 in both the buffered and unbuffered systems. Initial concentrations of TNT, RDX, and NG were 0.242 ± 0.001 mM (53.9 ± 0.2 ppm), 0.201 ± 0.001 mM (59.5 ± 0.3 ppm), and 0.307 ± 0.002 mM (69.7 ± 0.5 ppm), respectively. Vials were shaken at 100 rpm in a horizontal position on the platform of a rotary shaker in the glove box. At different elapsed times, two replicates were sacrificed for analysis. Aqueous samples were taken from each vial and passed through a 0.22-μm cellulose filter (Millipore, MA) for immediate analysis of TNT, RDX, or NG. Under identical conditions, control experiments were performed without either pyrite or magnetite.

2.3. Chemical analysis

TNT, RDX and NG were analyzed using a Varian HPLC (Walnut Creek, CA) equipped with a Supelguard guard column (20 mm × 4.6 mm, Supelco, Bellefonte, PA), a Supelco LC-18 column (250 mm × 4.6 mm, 5 μm), a UV detector (Varian 2510) and an isocratic pump (Varian 2550). A methanol–water mixture (55/45, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. Injection volumes for all samples were 10 μL and the wavelength for the UV detector was 254 nm.

3. Results and discussion

3.1. Transformation of TNT by pyrite and magnetite

Fig. 1 shows that TNT was transformed from solution by pyrite. In an unbuffered system, 27% of TNT was gradually
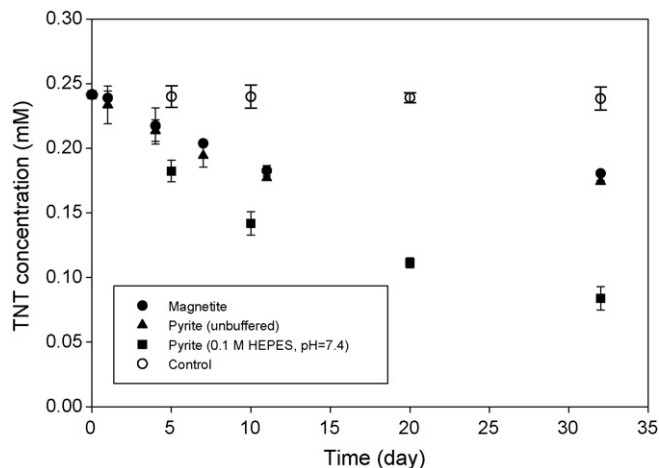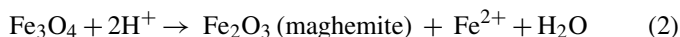

Fig. 1. Transformation of TNT with magnetite and pyrite. Data points are the average of duplicate samples and error bars represent standard deviations.

transformed within 11 days and pH dropped significantly from an initial 7.2 to 2.8. After 11 days, TNT concentration seemed to be constant until 32 days with no change of pH. It is likely that transformation of TNT by pyrite was negligible after 11 days, suggesting that pH was a key factor for controlling the transformation rate of TNT by pyrite. The anaerobic oxidation of pyrite by water molecules (or contaminants) may result in decreased pH [8]:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \tag{1}$$
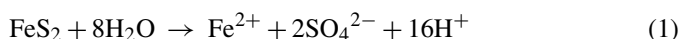
According to Eq. (1), the decrease of pH over reaction time in the unbuffered system could make anaerobic oxidation of pyrite much slower. To examine the role of pH in the transformation of TNT by pyrite, pH was maintained at 7.4 using HEPES buffer. As shown in Fig. 1, transformation of TNT by pyrite was greatly enhanced when pH was maintained at 7.4. In 10 days, 42% of TNT was transformed from solution in the presence of pyrite. Detectible transformation continued in the buffered system through day 32, albeit at slowly decreasing rates. Approximately 65% of initial TNT was transformed from solution in the presence of pyrite in 30 days. The pseudo-first-order rate constant was 0.037 ± 0.005 day^{-1} ($R^2 = 0.955$). The corresponding BET surface area-normalized rate was $(3.49 \pm 0.47) \times 10^{-3}$ L m^{-2} day^{-1}. These results indicated that the buffering capacity of soil or aquifer might be crucial for pyrite to transform TNT in subsurface environments. However, whether iron or sulfur species on the pyrite surface accounts for the reductive transformation of TNT still remains to be determined. In this study, we did not identify a well-known reduction product of reduction of TNT, 2,4,6-triaminotoluene (TAT). However, in TNT analysis by HPLC, as TNT concentration decreased, HPLC chromatograms showed unidentified peaks, which might be reduction intermediates, such as aminodinitrotolunes or diaminonitrotoluenes though we did not identified them due to lack of standard materials. The identification of reduction products also remains to be explored for future study.

TNT was also transformed in the presence of magnetite. Until 11 days, TNT was gradually transformed from solution by magnetite, with about 24% TNT removal in 11 days. Similar to the unbuffered pyrite system, transformation of TNT by magnetite was negligible after 11 days. An additional 1% of TNT was transformed from solution from 11 days to 32 days. Theoretically, for magnetite to generate electrons to reduce TNT, hydrogen ions should be consumed for the transformation of magnetite to maghemite as follows:

$$Fe_3O_4 + 2H^+ \rightarrow Fe_2O_3 \text{ (maghemite)} + Fe^{2+} + H_2O \tag{2}$$

Therefore, pH increased from 7.2 to 7.8 as 24% of TNT was transformed from solution by magnetite until 11 days. The pH did not change from 11 days to 32 days, indicating a lack of electron generation from magnetite may be responsible for the slow down of TNT transformation after 11 days. It does not appear that at slightly alkaline pH (7.8), magnetite could transform TNT effectively. As previously reported [12], acidic conditions may be needed for mag-
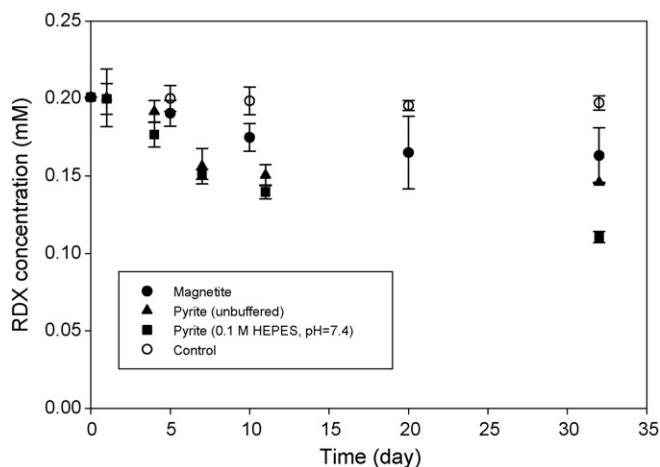

Fig. 2. Transformation of RDX with magnetite and pyrite. Data points are the average of duplicate samples and error bars represent standard deviations.

netite in the natural environment to effectively reduce oxidized contaminants.

The absence of significant transformation in the control samples (no pyrite or magnetite) suggests that the observed degradation is attributable to the mineral phases and not to alternative reaction mechanisms such as microbial or photocatalytic processes. In addition, it should also be noted that we did not make any attempts to examine the sorption of the explosives on the surface of pyrite/magnetite. Therefore, it could not be ruled out that the sorption of the explosives might be involved in the overall removal of the explosives in the magnetite/pyrite–water system.

3.2. Transformation of RDX by pyrite and magnetite

RDX was also transformed by pyrite. In the unbuffered system, 25% of initial RDX was transformed by pyrite as pH decreased from 7.1 to 3.0 in 11 days (Fig. 2). Similar to TNT transformation by pyrite (Fig. 1), transformation of RDX was much slower after 11 days. Approximately 27% of RDX was transformed by pyrite in 32 days. In a buffered system at pH 7.4, RDX was continuously transformed until 32 days showing 45% removal (Fig. 2). The extent and rate of RDX reduction by pyrite in the buffered system appear to be smaller and slower than TNT under identical conditions. The pseudo-first-order rate constant was calculated to be 0.021 ± 0.004 day^{-1} ($R^2 = 0.883$), corresponding to $(1.98 \pm 0.38) \times 10^{-3}$ L m^{-2} day^{-1}. Transformation of RDX by magnetite was also slower than that for TNT. In 32 days, only 19% of RDX was transformed from solution in the presence of magnetite. NH$_4{}^+$ (1.5 mg/L) was identified as one of the reduction products after 32 days in the pyrite–water system. The identification of other reduction products remains to be determined.

3.3. Transformation of NG by pyrite and magnetite

NG was also shown to be transformed by pyrite and magnetite. However, unlike TNT and RDX, NG was rapidly and continuously transformed from solution in the presence of pyrite
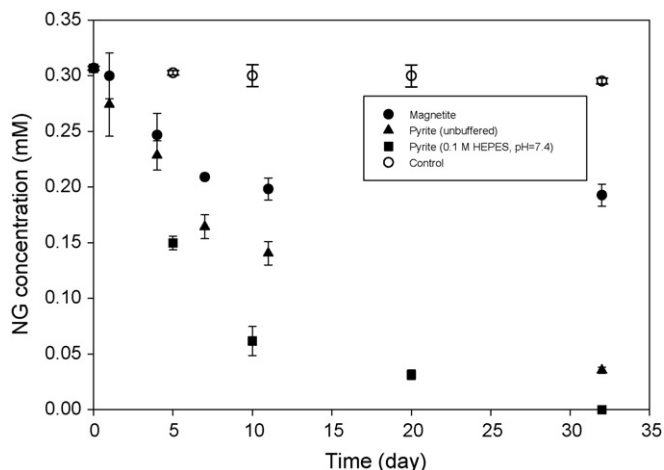
Fig. 3. Transformation of nitroglycerin with magnetite and pyrite. Data points are the average of duplicate samples and error bars represent standard deviations.

in the unbuffered system. As shown in Fig. 3, in 32 days, 89% of initial NG was transformed from solution as pH dropped from 7.2 to 2.9. It appears that, under acidic conditions, transformation of NG continued in the presence of pyrite. In the buffered system at pH 7.4, transformation of NG by pyrite was more rapid than TNT and RDX transformation by pyrite. About 90% of NG was transformed from solution in the presence of pyrite in 20 days. Complete transformation of NG was achieved in 32 days (Fig. 3). The pseudo-first-order rate constant for NG transformation was $0.147 \pm 0.011 \, \text{day}^{-1}$ ($(1.39 \pm 0.10) \times 10^{-2} \, \text{L m}^{-2} \, \text{day}^{-1}$) ($R^2 = 0.994$), which is about five- and sevenfold higher than the transformation rate of TNT and RDX, respectively. Reductive transformation of NG by magnetite was similar to what was observed for TNT and RDX, though the extent of NG transformation was somewhat enhanced under identical conditions. About 35% of initial NG was transformed from solution in the presence of magnetite in 11 days. Thereafter, transformation of NG was extremely slow until 32 days, showing only an additional 2% removal. NH_4^+ (9.8 mg/L) was identified as one of the reduction products after 32 days in the pyrite–water system. The identification of other reduction products remains to be determined.

4. Conclusions

In summary, our results show that pyrite and magnetite can reductively transform explosives under anaerobic conditions. Under buffered conditions at pH 7.4, TNT, RDX, and NG were continuously transformed from solution in the presence of pyrite.

Under unbuffered conditions, transformation of TNT and RDX decreased due to decreased pH. NG was continuously and more rapidly transformed by pyrite under both conditions. The explosives were also shown to be transformed in the presence of magnetite. The results suggest that abiotic transformations of the explosives by pyrite and magnetite should be considered when determining the fate of the explosives in natural attenuation processes under Fe/S-rich subsurface environments.

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