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Laboratory and pilot-scale bioremediation of Pentaerythritol Tetranitrate (PETN) contaminated soil

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HIGHLIGHTS

- Laboratory and pilot-scale bioremediation of PETN-contaminated soil.
- PETN-contaminated soil treated with granular iron and organic carbon materials.
- The amendment of carbon source effectively stimulated PETN biodegradation.
- The low efficiency of iron method was caused by the high concentration of nitrate.

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ABSTRACT

PETN (pentaerythritol tetranitrate), a munitions constituent, is commonly encountered in munitions-contaminated soils, and pose a serious threat to aquatic organisms. This study investigated anaerobic remediation of PETN-contaminated soil at a site near Denver Colorado. Both granular iron and organic carbon amendments were used in both laboratory and pilot-scale tests. The laboratory results showed that, with various organic carbon amendments, PETN at initial concentrations of between 4500 and 5000 mg/kg was effectively removed within 84 days. In the field trial, after a test period of 446 days, PETN mass removal of up to 53,071 mg/kg of PETN (80%) was achieved with an organic carbon amendment (DARAMEND) of 4% by weight. In previous laboratory studies, granular iron has shown to be highly effective in degrading PETN. However, for both the laboratory and pilot-scale tests, granular iron was proven to be ineffective. This was a consequence of passivation of the iron surfaces caused by the very high concentrations of nitrate in the contaminated soil. This study indicated that low concentration of organic carbon was a key factor limiting bioremediation of PETN in the contaminated soil. Furthermore, the addition of organic carbon amendments such as the DARAMEND materials or brewers grain, proved to be highly effective in stimulating the biodegradation of PETN and could provide the basis for full-scale remediation of PETN-contaminated sites.

1. Introduction

Intensive military activities over the past century have resulted in widespread contamination of soil and water with residues of explosives and related compounds [1]. It is currently estimated that explosives-contaminated sites could occupy millions of hectares of land in the U.S., while the global extent of contamination is difficult to assess [2]. Explosives are anthropogenic nitro-organic compounds with very few naturally occurring analogs. As a consequence, natural microbial populations are generally not acclimated and thus explosives tend to be persistent in the environment. The conventional method for remediation of explosives-contaminated soil is incineration. Because of the high cost and the associated disadvantages such as production of large volumes of unusable ash, increased attention has turned to alternative remediation methods, such as chemical reduction with metallic iron [3–7] and bioremediation including composting, bioslurry and landfarming [8].

Granular iron containing a zero-valent iron core has been shown to be an effective reductant for 2,4,6-trinitroluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) [3–5], both of which are nitrated munitions. In a field trial involving 70 kg of soil from a munitions wastewater disposal site, using iron (5%, w/w), RDX

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decreased from an average initial concentration of 12,100 mg/kg to 540 mg/kg, a 96% removal, within 120 days [6].

Explosive compounds have also been shown to be susceptible to biodegradation, with acclimated indigenous microbial communities which have been exposed to contaminants for a long period of time showing the greatest promise. For example, three species of the family *Enterobacteriaceae*, isolated from nitramines explosives-contaminated soil, can reduce both RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX) under anaerobic conditions [9]. Similarly, Marshall and White [10] isolated four anaerobic bacterial species of *Pseudomonas putida*, *Arthrobacter*, *Klebsiella* and *Rhodococcus* from glycerol trinitrate (GTN)-contaminated soil, all of which can use GTN as the sole nitrogen source.

The electron-withdrawing character of nitro groups in explosives is responsible for their low susceptibility to typical advanced oxidative catabolism [11]; therefore anaerobic bacteria hold greater potential for remediation of explosives-contaminated sites. Because of the low solubility of explosive compounds, an external co-substrate is commonly added to stimulate the growth of the explosive-degrading bacteria. For example, explosive compounds such as TNT, HMX and tetryl can all be effectively removed from contaminated soil by indigenous bacteria with the addition of molasses as a carbon source for bacterial growth [12–15].

To date, most studies on the degradation of explosives have focused on nitroaromatics and nitramines, particularly on TNT and RDX, but very little work has been reported on pentaerythritol tetranitrate (PETN), a nitrate ester compound. From laboratory tests performed with aqueous solutions, we previously reported [16] rapid degradation of PETN in the presence of granular iron. Half-lives were on the order of minutes, and the process appeared to follow sequential denitration. In a further laboratory study [17], using an anaerobic consortium from a contaminated site and with the addition of an organic carbon amendment, biodegradation of PETN was shown to be an effective process.

Our previous work, using laboratory-synthesized PETN in aqueous solution, showed that granular iron and biodegradation both had the potential to be effective technologies for remediation of PETN-contaminated sites. The goal of this study was to further evaluate the potential and possible limitations of both technologies for remediation of PETN present in solid and aqueous forms at heavily contaminated sites. In particular, both laboratory and small-scale pilot tests were performed using contaminated soil materials from a particular site located near Denver Colorado.

2. Materials and methods

2.1. PETN-contaminated soil

The contaminated site considered in this study is located approximately 40 km south of Denver, Colorado. The site consists of two settling ponds near a currently inactive explosive manufacturing facility, which received wastewater from PETN production for over 20 years (between 1967 and 1989). The ponds, each 119 m by 119 m, are lined with high-density PVC membrane with approximately 22–36 cm of clayey soil on top of the liner. The PETN concentration in the soil is highly variable, ranging from 1 to 200,000 mg/kg of dry soil. Because nitric acid and sulfuric acid were used in the process of PETN synthesis, concentrations of nitrate and sulfate are also high and generally variable, ranging from 1 to 10,000 mg/kg of dry soil.

The soil used in the laboratory experiments was obtained from the southwest corner of the south pond. The PETN concentration ranged from 65 to 600 mg/kg and high levels of nitrate and sulfate (8000–10,000 mg/kg) were also present. For the laboratory tests, the PETN concentration was increased to 4500–5000 mg/kg by spiking with pure PETN powder. Prior to PETN addition, a portion of the soil was leached several times with Millipore water to reduce the levels of nitrate and sulfate. On average, the concentrations of nitrate and sulfate were decreased to 1500 and 2500 mg/kg, respectively. The soil was air dried and ground to pass a 2 mm sieve before use. Soil used in the sterile controls was triple-autoclaved (1 h at 121 °C on three consecutive days). The soil had a total organic carbon content of 0.41%, including PETN.

2.2. Iron and organic materials

The granular iron was obtained from Connelly-GPM Inc. (Chicago, Illinois) and used without pretreatment. The iron material was characterized previously as containing 89.8% metallic iron with a surface layer of various forms of iron oxide (data provided by Connelly-GPM Inc.). The specific surface area of the iron used in this study was 1.02 m^2/g, measured by the BET (Brunauer–Emmett–Teller) method. The sources of organic carbon used in the laboratory tests included two different DARAMEND materials, D6390Fe20 and ADM-298500. The materials were provided by ADVENTUS Remediation Technologies (Mississauga, Ontario, Canada). The DARAMEND products are manufactured from plant materials rich in carbon and nutrients, though the precise composition is proprietary. D6390Fe20 and ADM-298500 are identical except that D6390Fe20 is fortified with 20% (by weight) fine granular iron. Brewers grain, a residual of the brewing process was tested as an alternative carbon source in the field pilot tests. This material was obtained from Teague Diversified, Inc., Ft. Morgan, CO. The brewers grain had a moisture content of 65% and is fibrous with a high protein content.

2.3. Laboratory batch experiment

A total of 12 treatments were conducted; set-1, set-2 and set-7 were control samples with no amendment added; set-3 to set-6 contained different percentages of granular iron ranging from 2 to 10% (by weight); and set-8 to set-12 tested the two types of organic materials (D6390Fe20 and ADM-298500) at 1% and 2% levels. The composition of each treatment is given in Table 1. Each treatment involved the same laboratory conditions with identical set-up and sampling and analysis procedures. Tests were conducted in 40 mL glass vials with screw caps fitted with Teflon-lined septa. Each vial contained 15 g of PETN-contaminated soil and the desired amount of a particular amendment (iron or DARAMEND materials), and was filled to the top with deoxygenated Millipore water before transferred to an anaerobic glovebox. A headspace was created once in the glovebox (5% H_2 + 5% CO_2 + 90% N_2) by removing 10 mL of water. The vials were vortexed for one minute and then incubated in the dark at room temperature (25 °C). Triplicate vials were sacrificed for analysis. Before analysis, the vials were centrifuged for 15 min at 1500 rpm. The aqueous solution was removed for inorganic analysis including nitrite, nitrate and sulfate. The soil was analyzed for PETN following the acetonitrile-sonication extraction method (US EPA Method 8330).

2.4. Field pilot test

The pilot test consisted of the following 10 treatments (% by dry weight): a control (no amendment), 10% iron, 1%, 2% and 4% of D6390Fe20, 2% and 4% of ADM-298500, and 1%, 2% and 4% of brewers grain. Because the dry weights of soil were not known precisely, the final percentages of the amendments in the treatments were somewhat different from the objective values, at 1.19%, 2.63% and 4.37% for D6390Fe20, 2.32% and 5.81% for ADM-298500, and 1.33%,