



Degradation of 2,4-dinitrotoluene by persulfate activated with iron sulfides

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ABSTRACT

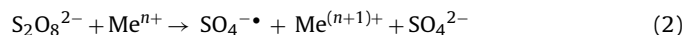
Of the many oxidants studied to date for subsurface remediation, persulfate ($S_2O_8^{2-}$) is particularly attractive for its stability under ambient conditions and high reactivity upon activation. In this study we evaluated a new approach to activate persulfate, namely using pyrite (FeS_2) or iron sulfide (FeS), with 2,4-dinitrotoluene (DNT) as a model contaminant. Pyrite was able to activate persulfate to degrade DNT. However, DNT degradation was rapidly halted presumably due to the low water solubility of pyrite and the presence of trace dissolved oxygen. In contrast, FeS was effective in activating persulfate to continuously and completely degrade DNT. Separate experiments with Fe^{2+} and HS^- suggest that Fe^{2+} , rather than HS^- , released from FeS was involved in persulfate activation and was necessary for rapid degradation of DNT. Further experiments show that reduction products of DNT were oxidized much faster than DNT by FeS -activated persulfate. These findings and their implications are discussed in the context of subsurface remediation strategies for hydrocarbons and reducible contaminants such as nitroaromatic compounds.

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1. Introduction

Over the last few decades, chemical oxidation of organic contaminants has been increasingly investigated as an *in situ* or *ex situ* remediation technology. H_2O_2 , $KMnO_4$, and O_3 are among the most well-examined oxidants in laboratory studies and field applications [1–6]. H_2O_2 has a high oxidation potential ($E^0 = 1.78$ V vs. SHE) and can degrade organic contaminants non-selectively. In soil, Fe^{2+} -bearing minerals can activate H_2O_2 and produce hydroxyl radical (OH^\bullet), a potent oxidant ($E^0 = 2.70$ V vs. SHE) involved in contaminant destruction [4]. However, H_2O_2 may be too reactive for subsurface remediation in some cases as it can be consumed during transport through soil and aquifer before reaching contaminants [5]. O_3 is a strong oxidant ($E^0 = 2.07$ V vs. SHE) that reacts somewhat selectively with electron-rich moieties [2]. However, O_3 is only sparingly soluble in water (~ 40 mg/L; [7]) and thus its *in situ* application may be limited by low delivery rates. In comparison, $KMnO_4$ ($E^0 = 1.68$ V vs. SHE) is a strong yet relatively soluble and stable oxidant, which makes it an attractive option [6]. Unfortunately, $KMnO_4$ reacts rather selectively (e.g., toward unsaturated moieties) which can limit its broad application [6].

In recent years, persulfate ($S_2O_8^{2-}$) has drawn increasing attention as an alternative for *in situ* oxidation of organic contaminants [9–20]. A strong oxidizing agent ($E^0 = 2.01$ V vs. SHE), persulfate is non-selective, soluble, and relatively stable at room temperature. Heat, transition metal ions (Me^{n+} , such as Fe^{2+}), and UV light can all activate persulfate to form the sulfate radical ($SO_4^{\bullet-}$), as shown in Eqs. (1) and (2). $SO_4^{\bullet-}$ is a thermodynamically stronger oxidant ($E^0 = 2.60$ V vs. SHE) than persulfate and is highly reactive towards a wide range of organic compounds [21,22].



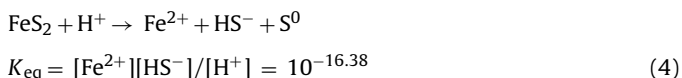
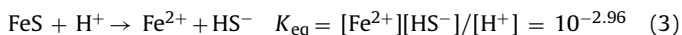
In a persulfate–water system, hydroxyl radical can also be formed and may participate in organic oxidation [13]. Destruction of organic contaminants, including methyl *tert*-butyl ether, benzene and alkylbenzenes, and chlorinated solvents by heat-activated $S_2O_8^{2-}$ has been demonstrated [8–10,13,16]. In addition, transition metal ions such as Ag^+ and Fe^{2+} have been used to activate persulfate for the oxidation of trichloroethene [11,12], 2,4-dichlorophenol [14,15], and other chlorinated phenols and polychlorinated biphenyls [17,18].

In a recent study we investigated the oxidation of polyvinyl alcohol (PVA) by persulfate activated with zero-valent iron ($Fe(0)$) [19]. We demonstrated that $Fe(0)$ could be a source of Fe^{2+} , which activated persulfate to form sulfate radical. In that study, we found the

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optimal persulfate-to-Fe(0) mole ratio was 1:1 and that PVA could be completely oxidized. We subsequently studied the degradation of nitroaromatic compounds (NACs) in a persulfate-Fe(0) system, using 2,4-dinitrotoluene (DNT) as a model compound. Unlike most compounds used in earlier persulfate work, DNT can also be rapidly reduced by Fe(0) [23]. We observed that, in an Fe(0)-persulfate system, DNT was transformed through a combination of reduction by Fe(0) and oxidation by Fe(0)-activated persulfate [24].

In contrast to Fe(0), iron sulfides, such as amorphous FeS, mackinawite (Fe_{0.93–0.96}S), troilite (FeS), greigite (Fe₃S₄), pyrite (FeS₂) and marcasite (FeS₂) are commonly formed in the subsurface through microbial activities and chemical weathering [25,26]. The ubiquity of iron sulfides in subsurface environments may represent an important advantage over Fe(0) for persulfate-based *in situ* remediation. Iron sulfides have been studied with respect to their ability to reductively transform contaminants including carbon tetrachloride [27], chlorinated ethenes [28–30], chlorinated pesticide [31], Cr(VI) [32–34], and 2,4,6-trinitrotoluene [35,36]. It is plausible that, similar to Fe(0), iron sulfides may activate persulfate to achieve *in situ* degradation of organic contaminants. Iron sulfides such as FeS and pyrite may activate persulfate by serving as precursors of dissolved or surface Fe²⁺ (i.e., adsorbed or structural Fe²⁺ at the mineral–water interface). The dissolution of amorphous FeS and pyrite can be expressed by the following equations [37]:



Based on the equilibrium constants (K_{eq} s), FeS is significantly more soluble than pyrite.

In this study, we investigated the degradation of DNT in the presence of persulfate and either FeS or FeS₂ to evaluate the potential of these iron sulfides for *in situ* and *ex situ* chemical oxidation. We chose DNT as the target contaminant because DNT was listed as a priority pollutant according to U.S. Environmental Protection Agency (EPA) [38]. The rates and extents of the degradation of DNT and its daughter products by iron sulfide-activated persulfate were assessed through batch experiments. Results and implications for *in situ* remediation are discussed, and potential application strategies for different types of organic contaminants are proposed.

2. Materials and methods

2.1. Chemicals

2,4-Dinitrotoluene (DNT, 97%), 2,4-diaminotoluene (DAT, 98%), 4-amino-2-nitrotoluene (4A2NT, 97%), 2-amino-4-nitrotoluene (2A4NT, 99%), Na₂S·9H₂O (>98%) and FeSO₄·7H₂O (>99%) were purchased from Aldrich (Milwaukee, WI). Na₂S₂O₈ (>98%) was acquired from Dong Yang Chemical Co. Ltd. (Seoul, Korea). HPLC-grade methanol was obtained from Burdick & Jackson (SK Chemicals, Ulsan, Korea). All chemicals were used as received.

Pyrite chips were acquired from Ward's Geology (Rochester, NY) and were pulverized and sieved to obtain fine particles of diameters less than 149 μm (–100 mesh). The pyrite has been reported to be 95% pure, with the remaining 5% being calcite [35]. FeS (100 mesh, 99.9%) was purchased from Aldrich (Milwaukee, WI). X-ray powder diffraction analysis showed that the FeS was poorly crystallized, though peaks of troilite and mackinawite were observed (data not shown). The specific surface areas of the pyrite and FeS were 0.143 ± 0.008 and 0.045 ± 0.008 m²/g, respectively, as determined by the Brunauer–Emmett–Teller (BET) method with N₂.

2.2. Batch oxidation experiments

Stock solutions of DNT (100 mg/L, or 0.55 mM) and persulfate (500 mg/L, or 2.6 mM) were prepared using deionized water and a magnetic stirrer (PC-420, Corning, Lowell, MA). For each batch experiment, 100 mL each of DNT and persulfate stock solutions were added simultaneously to a 500-mL Erlenmeyer flask, which was shaken at 180 rpm in a shaking water bath (HB-2053SW, Hanbaek Sci., Daejeon, Korea) at 22 ± 3 °C. The initial concentrations of DNT and persulfate were 50 mg/L and 250 mg/L, respectively. Flasks were prepared in duplicates for all experiments. To assess the ability of pyrite and FeS to activate persulfate, a per-determined mass of pyrite or FeS (0.02, 0.2, 0.5, and 1 g) was added to the DNT-persulfate solution. At different elapsed times, a 2-mL sample was collected from each flask, immediately passed through a 0.22-μm membrane filter (Millipore, MA), and quenched with 0.5 mL of methanol, an effective quenching agent for sulfate radical [17]. Samples were then shaken vigorously for 5 min using a vortex shaker to fully stop the reaction before chemical analysis. In order to analyze total organic carbon (TOC), KI was used as a quenching agent according to Liang et al. [11]. Controls without either pyrite/FeS or persulfate were run in parallel under identical conditions to assess the extents of DNT oxidation by persulfate alone and of DNT reduction by pyrite/FeS, respectively.

2.3. Chemical analysis

DNT, DAT, 4A2NT, and 2A4NT were analyzed using a Dionex Ultimate[®]-3000 HPLC (Sunnyvale, CA) equipped with a Dionex Acclaim[®] 120 guard column (4.3 × 10 mm) and an Acclaim[®] 120C-18 column (250 × 4.6 mm, 5 μm). A methanol–water mixture (50/50, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min for DNT, 4A2NT, and 2A4NT. The wavelength of the UV detector was set at 254 nm. Retention times for DNT, 4A2NT, and 2A4NT were 21.60, 10.12, and 11.26 min, respectively. For DAT, an acetonitrile–phosphate buffer (20 mM, pH 7.0, 30/70, v/v) was used as eluent at 1.0 mL/min. The wavelength of the UV detector was 224 nm and the retention time was 4.73 min for DAT. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, model TOC-V CPN, Japan). Solution pH and dissolved oxygen (DO) concentration were measured using an Orion[®] 5-Star meter (Thermo Fisher Scientific, Pittsburgh, PA). Concentrations of total dissolved iron were determined using the 1,10-phenanthroline method [39] and a UV–vis spectrophotometer (UVmini-1240, Shimadzu, Japan).

3. Results and discussion

3.1. Degradation of DNT by pyrite- and FeS-activated persulfate

Degradation of DNT in the presence and absence of persulfate and FeS/pyrite is shown in Fig. 1. DNT was not degraded by persulfate alone over 5 h under ambient conditions. In the persulfate-free control containing pyrite, approximately 30% of the DNT was removed in 30 min, after which the concentration of DNT in water remained constant. No intermediates or products were detected at any time except for traces of 4A2NT (<0.3 mg/L) at 180 and 240 min (data not shown). These results indicated that most of DNT removal by pyrite was probably due to sorption to pyrite surface. The introduction of pyrite into DNT solution dropped solution pH abruptly from 5.6 to 2.5. If pyrite had dissolved according to Eq. (4), then the solution pH should have increased due to proton consumption. The pH decrease suggests that the sulfide released was oxidized to sulfate, as shown in Eq. (5). In the DNT-free control,

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