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Degradation of 1,4-dioxane via controlled generation of radicals by pyrite-activated oxidants: Synergistic effects, role of disulfides, and activation sites

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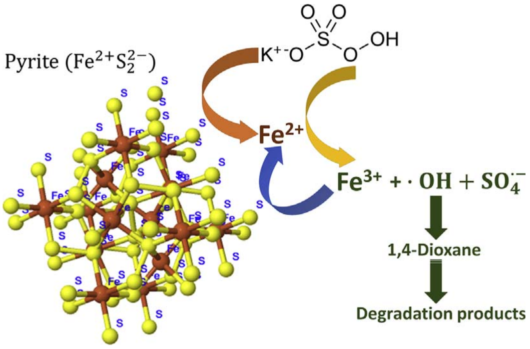
GRAPHICAL ABSTRACT


Pyrite ($Fe^{2+}S_2^{2-}$)
$K^+ {}^-O$
OH
Fe^{2+}
$Fe^{3+} + \cdot OH + SO_4^{\cdot -}$
1,4-Dioxane
Degradation products

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ABSTRACT

The controlled generation of radicals is an effective way to improve the stoichiometric efficiency of oxidants, particularly when treating highly recalcitrant contaminants. In this study, an innovative oxidation system was used to degrade extremely recalcitrant 1,4-dioxane. This system was based on a combination of pyrite, an abundant mineral used as a slow-release source of iron, and peroxymonosulfate (PMS). In addition, other oxidants, including hydrogen peroxide and peroxydisulfate, and their conditions were examined. PMS had the highest degradation performance of the oxidants tested. Near-100% degradation of 1,4-dioxane (50 mg L^{-1}) was achieved after 40 min using PMS; the corresponding degradation rates with peroxydisulfate and hydrogen peroxide were around 50% and 15%, respectively. The production of hydroxyl radicals and sulfate radicals by pyrite-activated PMS was confirmed by electron paramagnetic resonance. Neither solid pyrite nor dissolved Fe^{2+} or Fe^{3+} was directly involved in the degradation. Instead, the Fe^{2+} generated from pyrite oxidation activated PMS homogeneously. Quenching tests and the rapid degradation of nitrobenzene show that hydroxyl radicals were the major active species produced by pyrite-PMS. In contrast to the significant scavenging effect of Cl^- (3.0 mM) on Co^{2+}-PMS, no significant Cl^- (≤ 10 mM) scavenging was observed on pyrite-PMS. These results

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suggest that the use of pyrite-PMS mitigates the scavenging effects of Fe^{2+} and Cl^-, and, therefore, may increase the application of iron-based materials and PMS in the water treatment industry.

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1. Introduction

1,4-Dioxane ($C_4H_8O_2$, 1,4-D, Fig. S1), a cyclic compound containing two symmetrically reversed ether linkages, has been widely used as a stabilizer for chlorinated solvents, such as 1,1,1-trichloroethane [1]. It is also formed as a by-product during the fabrication of many consumer products [2]. Because of its toxicity, 1,4-D is considered to be an emerging contaminant and is classified as a Group 2B carcinogen by the International Agency for Research on Cancer. As a result of the improper disposal of industrial waste and the release of chlorinated solvents, 1,4-D is ubiquitous in environmental matrices, particularly in groundwater and soil [3]. As of 2007, over 31 sites on the EPA National Priorities List have been determined to contain 1,4-D [4]. Recent data show that 1,4-D is present at concentrations higher than $10\,mg\,L^{-1}$ in some polluted groundwater [5].

Because of its physical and chemical characteristics, 1,4-D contamination is difficult to resolve. For example, 1,4-D has a low Henry's law constant ($4.88 \times 10^{-6}\,atm\,m^3\,mol^{-1}$), a low octanol-water partition coefficient (−0.27), and is miscible with water [4]. These properties inhibit the removal of 1,4-D by volatilization and adsorption, and facilitate its rapid migration in water and soil. The symmetrical ether linkages stabilize 1,4-D, and are resistant to both biologically-mediated degradation and conventional chemical oxidation [3].

Advanced oxidation processes (AOPs), based on highly oxidative radicals, have been shown to effectively degrade 1,4-D. In addition to electrooxidation approaches [6,7], ultraviolet (UV) light-promoted hydrogen peroxide (H_2O_2) and ozone-promoted H_2O_2 are two commonly used hydroxyl radical ($\cdot OH$)-based AOPs for the ex-situ treatment of 1,4-D [8]. Although these processes are capable of degrading 1,4-D, they are not suitable for in-situ treatments. For UV-promoted treatment, good light transmission is necessary to ensure satisfactory performance. In addition, the generation of UV and ozone is costly, which limits the use of these techniques. Instead of UV activation, radicals such as $\cdot OH$ and sulfate radicals ($SO_4^{\cdot -}$) can be generated using Fe^{2+} as an activator (Eqs. 1–3) [9,10]. These oxidative combinations have shown great promise for the decontamination of chlorinated solvents [11]. Compared with UV activation, iron is significantly more cost-effective and suitable for in-situ decontamination. However, the use of Fe^{2+} has significant drawbacks. Firstly, Fe^{2+} is unstable; if Fe^{2+} is oxidized to ferric species, such as iron oxides or slurries, its reactivity is significantly reduced [12]. Secondly, the production of radicals is difficult to control because of the rapid reaction of Fe^{2+} with oxidants, particularly peroxymonosulfate (PMS, Eq. (3)), resulting in low radical utilization efficiency, particularly when high levels of scavengers are present [13]. Lastly, Fe^{2+} reacts rapidly with both $\cdot OH$ (Eq. (4)) [14] and $SO_4^{\cdot -}$ (Eq. (5)) [15], and therefore may act as a radical scavenger, particularly for $SO_4^{\cdot -}$, when present in excess [16,17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad k = 76\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\cdot -} + SO_4^{2-} \quad k = 27 - 32 M^{-1}\ s^{-1} \tag{2}$$

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{\cdot -} + OH^- \quad k = 3.0 - 3.56 \times 10^4\ M^{-1}\ s^{-1} \tag{3}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad k = 4.3 \times 10^8\ M^{-1}\ s^{-1} \tag{4}$$

$$Fe^{2+} + SO_4^{\cdot -} \rightarrow Fe^{3+} + SO_4^{2-} \quad k = 4.6 \times 10^9\ M^{-1}\ s^{-1} \tag{5}$$

Pyrite (FeS_2) is an abundant sulfide mineral containing structural Fe^{2+}, and has been proposed as an electron donor for the reductive removal of contaminants [18] and as an activator of either oxygen [19] or peroxides [20–22] to produce radicals. The reactivity of pyrite in Fenton-like reactions mainly results from the controlled release of iron that then reacts with oxidants via a Harber-Weiss-like mechanism. In the present study, we evaluated the activity of pyrite in the degradation of 1,4-D via the activation of three common oxidants: PMS, H_2O_2, and peroxydisulfate (PDS). Pyrite-PMS oxidation has not previously been evaluated in the degradation of pollutants. Thus, the present study emphasized the investigation of the dominant active species, activation sites, and the role of disulfide anions. To evaluate the applicability of pyrite-PMS, the effects of common water contaminants, including Cl^-, inorganic carbon, and organic matter, on pyrite-PMS activity were examined.

2. Materials and methods

2.1. *Chemicals and materials*

Anhydrous 1,4-D (99.8%), sodium PDS (≥98%), potassium PMS (as Oxone ($KHSO_5 \cdot 1/2KHSO_4 \cdot 1/2K_2SO_4$)), goethite (~35% Fe), iron(II) sulfide (FeS, 99.9% trace metals basis), and nanoparticulate Fe_3O_4 (50–100 nm, 97% trace metals basis) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%) was obtained from Aladdin Corporation (Shanghai, China) and purified according to the steps described in our previous study [23]. Iron disulfide (pyrite, 95%) was purchased from Strem Chemicals (Newburyport, MA, USA). A complete list of chemicals used is given in Note S1. Before use, the PMS content in Oxone was quantified iodometrically using a thiosulfate standard. All experimental solutions were prepared using ultrapure water with a resistivity of 18.0 MΩ cm from a Barnstead Easypure UV/UF purification system (Dubuque, IA, USA).

2.2. *Pretreatment and characterization*

Before use, the pyrite sample was passed through a 200-mesh sieve and washed with 0.1 M of HNO_3 under ultrasonication (Branson 8200, Danbury, CT, USA) to remove impurities formed by surface oxidation. During the cleaning process, a vacuum suction device with 0.45-µm cellulose nitrate membranes (Advantec MFS, Dublin, CA, USA) was used to remove the supernatant. The cleaned pyrite was vacuum dried at ambient temperature, stored in a Memmert electric oven (Schwabach, Germany) at 105 °C for no longer than two days. After two days, the pyrite was cleaned and dried according to the same procedures. A Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, Germany) with a Cu X-ray tube was used to characterize the crystallinity of the cleaned and used pyrite (Fig. S2). A Hitachi S-4800 field emission scanning microscope was used to determine the morphology of the cleaned pyrite (5–80 µm; Fig. S3). An ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific, Waltham, MA, USA) was used to investigate the S and Fe on the surface of pyrite and the spectra were record with a monochromatic Al Ka source. The iron content of the cleaned pyrite (45.6%) was quantified using an inductively coupled plasma optical emission spectrometer after dissolution in concentrated nitric acid. The atomic ratio of Fe and S on the surfaces of pyrite (~0.45) was determined using a Horiba EMAX energy dispersive X-ray detector (Table S1 and Fig. S4). The Brunauer-Emmett-Teller specific surface areas of the cleaned pyrite ($0.62\,m^2\,g^{-1}$), goethite ($15.1\,m^2\,g^{-1}$), and magnetite ($89.6\,m^2\,g^{-1}$) were analyzed using a micromeritics 3Flex surface characterization analyzer (Norcross, GA, USA). Iron(II) sulfide was passed through a 200-mesh sieve and cleaned according to the same procedure as for pyrite. In the following sections,

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