



Polyphosphate-enhanced production of reactive oxidants by nanoparticulate zero-valent iron and ferrous ion in the presence of oxygen: Yield and nature of oxidants

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ABSTRACT

The production of reactive oxidants from nanoparticulate zero-valent iron (nZVI) and ferrous ion (Fe(II)) in the presence of oxygen was greatly enhanced by the addition of tetrapolyphosphate (TPP) as an iron-chelating agent. Compared to other ligands, TPP exhibited superior activity in improving the oxidant yields. The nZVI/TPP/O₂ and the Fe(II)/TPP/O₂ systems showed similar oxidant yields with respect to the iron consumed, indicating that nZVI only serves as a source of Fe(II). The degradation efficacies of selected organic compounds were also similar in the two systems. It appeared that both hydroxyl radical ($\cdot\text{OH}$) and ferryl ion (Fe(IV)) are produced, and $\cdot\text{OH}$ dominates at acidic pH. However, at pH > 6, little occurrence of hydroxylated oxidation products suggests that Fe(IV) is a dominant oxidant. The degradation rates of selected organic compounds by the Fe(II)/TPP/O₂ system had two optimum points at pH 6 and 9, and these pH-dependent trends are likely attributed to the speciation of Fe(IV) with different reactivities.

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1. Introduction

Zero-valent iron (ZVI) is known to produce reactive oxidants such as hydroxyl radical ($\cdot\text{OH}$) and ferryl ion (Fe(IV)) when corroded by oxygen. The oxidative degradation of herbicides, aromatic compounds, alcohols, and arsenic has been demonstrated in aqueous solution containing nanoparticulate ZVI (nZVI) (or granular ZVI) in the presence of oxygen (Joo et al., 2004, 2005; Feitz et al., 2005; Katsoyiannis et al., 2008; Lee et al., 2014). The reaction of ferrous ion (Fe(II)) with oxygen also produces reactive oxidants under neutral pH conditions, leading to the oxidation of organic compounds (Keenan and Sedlak, 2008a). nZVI and Fe(II) with a supply of oxygen (i.e., the nZVI/O₂ and the Fe(II)/O₂ systems) have been proposed as potential agents for in situ chemical oxidation (ISCO) to rapidly oxidize refractory organic compounds in

groundwater. However, a major limitation of the nZVI/O₂ and the Fe(II)/O₂ systems was the low yield of reactive oxidants. The oxidant yields were only less than 10% with respect to nZVI and Fe(II) added (Keenan and Sedlak, 2008a). The yields from nZVI were no greater than those from Fe(II), indicating that the oxidant production from nZVI is mainly due to the oxidation of Fe(II) released from nZVI. The four-electron transfer from nZVI to oxygen (involving the direct conversion of oxygen to water) and the iron precipitation at neutral pH were responsible for the low oxidant yields.

The addition of iron-chelating agents such as oxalate, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid (NTA) enhanced the oxidant production from nZVI and Fe(II) by increasing the iron solubility (Seibig and Eldik, 1997; Keenan and Sedlak, 2008b; Belanzoni et al., 2009). In addition, the coordination of Fe(II) with these ligands appeared to alter the mechanism of the Fenton reaction to favor the production of $\cdot\text{OH}$ relative to Fe(IV). Polyoxometalate (POM) such as polyoxotungstate, polyoxosilicate, and polyoxomolybdate also increased the oxidant yields in the

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nZVI/O₂ and the Fe(II)/O₂ systems by mediating the electron transfer from nZVI to oxygen (i.e., changing the four-electron transfer to a two-electron transfer) as well as by forming soluble complexes with iron at neutral pH (Lee et al., 2008a). However, the use of organic ligands is problematic with chemical oxidation applications due to issues such as the scavenging of oxidants and the subsequent self-destruction by oxidation. POM, as an inorganic compound, is resistant to oxidation, but is known to undergo hydrolysis at neutral pH. The stability issue remains unresolved (Kyle, 1983; Jürgensen and Moffat, 1995; Lee et al., 2008a).

It was recently reported that tetrapolyphosphate (TPP) is a stable inorganic ligand that improves oxidant production from Fe(II) and nZVI (Wang et al., 2013, 2014). Effective degradation of atrazine and pentachlorophenol was demonstrated in nZVI/O₂ and Fe(II)/O₂ systems with TPP. In particular, atrazine degradation by the nZVI/O₂ system was dramatically enhanced in the presence of TPP, which could not be explained by the role of the released Fe(II)-TPP complexes. Therefore, it was suggested that TPP promotes electron transfer from the nZVI core to the surface-bound Fe(II), increasing the electron density available for oxygen activation (Wang et al., 2014). In spite of these studies, the oxidant yields have not been quantified in TPP-enhanced nZVI/O₂ and Fe(II)/O₂ systems. The quantitative measurement of oxidant yields can provide new insight into the mechanism of oxidant production. In addition, there has been little discussion on the nature of oxidants produced by those systems (especially, the possible generation of Fe(IV) species).

The primary objectives of this study were to quantify the oxidant yields from nZVI/O₂ and Fe(II)/O₂ systems with TPP and to explore the nature of oxidants produced by the systems. For these purposes, excess probe compounds were employed, and the formation of their oxidation products was quantified. In addition, the oxidative degradation of selected organic compounds at low concentrations was examined under different conditions. To test the practical applicability, some of the experiments were conducted in natural water and the possible effects of water constituents on the efficiency of the system are discussed.

2. Materials and methods

2.1. Materials

All chemicals were of reagent grade and were used as received without further purification except for 2,4-dinitrophenyl hydrazine (DNPH). DNPH was purified three times by recrystallization in acetonitrile. Chemicals used in this study include methanol, formaldehyde (HCHO), DNPH, benzoic acid, *para*-hydroxybenzoic acid (*p*-HBA), coumarin, 7-hydroxycoumarin (7-HC), cimetidine (CMT), acetaminophen (AAP), carbamazepine (CBZ), Reactive Black 5 (RB5), oxalic acid, EDTA, NTA, sodium polyoxotungstate (used as POM), sodium hexametaphosphate (HMP), ferric perchlorate, ferrous sulfate, hydrogen peroxide, sodium chloride, sodium bicarbonate, sodium hydroxide, perchloric acid, hydrochloric acid (all from Sigma–Aldrich Co.), acetonitrile (J.T. Baker Co.), Suwannee river humic acid (International Humic Substances Society), and sodium tetrapolyphosphate (International Laboratory Co.). All stock solutions were prepared in deionized water (18 MΩ cm Milli-Q water from a Millipore system). nZVI was synthesized by the aqueous-phase reduction of ferrous sulfate solution using sodium borohydride as a reducing agent; nZVI so produced forms aggregates of spherical single nanoparticles (10–80 nm). The detailed synthetic procedure is described elsewhere (Lee et al., 2008b). Stock solutions of nZVI and Fe(II) were freshly prepared prior to the experiments.

2.2. Experimental setup and procedure

All experiments were performed with 100 mL solutions (in 125 mL of Erlenmeyer flasks) open to the atmosphere at room temperature (22 ± 2 °C). The solution pH was initially adjusted using 1 N HClO₄ and 1 N NaOH solutions, and the pH variations were less than 0.1 units during the reaction for all experiments (polyphosphates partially serve as pH buffers). The reaction was initiated by adding an aliquot of nZVI or Fe(II) stock solution to a pH-adjusted reaction solution containing all other compounds (probe compounds, target organic compounds, iron-chelating agents including TPP, etc. depending on the experiment). The amount of nZVI and Fe(II) used was typically 0.168 mM as Fe (10 mg/L for nZVI). Samples were withdrawn using a 1 mL plastic syringe or a 10 mL glass syringe at predetermined timed intervals, and were immediately filtered with a 0.2-μm hydrophilic polytetrafluoroethylene syringe filter. For experiments needing deaeration, ultrapure nitrogen gas was bubbled through the reaction solution with a needle-type diffuser for 30 min prior to initiation and throughout the entire reaction.

In experiments to quantify oxidant yields, methanol was introduced as a probe compound to capture reactive oxidants (both •OH and Fe(IV)), and its oxidized product (HCHO) was analyzed (Keenan and Sedlak, 2008a). Typically, an excess amount of methanol (200 mM) was used to ensure that all oxidants were scavenged. Benzoic acid (10 mM) and coumarin (1 mM) were used as probe compounds for •OH, and their hydroxylated products (*p*-HBA and 7-HC, respectively) were analyzed (Joo et al., 2005; Louit et al., 2005).

For experiments using natural water, raw water was obtained from the Nak-Dong river (ND river water) and from an aquifer in the Jeon-Buk province (JB groundwater). The quality parameters of the natural water samples are summarized in the supplementary data, Table S1. The natural water samples were filtered with a 0.45-μm filter within 24 h after sampling and stored at 4 °C until use.

2.3. Analytical methods

The concentration of HCHO was measured by DNPH derivatization and subsequent HPLC analysis (UV absorbance detection at 350 nm) (Zhou and Mopper, 1990). *p*-HBA, 7-HC, CMT, AAP, and CBZ were also analyzed by HPLC with UV detection at 270, 320, 230, 241, and 285 nm, respectively. Separation was performed on an Agilent – Eclipse XDB C18 column (150 mm × 4.6 mm, 3.5 μm) using a binary mixture of 0.1% (w/w) aqueous phosphoric acid and neat acetonitrile as the eluent at a flow rate of 1.5 mL/min. RB5 was spectrophotometrically analyzed by measuring visible light absorbance at 597 nm. Total dissolved iron was analyzed by atomic absorption spectroscopy at 248.3 nm (AAnalyst 700, Perkin–Elmer Co.). The concentration of dissolved Fe(II) was quantified by the 1,10-phenanthroline method (Tamura et al., 1974).

3. Results

3.1. Oxidative transformation of methanol and benzoic acid

Methanol and BA were used as probe compounds for detecting reactive oxidants. To ensure that all of the oxidants were scavenged by the probe compound, an excess of probe compound was employed, and the major oxidized product was quantified. The production of HCHO and *p*-HBA (by the oxidation of methanol and BA, respectively) was monitored in the nZVI/O₂ and Fe(II)/O₂ systems with and without TPP at neutral pH (Fig. 1a and b). The concentrations of HCHO and *p*-HBA increased instantaneously in the initial stage of the reaction, and the increase gradually slowed over time. The nZVI/O₂ and the Fe(II)/O₂ systems without TPP produced

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