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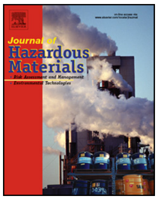

Oxidant production from corrosion of nano- and microparticulate zero-valent iron in the presence of oxygen: A comparative study

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HIGHLIGHTS

- Oxidants from zero-valent iron were quantified in the presence of oxygen and EDTA.
- The oxidant yields of nano- and microparticulate zero-valent iron were compared.
- Microparticulate zero-valent iron produced higher oxidant yields.
- The factors affecting the oxidant production from zero-valent iron were discussed.

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ABSTRACT

In aqueous solution, zero-valent iron (ZVI, Fe^0) is known to activate oxygen (O_2) into reactive oxidants such as hydroxyl radical and ferryl ion capable of oxidizing contaminants. However, little is known about the effect of the particle size of ZVI on the yield of reactive oxidants. In this study, the production of reactive oxidants from nanoparticulate and microparticulate ZVIs (denoted as nZVI and mZVI, respectively) was comparatively investigated in the presence of O_2 and EDTA. To quantify the oxidant yield, excess amount of methanol was employed, and the formation of its oxidation product, formaldehyde (HCHO), was monitored. The concentration of HCHO in the nZVI/O_2 system rapidly reached the saturation value, whereas that in the mZVI/O_2 system gradually increased throughout the entire reaction time. The mZVI/O_2 system exhibited higher yields of HCHO than the nZVI/O_2 system under both acidic and neutral pH conditions. The higher oxidant yields in the mZVI/O_2 system are mainly attributed to the less reactivity of the mZVI surface with hydrogen peroxide (H_2O_2) relative to the surface of nZVI, which minimize the loss of H_2O_2 by ZVI (i.e., the two-electron reduction of H_2O_2 into water). In addition, the slow dissolution of Fe(II) from mZVI was found to be partially responsible for the higher oxidant yields at neutral pH.

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1. Introduction

The corrosion of zero-valent iron (ZVI, Fe^0) by dissolved oxygen (O_2) in water produces reactive oxidants capable of oxidizing organic and inorganic contaminants. Previous studies have demonstrated that the ZVI/O_2 systems using granular or nanoparticulate ZVI (nZVI) can effectively oxidize various contaminants such as arsenite (As[III]), herbicides, phenolic compounds, chelating agents, and dyes [1–5]. It has also been reported that the oxidative stress induced by nZVI leads to the microbial inactivation [6,7].

The mechanism for the oxidant production by the ZVI/O_2 system involves the in situ formation of hydrogen peroxide (H_2O_2) and the subsequent Fenton reaction. As the first step, H_2O_2 is formed on the surface of ZVI by two-electron reduction of O_2 (reaction (1)). H_2O_2 so produced is either reduced to water by another two-electron transfer from ZVI (reaction (2) [8,9]), or is converted into reactive oxidants such as hydroxyl radical ($^\bullet$OH) and ferryl ion (Fe[IV]) by reaction with Fe(II) (i.e., Fenton reaction; reaction (3)).

$$Fe^0_{(s)} + O_2 \xrightarrow{2H^+} Fe(II) + H_2O_2 \qquad (1)$$

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$$Fe^0_{(s)} + H_2O_2 \xrightarrow{2H^+} Fe(II) + 2H_2O \quad (2)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^\bullet OH + OH^- \quad \text{or} \quad Fe(IV) + H_2O \quad (3)$$

The oxidation of Fe(II), the primary corrosion product of ZVI (from reactions (1) and (2)), also produces reactive oxidants under neutral pH conditions. Fe(II) reduces O_2 into H_2O_2 via a series of one-electron transfer (reactions (4) and (5)), and the subsequent Fenton reaction (reaction (3)) produces reactive oxidants [10,11].

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2{}^{\bullet -} \quad (4)$$

$$Fe(II) + O_2{}^{\bullet -} \xrightarrow{2H^+} Fe(III) + H_2O_2 \quad (5)$$

The ZVI/O_2 system is an interesting tool of activating O_2 for contaminant oxidation. However, the low yields of reactive oxidants can limit the application of this system. According to a previous study [12], the oxidant yields based on the dose of ZVI (i.e., $\Delta[\text{Oxidants}]/\Delta[Fe^0]$) are less than 10% in the nZVI/O_2 system, even if the theoretical maximum of the value is 100% when only reactions (1) and (3) are taken into account. It was also found that in the nZVI/O_2 system the production of oxidants at neutral pH values mainly results from the oxidation of Fe(II) by O_2 (reactions (4) and (5)) [12]. For the low oxidant yields, the loss of H_2O_2 by two-electron reduction on the surface of ZVI (reaction (2)) is the primary cause [12], and the passivation of ZVI surfaces and the co-precipitation of Fe(II) and Fe(III) species at neutral pH are also partially responsible [12,13]. In order to improve the oxidant production by the ZVI/O_2 system, several approaches such as the addition of iron-chelating ligands [4,14] or polyoxometalates [15,16], and the introduction of secondary metal (e.g., nickel–iron bimetal) [17] have been attempted.

The yields of reactive oxidants produced by nZVI in the presence of O_2 are relatively well-documented with influences of reaction parameters and additives [12,14,16]. However, the oxidant yields from microparticulate granular ZVI have not been explored. The objective of this study was to quantify and compare oxidant yields from nZVI and microparticulate granular ZVI (mZVI) in the presence of O_2 and EDTA, and to provide a mechanistic interpretation for the observations. A series of experiments was carried out using a probe compound, methanol that are known to form formaldehyde (HCHO) by the reaction with ${}^\bullet$OH or Fe(IV). The formation of HCHO and the dissolution of Fe(II) were examined under various conditions.

2. Materials and methods

2.1. Reagents and synthesis of nZVI

All chemicals were of reagent grade (obtained from Sigma–Aldrich Co., USA) and were used without further purification except for 2,4-dinitrophenyl hydrazine (DNPH). DNPH was recrystallized three times from acetonitrile prior to use. 18 MΩ cm Milli-Q water from a Millipore system was used to prepare solutions. Iron powder (obtained from Acros Organics Co., USA) smaller than 70 mesh was used as a source of mZVI; the average particle size of mZVI was approximately 95 μm. nZVI was synthesized by aqueous-phase reduction of ferrous sulfate solution using sodium borohydride as a reducing agent, and the details are described elsewhere [6,18]. nZVI so produced exhibits chain-shaped aggregates of spherical nanoparticles of which average diameter is approximately 35 nm [6]. TEM and SEM images of nZVI and mZVI are presented in Fig. S1 (the supplementary data). The suspension of nZVI was prepared daily and dried at room temperature (22 ± 2 °C) prior to use. The stock solution of ferrous sulfate (50 mM) was also prepared daily in 0.1 mM HCl solution.

2.2. Measurement of oxidant yields

In order to detect reactive oxidants, methanol was used as a probe compounds. An excess amount of methanol (200 mM) was employed to ensure that all the oxidants (i.e., ${}^\bullet$OH and Fe(IV)) were scavenged, and the concentration of its oxidation product (HCHO) was monitored. Methanol has a low affinity for surfaces of metal oxides and is present as a neutral species over the pH range of interest. It appears that methanol reacts with both ${}^\bullet$OH and Fe(IV) to produce a stoichiometic amount of HCHO [12]. More details regarding the measurement of oxidant yields (the selection of probe compounds and the analyses of their oxidation products) are described in previous studies [12,16,17].

2.3. Experimental setup and procedure

All experiments were carried out at room temperature (22 ± 2 °C) in 100 mL solution open to the atmosphere. For some experiments needing deaeration, the solution was sparged with ultrapure N_2 gas using a needle-type diffuser for 10 min prior to the reaction and during the entire experiment. The solution pH for experiments conducted under acidic condition (pH 3) was adjusted using 1 N $HClO_4$ solution (perchlorate ion is inert). The solution pH of neutral solutions (pH 7) was buffered with 1 mM piperazine-*N*,*N*′-bis(ethanesulfonic acid) (PIPES) [19]. For all experiments, the pH variations were less than 0.2 units during the reaction. The experiments were initiated by adding pre-weighed nZVI or mZVI powder to a pH-adjusted solution. The dose of nZVI and mZVI added was typically 0.25 mM (14 mg/L) as Fe. Samples were withdrawn using a 10 mL glass syringe at predetermined timed intervals and filtered immediately through a 0.22-μm nylon filter. All experiments were carried out at least in triplicate, and the mean values and standard deviations are presented. The oxidation reduction potential in the ZVI/O_2 systems in the absence and presence of EDTA was monitored (Fig. S2 in the supplementary data).

2.4. Analytical methods

The concentration of HCHO was determined using the DNPH derivatization followed by HPLC analysis with UV absorbance detection at 350 nm [20]. Separation was performed on a Dionex – Acclaim C18 column (250 mm × 4.6 mm, 5 μm) using 10 mM aqueous solution of nitric acid and neat acetonitrile as the eluent at 1.0 mL min^{-1} flow rate. Fe(II) was analyzed spectrophotometrically using the 1,10-phenanthroline method [21], and for the analysis of total iron concentration, Fe(III) was reduced to Fe(II) with hydroxylamine prior to the analysis of Fe(II). The X-ray diffraction (XRD) patterns were recorded with a diffractometer (Bruker, D8 Advanced).

3. Results

3.1. Oxidant production from Fe(II), nZVI, and mZVI

The production of reactive oxidants and the iron dissolution by the Fe(II)/O_2, the nZVI/O_2, and the mZVI/O_2 systems were examined in the absence and presence of EDTA under acidic (pH 3, Fig. 1) and neutral (pH 7, Fig. 2) conditions. The formation of HCHO, Fe(II), and total dissolved iron was monitored during the reaction time of 4 h in each system.

At pH 3, in the absence of EDTA, less than 15 μM of HCHO was produced from each system, exhibiting increasing yields in the order of Fe(II) < nZVI < mZVI (Fig. 1a). In the presence of EDTA, the production of HCHO was greatly enhanced; the concentrations of HCHO after 4 h reaction were 54, 55, and 84 μM for Fe(II), nZVI, and mZVI, respectively. The HCHO concentration in the nZVI/O_2 system

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