Short communication

Effect of magnetic field on the zero valent iron induced oxidation reaction

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ABSTRACT

The magnetic field (MF) effect on the zero valent iron (ZVI) induced oxidative reaction was investigated for the first time. The degradation of 4-chlorophenol (4-CP) in the ZVI system was employed as the test oxidative reaction. MF markedly enhanced the degradation of 4-CP with the concurrent production of chlorides. The consumption of dissolved O_2 by ZVI reaction was also enhanced in the presence of MF whereas the competing reaction of H_2 production from proton reduction was retarded. Since the ZVI-induced oxidation is mainly driven by the in situ generated hydroxyl radicals, the production of OH radicals was monitored by the spin trap method using electron spin resonance (ESR) spectroscopy. It was confirmed that the concentration of trapped OH radicals was enhanced in the presence of MF. Since both O_2 and Fe^0 are paramagnetic, the diffusion of O_2 onto the iron surface might be accelerated under MF. The magnetized iron can attract oxygen on itself, which makes the mass transfer process faster. As a result, the surface electrochemical reaction between Fe^0 and O_2 can be accelerated with the enhanced production of OH radicals. MF might retard the recombination of OH radicals as well.

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1. Introduction

Iron is abundant and low cost material and it has been widely used in water treatment as flocculant or Fenton reagent in a salt form. For the past decade, the metallic iron, which is commonly referred as zero-valent iron (ZVI), has been intensively studied as a new reactive material for water treatment. The oxidation of iron (i.e., corrosion) can be coupled with the reductive conversion of a variety of organic and inorganic pollutants in water. Although the reductive conversion in the ZVI process has been extensively studied [1–4], its applications to the oxidative conversion of aquatic contaminants were only recently recognized [5–9]. The ZVI-induced oxidative transformation is based on the reductive activation of O_2 by ZVI ($E^0(Fe^{2+}/Fe^0) = -0.44\,V_{NHE}$), which leads to the generation of H_2O_2 which subsequently decomposes into OH radicals through Fenton type reaction.

Many methods have been tested to increase the efficiency of the ZVI-based treatment with combining the ZVI redox reactions with other processes. The addition of H_2O_2 [10] or electron shuttles [11–13], UV irradiation [14], ultrasonication [15], and microwave radiation [16] were coupled with the ZVI reaction to enhance the degradation of aquatic contaminants. However, the overall process efficiency still needs to be improved significantly.

Here we focus on the possible effects of magnetic field (MF) on the ZVI treatment process for the first time. The presence of MF may affect the ZVI-based chemical reactions through various mechanisms. Kishioka et al. reported that the dissolution of O_2 in water is enhanced under MF [17,18]. Because of the paramagnetic nature of oxygen molecule, it is reasonable to consider that O_2 would be attracted by magnetic force. Another effect is to increase the dissolution of iron. Rakoczy reported that rotating magnetic field enhances solid dissolution process [19,20]. MF can also influence the lifetime of radicals by inhibiting their recombination reactions through the interaction with electron spins [21]. Krzemieniewski et al. found that MF enhances the Fenton process [22,23]. Hao et al. reported as well that MF accelerates the decomposition rate of H_2O_2 and the conversion rate of Fe^{2+} in Fenton reaction [24]. The MF-enhanced effect in Fenton reaction was ascribed to the suppression of recombination between radical pairs. ZVI-induced oxidative processes are essentially in situ Fenton reaction and they can be affected by MF as well. In this study, we investigated the effects of MF on ZVI oxidative reaction by selecting 4-chlorophenol (4-CP) as a model substrate.

2. Experimental

2.1. Chemicals and materials

Chemicals used in this study include: 4-chlorophenol (4-CP, Sigma), sodium chloride (Samchun), perchloric acid (Aldrich), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, Sigma), all of which were of reagent grade and used as received. Deionized water used was ultrapure (18 MΩ cm) and prepared by a Barnstead purification system. Iron powder (100 mesh) was purchased from Fischer Scientific

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and used as received. The magnetic field was established by positioning a thin cylindrical magnet (1 cm diameter × 0.25 cm high) under the reactor. The magnetic flux density was measured by Teslameter (PHYWE, Germany) to be about 40 mT at the bottom of the ZVI reactor.

2.2. Experimental procedure

Typical iron powder slurry in water was prepared at a concentration of 0.2 g/L. Aliquots of 4-CP stock solution (2 mM) were then added to make a desired concentration (typically 0.1 mM). The iron powder slurry was unbuffered and air-equilibrated. The initial pH of the slurry was adjusted to 2.0 with using $HClO_4$ solution. The reaction was carried out in a 120 mL glass bottle that was slowly stirred on a rotary shaker, and the magnet was fixed under the center of the reactor. Because of the magnetic force, iron powder was concentrated at the bottom of the reactor over the magnet. The reactor was either exposed to air to continuously provide dissolved oxygen or sealed with a rubber septum when hydrogen and oxygen gas in the headspace were analyzed. Sample aliquots of 1 mL were withdrawn at a regular time interval from the reactor with a syringe, passed through a 0.45 μm PTFE filter (Millipore), and injected into a 2 mL sampling vial. The headspace gas was sampled from the sealed reactor using a gas-tight syringe. Multiple experiments were carried out for a given condition to confirm the reproducibility.

2.3. Analysis

Quantitative analysis of 4-CP was done by using a high performance liquid chromatograph (HPLC Agilent 1100) equipped with a C-18 column (Agilent Zorbax 300SB) and a diode-array detector. The eluent consisted of a binary mixture of 0.1% phosphoric acid and acetonitrile (8:2, v/v). Quantification of chloride production from the degradation of 4-CP was performed by using an ion chromatograph (IV, Dionex DX-120). The IC system was equipped with a Dionex IonPac AS-14 (for anion analysis) and a conductivity detector. The quantitative analyses of hydrogen and oxygen were performed by a gas chromatograph (GC, HP6890N) with a thermal conductivity detector using N_2 as carrier gas.

The in situ generation of •OH in the ZVI slurry was measured by the spin trap method. The spin trapping employed diamagnetic DMPO as a spin trap to generate a stable paramagnetic spin-adduct with OH radical as shown in reaction 1 [25]. The in situ production of the spin-adducts in ZVI oxidative reaction was monitored by electron spin resonance (ESR) spectroscopy. An ESR spectrometer (Jeol JES-FA100) was operated under the conditions of MF 324 ± 15 mT, power 10 mW, modulation frequency 100 kHz, sweep time 30 s, and time constant 0.03 s.

$$\bullet OH + DMPO \rightarrow DMPO–\bullet OH \, (radical \, OH \, adduct) \tag{1}$$

3. Results and discussion

The effects of MF on the ZVI-induced oxidative process were investigated with monitoring the degradation of 4-CP in aqueous iron slurry. The ZVI-induced oxidation is initiated via reactions 2–3.

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \tag{3}$$
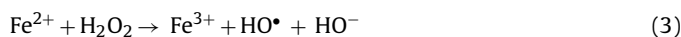
It is well established that 4-CP is degraded via the OH radical mediated pathway in the ZVI system [26]. Fig. 1(a) shows that MF clearly enhanced the degradation of 4-CP although the presence of MF made the iron particles highly aggregated with keeping them from dispersing in the solution. The MF-induced aggregation of iron powder should not be a practical problem considering that most of
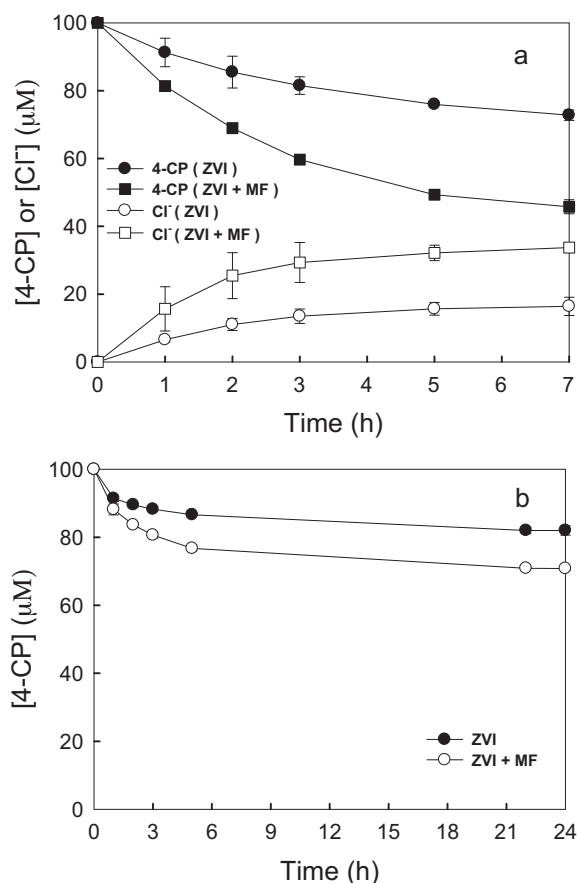

Fig. 1. (a) The degradation of 4-CP and the accompanying production of chlorides in ZVI slurry open to the air with or without magnetic field ([ZVI] = 0.2 g/L, pH_i 2.0). (b) The degradation of 4-CP in the ZVI reactor closed with a rubber septum (headspace = 5 mL, [ZVI] = 0.2 g/L, pH_i 2.0).

ZVI applications employ the packed iron powder. With MF alone in the absence of ZVI, the removal of 4-CP was completely absent. This excludes any possibility of the direct magnetic effect on 4-CP under the ambient experimental condition. The concurrent production of chloride indicates that 4-CP removal was not the adsorption on ZVI surface, but the degradation.

We first considered the possibility that this MF effect can be ascribed to more dissolved O_2 in the presence of MF. It was previously reported that more O_2 can be dissolved into water from air by a magnetic force acting on oxygen molecules [17,18]. Fig. 1(b) compares the ZVI-induced degradation of 4-CP in a closed reactor with and without MF where no additional oxygen can be supplied from the ambient air. The MF effect was also clearly observed until the degradation reaction stopped (around at 22 h) even when the total amount of O_2 was limited in the closed reactor. This indicates that the MF effect should not be related with higher concentration of dissolved O_2. The previous observation [17,18] that more O_2 was dissolved in water in the presence of MF was done with much higher magnetic field density (around a few T) while the present work was done under 40 mT.

The ZVI oxidative reaction is initiated by the electron transfer from Fe^0 to dissolved O_2 and therefore the mass transfer of O_2 onto the ZVI surface is critical. Since both oxygen and Fe^0 are paramagnetic, the diffusion of O_2 onto the iron surface might be accelerated by a magnetic force. The magnetized iron can attract oxygen on itself, which makes the mass transfer process faster. As a result, the surface electrochemical reactions can be enhanced under MF. To further test the MF effect on the related chemical reactions, the consumption of O_2 (via reaction (2)) and the generation of H_2 (reac-
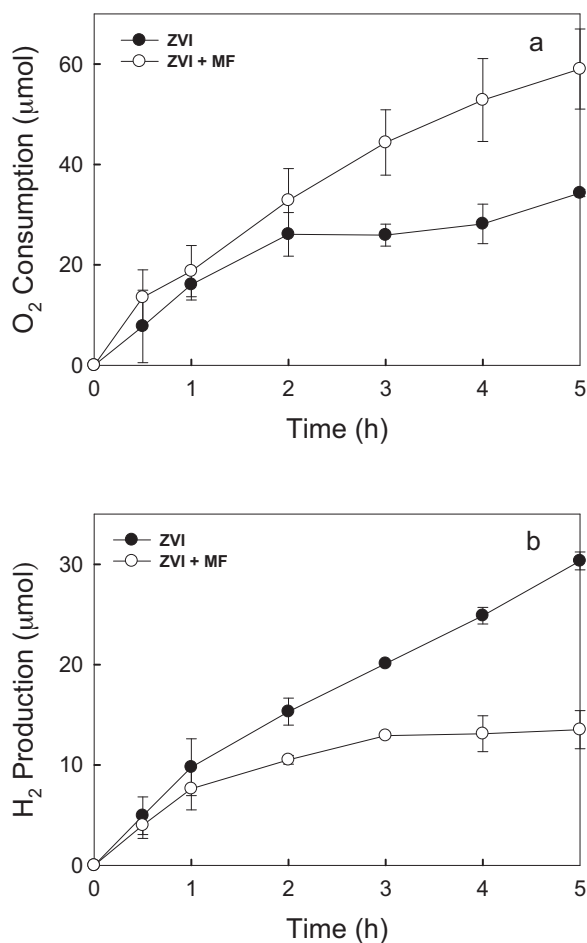
Fig. 2. Time profiles of (a) the consumption of O_2 and (b) the production of H_2 in the headspace of a closed ZVI reactor with or without magnetic field ([ZVI] = 0.2 g/L, pH_i 2.0).

Fig. 3. (a) ESR spectra of DMPO–•OH radical adduct generated in situ in the aqueous slurry of ZVI with or without magnetic field. The reaction time was 5 min. (b) Time profiles of the production of the DMPO–•OH radical adduct where were obtained with or without magnetic field ([ZVI] = 0.5 g/L, [DMPO] = 0.3 M, pH_i 2.0).

tion (4)) were monitored in the aqueous slurry of ZVI as a function of time in the absence and presence of MF (Fig. 2). The reducing power of ZVI continuously consumes dissolved O_2 and depletes O_2 in the reactor headspace. On the other hand, ZVI can reduce water (or protons) with producing H_2.

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{4}$$

Fig. 2 shows the in situ consumption of O_2 and production of H_2, which were simultaneously monitored in a ZVI reactor sealed with a rubber septum. The presence of MF clearly enhanced the consumption of O_2 but inhibited the production of H_2 on the contrary. It should be noted that both oxygen molecules and protons are competing electron acceptors (oxidants) of Fe^0 (reaction (2) vs (4)). Therefore, when the reaction between Fe^0 and paramagnetic O_2 is enhanced by the magnetic force, the reaction of Fe^0 with protons should be suppressed instead. The behavior shown in Fig. 2 implies that MF magnetizes ZVI and subsequently attracts paramagnetic oxygen molecules onto the surface region with accelerating the rate-limiting mass transfer. The enhanced reduction of O_2 on ZVI should lead to the enhanced production of OH radicals via reactions (2) and (3).

The spin trap experiment done with ESR provides a direct evidence for that MF enhances the generation of OH radicals on ZVI surface. The ESR spectra shown in Fig. 3(a) show the clear distinction between ZVI alone and ZVI+MF systems. The characteristic ESR signal (a quartet signal with 15 gauss spacing) for the trapped OH radicals (DMPO–•OH) clearly appeared in the presence of MF
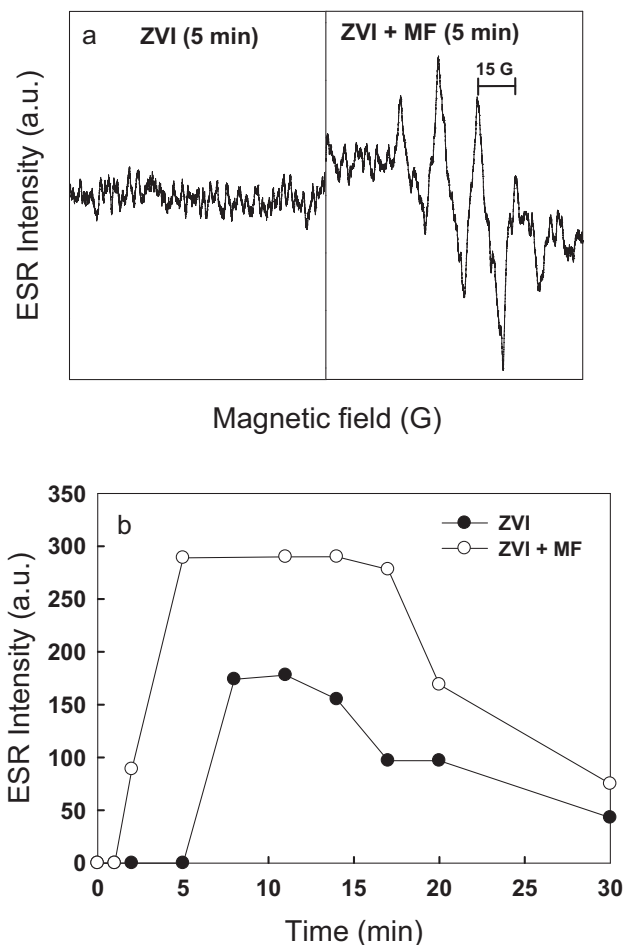
whereas that was not observed in the absence of MF. The time profiles of the ESR signal intensity (Fig. 3(b)) also show that the production of OH radicals started earlier and remained higher throughout the ZVI reaction in the presence of MF. Therefore, the positive effects of MF on the ZVI reaction were confirmed by both chemical reaction kinetics (Figs. 1 and 2) and spectroscopy (Fig. 3).

The enhanced production of OH radicals in the ZVI + MF system should be ascribed to not only the enhanced mass transfer of O_2 but also the retarded recombination of active radical species in the presence of MF [21,27–30]. The in situ generated OH radicals should be also influenced by a magnetic force. Radicals with non-paired electrons form radical pairs in an electron spin-correlated singlet or triplet state. The recombination reaction between radicals takes place in singlet state. MF should have a larger effect on the radical recombination in the ZVI system than the homogeneous Fenton system since OH radicals are generated on the iron surface and the recombination of surface radicals is more favored than in the homogeneous phase. It is well known that MF has an influence on the spin state of radical pairs [31]. For example, it was reported that the recombination of neutral organic radicals is markedly retarded in the presence of MF of 21 mT [29], which is comparable to the MF density employed in this study (40 mT). The retarded recombination of OH radicals should lead to the enhanced oxidation kinetics, which is supported by the present observation. Although the interesting phenomenon of MF effect was identified in this study, more thorough investigation should be needed to understand the MF

effects on the ZVI process in detail. Incidentally, the application of MF in the ZVI process can be also combined with other physicochemical methods (*e.g.*, sonication, UV irradiation), which can be the subject of further studies.

4. Conclusion

This study observed that the application of MF on the ZVI slurry markedly enhanced the oxidative degradation under air equilibrated condition. The MF effects can be briefly summarized as follows:

(1) The ZVI-induced oxidative degradation of 4-CP was accelerated along with the enhanced consumption of O_2 in the presence of MF. The enhanced oxidation should be ascribed to the production of more OH radicals, which was experimentally confirmed by the ESR spin trap method.
(2) Both Fe^0 and O_2 are paramagnetic, which can be influenced by magnetic force. The magnetized iron can attract paramagnetic oxygen molecules on the surface with facilitating the mass transfer process. In addition, the recombination of paramagnetic radicals can be retarded under MF with extending their lifetime.

Acknowledgements

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