Reduction of nitroaromatic pesticides with zero-valent iron

Young-Soo Keum, Qing X. Li *
Department of Molecular Biosciences and Bioengineering, University of Hawaii, 1955 East-West Road, Ag Sci 218, Honolulu, HI 96822, USA

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Abstract

Reduction of eleven nitroaromatic pesticides was studied with zero-valent iron powder. Average half-lives ranged from 2.8 to 6.3 h and the parent compounds were completely reduced after 48–96 h. The di-nitro groups of the 2,6-dinitroaniline herbicides were rapidly reduced to the corresponding diamines, with a negligible amount of partially reduced monoamino or nitroso products. Low levels of de-alkylated products were observed after 10 days. The nitro group of the organophosphorus insecticides was reduced dominantly to the monoamines but in a slower rate than the 2,6-dinitroanilines. A trace amount of oxon products was found. Reduction of nitro to amino was also the predominant reaction for the diphenyl ether herbicides. Aromatic de-chlorination and de-alkylation were minor reactions. These amine products were more stable than the parent compounds and 60% or more of the amines were detected after two weeks. Humic acid decreased the reduction rates of pendimethalin, and dichlone (a known quinone redox mediator) counteracted the effect of humic acid on the reactivity. Storage of iron powder under air decreased the reactivity very rapidly due to iron oxidation. Repeated use of iron powder also showed similar results. The reduced activity of air-oxidized iron was recovered by purging with hydrogen, but not nitrogen. Integration of iron powder with hydrogen- and quinone-producing microbial technologies may be a viable mean for remediation of highly oxidized xenobiotics in the environment.

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1. Introduction

Reductive technologies have been extensively studied for the removal of highly oxidized chemicals, particularly polyhalogenated chemicals from contaminated sites. Those chemicals include polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated biphenyls (PCBs) (Adriaens et al., 1996; Burris et al., 1996; Wang and Zhang, 1997; Woods et al., 1999; Kao et al., 2001), pesticides (Sayles et al., 1997; Eykholt and Davenport, 1998; Ghauch et al., 1999, 2001; Ghauch and Supitil, 2000; Loch et al., 2000; Ghauch, 2001), halogenated phenols (Kim and Carraway, 2000), nitroaromatics (Hundal et al., 1997; Klausen et al., 2001), and polychloroalkane (Loraine, 2001). Various types of reducing agents exist in the environment, especially in anaerobic sediment and soil (Kao et al., 2001). Studies were done with natural and synthetic reductants such as zero-valent metal (Adriaens et al., 1996; Arienzo et al., 2001), metal sulfide (Butler and Hayes, 1998; Loch et al., 2000), quinone (Adriaens et al., 1996; Kao et al., 2001) and vitamin B12 (Burris et al., 1996; Glod et al., 1997).

Iron (Fe^{2+} or Fe^{3+})-catalyzed Fenton reaction is a widely accepted remediation technology to decompose recalcitrant pollutants including PCDDs (Kao and Wu, 2000; Arienzo et al., 2001). Zero-valent iron is also employed in many environmental reclamation projects as a permeable reactive barrier (US EPA, 1997). Zero-valent iron-based reductive methods can be applicable to...
non-halogenated pesticides (Ghauch, 2001; Ghauch et al., 2001), PCDDs (Kluyev et al., 2002) and azo dye (Nam and Trantnyek, 2001). However, corrosion of zero-valent iron produces various kinds of oxide, hydroxide, ferrous and/or ferric ions. Under oxygen-limited conditions such as groundwater, sediment and/or deep soil, hydrogen and electron are produced with ferrous conditions such as groundwater, sediment and/or deep oxide, ferrous and/or ferric ions. Under oxygen-limited zero-valent iron produces various kinds of oxide, hydrous and electron can enhance the contaminant degradation via Fenton reaction (He et al., 2002), formation of oxide layer generally prevents the adsorption of contaminants on fresh iron surface and results in an inhibition of reduction reaction. Acid washing is generally used to remove such an oxide and hydroxide layer (Lavine et al., 2001), but the recovery of reductive activity of oxidized iron surface is not well understood.

The reactivity is often determined by surface-related properties including specific surface area of iron (Wang and Zhang, 1997) and adsorption coefficient of contaminants (Kim and Carraway, 2000) because the reaction occurs on the surface. Compounds that adsorb on the iron surface competitively with contaminants can affect the reductive removal of contaminants. Humic acid, a ubiquitous natural organic material (NOM), can be adsorbed easily on iron surface, and consequently, inhibits contaminant remediation (Trantnyek et al., 2001). Humic acid may also enhance the reaction via a redox mediation mechanism (Dunnivant et al., 1992). The effects of humic acid on the reduction of nitroaromatic compounds were not well studied. Simple nitroaromatic compounds were reduced rapidly with zero-valent iron to the anilines as a stable product (Klausen et al., 2001). Parathion, having a nitrophenyl group, was also reduced rapidly with zero-valent iron (Ghauch et al., 1999), however, reduction products were not identified. It is not important to understand the effects of environmental factors such as humic acid, atmospheric oxidation or repeated use of iron powder on the reduction processes and kinetic rates, and to identify reaction intermediates and products. Few studies have been done on the reductive removal of nitroaromatic pesticides. In this study, 11 pesticides, for which reductive remediation studies were not found, were selected to represent the wide structural diversity and reactivity of nitroaromatic pesticides. Effects of humic acid, a quinone mediator, hydrogen purging, and atmospheric oxidation and repeated use of iron powder on the zero-valent iron-catalyzed reduction were studied.

2. Materials and methods

2.1. Reagents

The 11 pesticides were (a) 2,6-dinitroaniline herbicides of benfluralin, ethalfluralin, nitrалin, oryzalin, pendimethalin and trifluralin, (b) diphenyl ether herbicides of bifenox, nitrofen and oxyfluorfen, and (c) organophosphorus insecticides of fenithrothion and methyl parathion (Fig. 1). The purity of these pesticides was 99% or higher. 2,3-Dichloro-1,4-napthoquinone (dichlorone, 98% purity) was obtained from the US Environmental Protection Agency (US EPA) (Triangle Park, NC). Powdery iron (99%, <325 mesh) and ferrous sulfate were purchased from Aldrich (Milwaukee, WI). Iron (III) hydroxide (α-FeO2H, goethite) was obtained from Alfa Aesar (Ward Hill, MA). Acetonitrile and chloroform were from Fisher Scientific (Pittsburgh, PA).

2.2. Reduction with zero-valent iron powder

Phosphate buffer (20 ml, potassium phosphate, pH 6.5, 100 mM) was fortified with the pesticides dissolved in acetonitrile at a final concentration of 10 μM, followed by addition of zero-valent iron powder (1 g).

After hydrogen purging for 5 min, the reaction vial was sealed tightly and stirred at 35 °C. Control experiments were done with the same concentration of pesticides (10 μM) in phosphate buffer without iron powder. In each sampling event, the contents in the vial were extracted with chloroform (3×10 ml). After removal of the organic solvent, residues were re-dissolved in acetonitrile (1 ml) and were analyzed with high performance liquid chromatography (HPLC). An aliquot of the sample was analyzed with gas chromatography–mass spectrometry (GC–MS). The products were tentatively identified by comparing of resulting mass spectra with NIST/EPA/NIH mass spectral library (NIST).

2.3. Effects of humic acid and quinone on reduction

Humic acid (20 mg l⁻¹) was dissolved in phosphate buffer (20 ml, pH 6.5, 100 mM), followed by addition of zero-valent iron powder (1 g). 2,6-Dinitroaniline pesticides were subsequently added at a concentration of 10 μM. After hydrogen purging for 5 min, samples were capped tightly and stirred at 35 °C. In the case of benfluralin, additional experiments were done in different orders of reagent additions. The pesticide standard solution was added first to phosphate buffer and sat for 5 min at 35 °C, followed by humic acid (a final concentration of 10 μM and 20 mg l⁻¹ for benfluralin and humic acid, respectively). In the case of quinone-mediated reactions, dichlorone (a final concentration of 20 mg l⁻¹) was added to a mixture of humic acid (20 mg l⁻¹) and iron powder (1 g/20 ml) in phosphate buffer, followed by pendimethalin (10 μM) addition. The controls did not contain humic acid.
2.4. Repeated use and storage of iron powder under atmospheric condition

Pendimethalin standard solution was added to phosphate buffer (20 ml, pH 6.5, 100 mM) at a final concentration of 10 \mu M, followed by zero-valent iron (1 g). The reaction mixture sat for 48 h, and then, the iron powder was filtered and washed with degassed acetonitrile (2 \times 100 ml) and phosphate buffer (100 ml). Pendimethalin was added again after re-suspension of the iron powder in phosphate buffer. Pendimethalin degradation was monitored after another 48-h incubation.

Fresh iron powder was exposed to air for 3, 7 and 10 days at 35 °C to examine effects of atmospheric oxidation on the reduction reaction. An aliquot amount of the air-exposed iron (1 g) was added into pendimethalin solution (20 ml, 10 \mu M in 100 mM-phosphate buffer, pH 6.5) and incubated for 96 h at 35 °C. Hydrogen or nitrogen gas was purged through the samples for 5 min and re-incubated. The control contained iron hydroxide suspension (50 g l\(^{-1}\)) or ferrous sulfate (10 mM) instead of iron powder.

2.5. Hydrogen and nitrogen purging

Iron powder (50 g l\(^{-1}\)) that was exposed to air for 10 days was poured into pendimethalin solution (10 \mu M in 100 mM-phosphate buffer, pH 6.5) and incubated for 96 h at 35 °C. Hydrogen or nitrogen gas was purged through the samples for 5 min and re-incubated. The control contained iron hydroxide suspension (50 g l\(^{-1}\)) or ferrous sulfate (10 mM) instead of iron powder.

2.6. Instrumental analysis

Reaction and products were monitored with HPLC and GC–MS. The HPLC system consisted of a Shimadzu LC-10S pump, Perkin-Elmer UV/VIS detector and a VyDac C18 column (250 mm, 4.6 mm, 5 \mu m). The mobile phase was 70% aqueous acetonitrile at a flow rate of 0.6 or 0.8 ml min\(^{-1}\) varying with analytes. The detection wavelength was 210 nm.

The GC–MS consisted of a Varian CP-3800 gas chromatograph, Saturn 2000 ion trap MS, Varian CP-8400 autosampler, and a ZB-1 column (60 m, 0.25 \mu m film thickness, Phenomenex, USA). The carrier gas was helium at a flow rate of 2 ml min\(^{-1}\). The MS was operated in electron impact mode (70 eV). Injection port and ion source temperatures were 250 °C and the column temperature started at 35 °C for 2 min, was jumped up to 280 °C at a rate of 4 °C min\(^{-1}\) and was finally held for 10 min.

![Fig. 1. Structures of eleven nitroaromatic pesticides.](image-url)
3. Results and discussions

3.1. Reduction of nitro group by zero-valent iron powder

All the pesticides in phosphate buffer were decomposed rapidly by zero-valent iron $[\text{rate}] = k/C_0$ to $0.25 \text{ h}^{-1}$, half-lives ($t_{1/2} = 2$) were $4.3 \pm 0.9$ to $34.8 \pm 0.0$ h (Table 1). In all the cases, the reaction followed pseudo-first order kinetics. Although an initial lag phase was reported (Lavine et al., 2001), it was not observed in this study, which may be attributed to strong hydrophobicity of the test chemicals and subsequent rapid adsorption on iron surface. Reduction of the two organophosphates was generally slower than the 2,6-dinitroaniline herbicides. It appeared that the methyl group adjacent to the nitro group in fenitrothion slightly enhanced the reduction in relation to its close analog methyl para-thion. However, the electron withdrawing groups of the methoxycarbonyl group in bifenox and the ethoxy in oxyfluorfen lowered the reaction rate in comparison with nitrofen that has no substitution group adjacent to the nitro group.

The GC–MS results showed that reduction of nitro-to-amino was a dominant reaction for all the tested compounds (Table 2). The nitro group of the diphenyl ether herbicides was completely reduced to amino within 48 h and the corresponding amines persisted even after 96 h. Trace quantities of dechlorinated amino products were found after 72 h and continuously increased during the course of the experiment. The result showed that the reductive aromatic dechlorination was much slower than the reduction of nitro groups. Such a stability of aromatic chlorine to iron-mediated reduction was reported with $p,p'$-DDT (Sayles et al., 1997). The nitro group of fenitrothion and methyl parathion was labile to reduction and the corresponding amines were the most abundant reaction products (>90%). Small quantities of the oxon and amino-oxon derivatives were found during the first 48 h (<1%). All the oxon products disappeared after 72 h. It is known that the oxon products are more toxic than the parent organophosphorus insecticides. Therefore, occurrence of the oxon products should be monitored in iron-mediated reactions. The iron-free reaction (control) produced a similar amount of oxon as the iron mediated reaction, which suggested that the toxic oxon was not produced from zero-valent iron catalysis. However, the oxon products were more resistant to degradation in control samples and found even after 72 h.

The two nitro groups of the 2,6-dinitroaniline herbicides were reduced readily to yield the corresponding 2,6-diamines as exemplified in Fig. 2. The monoamino products from the diphenyl ethers and organophosphates and di-amino derivatives from the 2,6-dinitroanilines were fairly stable relative to their corresponding parent compounds. These amino products had a $t_{1/2}$ of longer than two weeks. Though the nitro groups can be reduced stepwise [Eq. (1)] (Klausen et al., 2001), only trace quantities of the intermediates were found.

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Chemical name</th>
<th>$-k$, $\text{h}^{-1}$</th>
<th>$t_{1/2}$, h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Humic acid free</td>
<td>Humic acid $^b$</td>
</tr>
<tr>
<td>2,6-Dinitroaniline</td>
<td>Benfluralin</td>
<td>0.19 ± 0.02</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Ethalfluralin</td>
<td>0.18 ± 0.03</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Nitratin</td>
<td>0.16 ± 0.01</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>Oryzalin</td>
<td>0.16 ± 0.03</td>
<td>0.04 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>Pendimethalin</td>
<td>0.13 ± 0.01</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>Trifluralin</td>
<td>0.13 ± 0.02</td>
<td>0.03 ± 0.00</td>
</tr>
<tr>
<td>Diphenyl ether</td>
<td>Bifenox</td>
<td>0.16 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrofen</td>
<td>0.25 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxyfluorfen</td>
<td>0.12 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Organophosphate</td>
<td>Fenitrothion</td>
<td>0.13 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl parathion</td>
<td>0.11 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Quinone$^d$</td>
<td>Dichlone</td>
<td>0.01 ± 0.00</td>
<td>0.010 ± 0.00</td>
</tr>
</tbody>
</table>

$^a$ Average values ± standard deviation, values of three separate experiments.

$^b$ The concentration of humic acid was 20 mg l$^{-1}$.

$^c$ Benfluralin was added prior to the addition of humic acid.

$^d$ Dichlone is used as redox mediator in the study of the effect of humic acid.
Monoamino and nitroso products were found in the initial reaction mixtures of benfluralin, pendimethalin and trifluralin. The monoalkyl nitrobenzimidazole was also found in the initial reaction stage of trifluralin (Fig. 2), but it disappeared after 72 h. It may be formed by an intra-molecular ring closure from the partially reduced products.

3.2. Effects of humic acid and quinone

All the above iron-mediated reactions were performed in phosphate buffer without any other additives. Environmental matrices contain various solutes including different inorganic salts and humic materials. Humic acid and related NOMs are ubiquitous in soil, sediment, and natural waters and exist on soil minerals or in aqueous solutions. Because of its strong adsorption on iron surface, NOM can affect the reduction with zero-valent iron (Trantnyek et al., 2001). It can inhibit the reaction by competitive surface adsorption (Dunnivant et al., 1992; Curtis and Reinhard, 1994; Trantnyek et al., 2001). It may also enhance the reaction by electron shuttle mechanisms through quinones (Dunnivant et al., 1992).

In this study, humic acid decreased the reaction rate of the 2,6-dinitroaniline herbicides for 1.2–10 fold (Table 1). In addition to inhibitory effects of the competitive binding, humic acid and related NOM can form micelles and consequently trap the contaminants in the micelles (Trantnyek et al., 2001), which can limit the actual amount of contaminants to react with iron. The rapid reaction of benfluralin \(k = -0.20 \text{ h}^{-1}\), when it was treated prior to the addition of humic acid, suggested that the adsorption of the contaminants is critical for the reduction. The inhibitory effect of humic acid can be a serious problem for the application of zero-valent iron in the environment since NOM is ubiquitously distributed in the environment. Therefore, methods to minimize the inhibitory effect of humic acid and NOM or to enhance the reaction should be studied.

Opposite to humic acid, several natural quinones (constituents of humic materials) are known to enhance reduction by a rapid quinone-hydroquinone interconversion (Weber, 1996; Trantnyek et al., 2001). Dichlone (a known quinone redox mediator) enhanced the iron mediated reduction rate of pendimethalin with humic acid from \(k = -0.01 \text{ h}^{-1}\) to \(k = -0.12 \text{ h}^{-1}\), close to those of the dichlone-iron treatment \(k = -0.12 \text{ h}^{-1}\) and iron control \(k = -0.13 \text{ h}^{-1}\) (Fig. 3, and Table 1). The partial recovery may be due to (a) a slow diffusion of the redox mediator dichlone from iron surface to the target molecules, (b) a slow reaction between quinone and pendimethalin or (c) a competitive binding of dichlone and...
pendimethalin reduction rate in the dichlone-iron treatment would be faster than that of the iron control if a simple additive effect of dichlone on the reaction rate exists. A slight decrease of the pendimethalin reduction rate in the dichlone-iron treatment suggests a possible competitive binding between pendimethalin and dichlone on iron surface, which may result in a slow reaction. In addition, degradation of dichlone by zero-valent iron can be another cause of such non-additive nature. If the redox mediation was achieved without other reaction, namely dechlorination or polymerization, the concentration of dichlone should be kept constant. However, dichlone concentration decreased slowly (Table 1), which may result in loss of redox mediation activity. It should be pointed out that the dichlone-mediated reactions gave the same products and the according diamine being the most abundant product as the other treatments.

3.3. Effects of repeated use and storage under air

Disadvantages of using zero-valent iron for remediation include gradual loss of reactivity and permeability. These phenomena occur mainly by the formation of iron oxide and hydroxide layer (US EPA, 1998; Phillips et al., 2000). Plugging by iron-oxidized products is a serious problem in many permeable reactive barrier technologies. In aerobic or partially aerobic aqueous solution, such an iron hydroxide (e.g., goethite) can inhibit further corrosion by which formation of hydrogen or electron (i.e., reductant) is also inhibited. In addition, an iron hydroxide layer inhibits adsorption of contaminants on fresh iron surface. High concentration of dissolved oxygen can compete as an electron acceptor with contaminants (US EPA, 1998; Lavine et al., 2001).

In this study, repeated use and air exposure of fresh iron powder were studied to correlate the reaction rate with the status of iron surface. The removal rate of pendimethalin gradually slowed down as iron powder was repeatedly used (Fig. 4A). In addition to the formation of an iron hydroxide layer, accumulation of reduction products such as the aromatic diamines may retard the reaction since aromatic amine is known as corrosion inhibitor (Tan and Blackwood, 2003). In this study, iron powder was completely washed with organic solvent for the subsequent use. Therefore, the reduction products would not be accumulated on the iron surface. As the repeated exposure to new batches of pesticide solutions, surface iron can be oxidized by trace oxygen. The pendimethalin reduction rates by the first (fresh iron), second and third repeated uses of iron powder were 0.13, 0.06, and 0.02 h\(^{-1}\), respectively. A negative correlation between storage period and reduction rate (Fig. 4B) suggested that the surface oxidation slowed down the reaction. In many remediation projects, loss of long-term performance of a permeable reactive iron
barrier was caused by such an oxidation (US EPA, 1998; Farrell et al., 2000; Phillips et al., 2000).

3.4. Reactivity recovery for air oxidized iron powder using hydrogen gas

Although hydrogen and electron are produced from the corrosion of surface iron, such corrosion and concomitant formation of oxide or hydroxide layer inhibit further reaction. Studies were done to improve the performance and duration of zero-valent iron reactive permeable barrier. Those include combined treatment of aluminosilicate mineral (Powell and Puls, 1997), quinones (Curtis and Reinhard, 1994), or organic solvent and surfactant (Loraine, 2001). Integration of zero-valent iron into different technologies was also studied, for example, iron and anaerobic bioremediation (Weathers et al., 1997; Gerlach et al., 2000) or oxidative reaction (Krishna et al., 2001). Acid washing is often used to remove iron oxide and hydroxide from the surface (Lavine et al., 2001). Hydrogen can increase the dissolution rate of metals by which hydrogen or electron can be produced more rapidly (Wallinder et al., 2001) and the growth of anaerobic microorganism, having reductive activity, can be stimulated (Weathers et al., 1997), hydrogen can be a possible candidate to improve the performance of zero-valent iron permeable reactive barrier or combined technologies of zero-valent iron and bioremediation.

Hydrogen gas purging restored lost reactivity of air-oxidized iron powder for the reduction of pendimethalin, by increasing the reaction rate from 0.003 to 0.16 h\(^{-1}\), but not nitrogen (Fig. 5A). But the rate enhancement was not found with freshly prepared iron powder. Hydrogen purging without iron powder did not change the reduction rate of pendimethalin in buffer, ferrous sulfate solution, and iron hydroxide suspension (Fig. 5B). Numerous studies were done for the effects of solution pH on the zero-valent iron mediated reaction (Powell and Puls, 1997; Lavine et al., 2001), however, none were found on recovering the reactivity of oxidized iron by hydrogen. Apparent recoveries of the reactivity by hydrogen may be explained by possible (a) reduction of iron oxide and hydroxide to more reactive species or (b) catalytic hydrogenation by purging hydrogen gas on the active surface (Odziemakowski et al., 2000). Although hydrogen gas was supplied artificially in this study, the results suggest a possibility of using hydrogen producing microorganisms and zero-valent iron for removal of

Fig. 4. Repeated uses of zero-valent iron (A) and effects of atmospheric oxidation (B) of zero-valent iron on reduction of pendimethalin in phosphate buffer solution.

Fig. 5. Effects of hydrogen and nitrogen purging on pendimethalin reduction by air-oxidized iron powder (A) and effects of hydrogen purging on pendimethalin reduction by iron hydroxide, ferrous sulfate and phosphate buffer as control (B). The start time of hydrogen and nitrogen purging was marked with an arrow.
highly oxidized pollutants. Hydrogen purging may be applicable to remediation of nitroaromatic pesticides.

4. Conclusion

The nitroaromatic pesticides were rapidly reduced with zero-valent iron to the corresponding amines as major reduction products. Nitroso intermediates were found only at very small quantities in some reactions. Dichlone, a quinone, neutralized the inhibitory effect of humic acid on the catalysis ability of zero-valent iron for the reduction reaction of pendimethalin, which suggests that some natural quinones be relevant to pollutant degradation via iron-catalyzed reduction in the environment. Although use of zero-valent iron for environmental remediation is economical and feasible, it is important to develop ways to enhance and stabilize its catalytic capability and recover the activity of oxidized iron. Hydrogen gas purging rapidly recovered the catalysis ability of air-exposed iron to reduce pendimethalin, which implies hydrogen purging as a possible mean to maintain a reactive zero-valent iron barrier for the associated remediation technologies. It is possible to use zero-valent iron in conjunction with microbial approaches that may provide hydrogen and quinones for reduction of highly oxidized pollutants.

Acknowledgements

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