

FENTON-LIKE OXIDATION OF TRICHLOROETHYLENE IN THE PRESENCE OF NATURAL PYRITE

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Abstract

Degradation of trichloroethylene (TCE) by Fenton-like system in the presence of naturally occurring pyrite was investigated in a batch suspension system. Pyrite was selected by evaluating the effect of different iron sources (nZVI, Iron(II, III) oxide, ferrous sulfate, and pyrite). The evaluation experiments were conducted at pH 3 with 2.14-12.8 g/L iron sources and 54-163 mM hydrogen peroxide in a dark room. TCE removal efficiency was affected by Fe(II) content of the iron sources. Oxidation reaction occurred on the surface of pyrite and its reaction rate constants were estimated to be 0.2336, 0.0737, and 0.0253 min⁻¹ for 12.82, 4.27, and 2.14 g/L pyrite, respectively. Pyrite showed higher reactivity than any other iron sources even in the low concentration (2.14 g/L). Fenton-like oxidation using pyrite could be applied to the soil and groundwater contaminated with chlorinated organics as a potential remedial alternative for in-situ and ex-situ chemical oxidation process.

Introduction

Trichloroethylene (TCE) is a widely used industrial solvent in vapor degreasing of fabricated metal parts, dry cleaning, paint stripping, and chemical, pharmaceutical, and plastics manufacturing. The contamination of soils and groundwater by TCE having cytotoxicity and subsequent carcinogenicity has become an important environmental concern. Although bioremediation and biodegradation have been considered as economical treatment for the contaminated site cleanup, advanced oxidation processes (AOPs) can provide fast degradation kinetics for the treatment of refractory chemical compounds such as chlorinated aliphatics, halogenated aromatics, and PAHs [1].

Among various oxidation process explored for in situ oxidation of contaminants, Fenton oxidation has attracted a significant attention, due to its strong oxidation capabilities and low environmental impacts [2]. In classic Fenton oxidation, iron(II), typically ferrous sulfate, catalyzes the decomposition of hydrogen peroxide (H₂O₂) to hydroxyl radicals (OH•) [3]. Previous studies have suggested the basic reaction mechanisms of Fenton reaction as followed.



Hydroxyl radical is the strongest oxidant among hydroxyl radical, hydroperoxyl radical, hydrogen peroxide, and oxygen [2]. The reaction efficiency of the Fenton oxidation is largely influenced by Fe²⁺ and H₂O₂ concentrations. Classic Fenton oxidation can degrade bio-refractory contaminants in a short time and keep the cost of the remediation low. However, this process is terminated rapidly through precipitation of dissolved iron with hydroxyl radicals.

Instead of using soluble iron as a Fenton reagent, heterogeneous iron sources such as nZVI and iron (II)-bearing soil minerals playing a role of surface catalyst have been used to generate hydroxyl radicals during the Fenton reaction. Pyrite, one of iron(II)-bearing soil minerals, is highly reactive due to its high specific surface and high porosity [4]. It could be an effective and maintainable reactant producing less precipitates than aqueous Fe(II) due to the low solubility in solution. The goal of this study is to investigate TCE degradation kinetics during the Fenton-like oxidation with pyrite and evaluate the effect of different iron source and contents of pyrite and hydrogen peroxide on the degradation kinetics. All experiments were conducted using the batch system to characterize the degradation of TCE during the Fenton-like oxidation. This process can be applied to in-situ and

ex-situ chemical oxidation process for the remediation of soils and groundwater contaminated with chlorinated organics.

Materials and Methods

Materials. TCE stock solution was prepared by diluting TCE (99.5%, Sigma-Aldrich) in n-hexane (98%, Merck). Hydrogen peroxide (30%) was purchased from Kanto. Iron(II, III) oxide (98%) with particle size less than 5 μm , ferrous sulfate hepta-hydrate (99%), and 1,2-Dibromopropane (97%) were obtained from Sigma-Aldrich. Natural pyrite (Zacatecas, Mexico) was purchased from ward's natural science and milled with particle size less than 150 μm . H_2SO_4 was obtained from DC Chemical, methanol (99%) was obtained from Merck. nZVI was synthesized by reducing 0.11 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with 0.9 M NaBH_4 solution, modifying Wang's method [5]. Fe(III) was reduced to Fe(0) by hydrogen generated during the synthesis. The precipitates in the solution were washed with DDW twice and then with acetone. Synthesized nZVI was dried and kept in the anaerobic chamber and used in a week. Deionized water was purified to obtain 18 M Ωcm pure water using a ELGA PURELAB Classic system.

Procedure. The experiments to characterize the TCE degradation kinetics by Fenton-like oxidation using different iron sources (nZVI, Iron(II, III) oxide, ferrous sulfate and pyrite) were conducted in closed batch reactors (24 mL of amber vials sealed with PTFE septum caps) at room temperature (25 ± 0.5 °C) in the dark room. Exact amounts of iron sources (0.3 g) were added to the reactors. Deionized water which was adjusted to pH 3 by 1M H_2SO_4 was poured into each reactor. TCE stock solution (124 mM) in methanol was spiked to each reactor (diluted to 0.53 mM) and reactions were initiated by adding 163 mM H_2O_2 . Reactors were mixed by a tumbler at 7 rpm. Control samples were prepared to check possible loss by volatilization and adsorption in the batch reactor and all samples were prepared in duplicate. Batch kinetic experiments were also conducted to investigate the effect of contents of pyrite (0.05, 0.1, and 0.3g) and H_2O_2 (54 and 163 mM) by following the same experimental procedure above.

The degradation kinetics was estimated by measuring the concentration of TCE in aqueous solution. Retrieved vials were centrifuged at 3000 rpm for 5 min. An exact amount of supernatant (100 μL) was transferred to 2 mL vial containing 1.4 mL of extractant (hexane with 0.05 mM 1,2-dibromopropane as an internal standard). Extraction was conducted by mixing the vial on an orbital shaker for 30 min at 200 rpm and 1 μL of extractant was injected into the GC injector.

Analytical methods. Target organic was measured by a Hewlett Packard 5890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and a HP-5 column (30 m \times 0.32 mm \times 0.25 μm). The temperature of injector and detector was 175 and 200 °C, respectively and oven temperature was isothermal at 80 °C.

Result and Discussion

Figure 1 shows oxidative degradation kinetics of TCE using different iron sources at pH 3. TCE removal has been shown by the different iron sources in the following order: pyrite > ferrous sulfate > Iron(II, III) oxide > nZVI. Pyrite and ferrous sulfate were more effective reactants than Iron(II, III) oxide and nZVI for the TCE degradation. This is mainly due to the higher Fe(II) contents of pyrite and ferrous sulfate than those of iron oxide and nZVI indicating that TCE removal by the heterogeneous Fenton oxidation is significantly influenced by Fe(II).

Fenton-like oxidation using pyrite was more efficient than classic Fenton reaction. Classic Fenton reagent, ferrous sulfate, is soluble while pyrite is insoluble mineral. Fenton-like oxidation system was an aqueous suspension condition and pyrite was acted as surface catalyst with high specific surface and high porosity. Heterogeneous Fenton-like reaction on pyrite surface was more effective than homogeneous classic Fenton reaction when pyrite has high specific surface.

The results for Fenton-like oxidation using pyrite at different concentration of H_2O_2 were shown in Figure 2. In this system, TCE degradation by the oxidation seemed to be properly described as a second-order rate law. Lower concentration of H_2O_2 (54 mM) was insufficient to produce enough hydroxyl radical to completely degrade TCE, while higher concentration (163 mM) showed full degradation in 25 min. This indicates that the oxidation by the heterogeneous Fenton in this research was limited by the concentration of H_2O_2 resulting in the reactive hydroxyl radical under constant amount of pyrite.

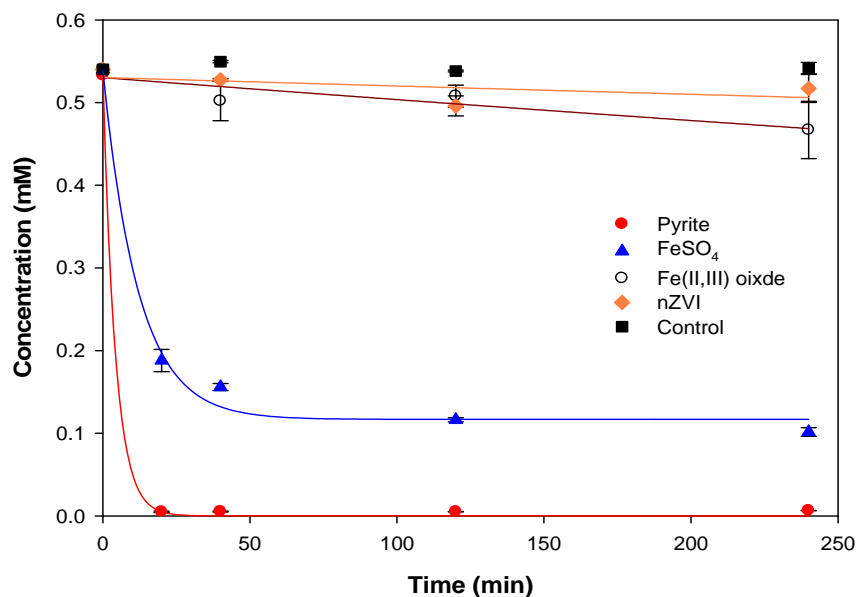


Figure 1. TCE (0.53 mM) degradation by Fenton oxidation using different iron sources at pH 3; [H₂O₂]=163 mM, [iron sources] = 12.82 g/L

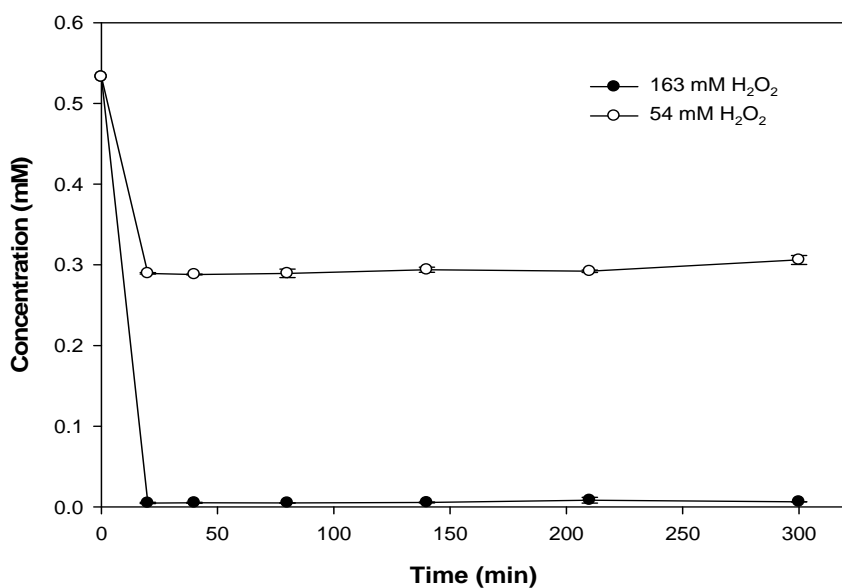


Figure 2. TCE (0.53 mM) degradation by Fenton-like oxidation using pyrite (12.82 g/L) and different concentration of H₂O₂ at pH 3; [H₂O₂]=54mM and 163 mM

Figure 3 shows the effect of pyrite concentration on TCE degradation during the heterogeneous Fenton reaction. Each sample under different loading showed a different rate constant. The estimated kinetic rate constants were 0.2336 min⁻¹ for 12.82 g/L pyrite, 0.0737 min⁻¹ for 4.27 g/L, and 0.0253 min⁻¹ for 2.14 g/L, respectively. Higher pyrite content containing more reactive surfaces showed faster oxidation kinetics under constant TCE concentration.

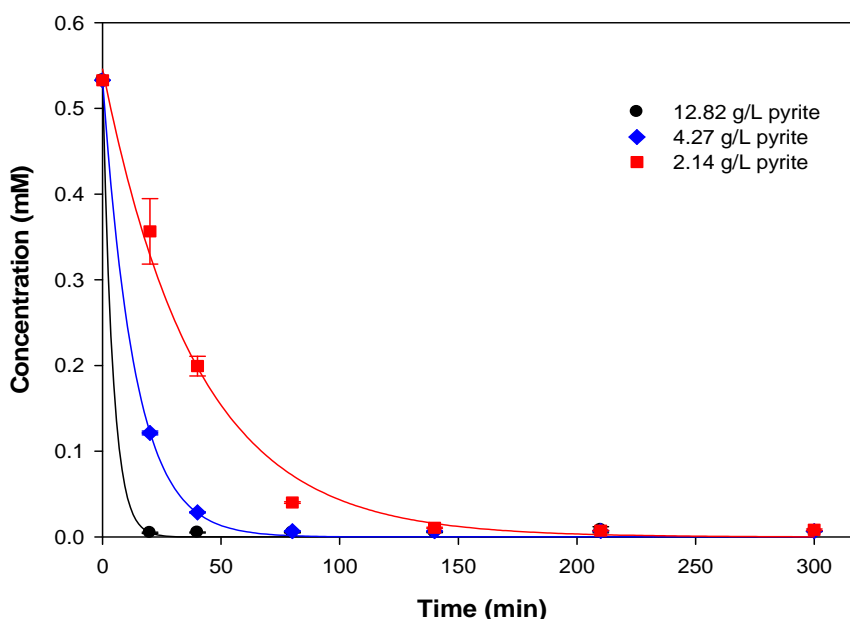


Figure 3. TCE (0.53 mM) degradation by Fenton-like oxidation using different concentration of pyrite and H₂O₂ (163 mM) at pH 3; [pyrite]=12.82 g/L, 4.27 g/L and 2.14 g/L

Based on the comparison between TCE degradation with ferrous sulfate (12.82 g/L, Figure 1) and with pyrite (2.14 g/L, Figure 2), TCE degradation by Fenton-like oxidation using pyrite showed higher TCE removal than classic Fenton oxidation. The result demonstrates that pyrite is the most effective reactant for the Fenton-like oxidation system. This is partly because the classic Fenton system is terminated earlier by the precipitation of dissolved iron with hydroxyl radicals, while pyrite produces less precipitates than aqueous ferrous sulfate.

The experimental results for Fenton-like oxidation with pyrite suggested in this research can be applied to a potential remedial alternative for the in-situ and ex-situ chemical oxidation process to treat the soils and groundwater contaminated with chlorinated organics.

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