Treatment of TCE-Contaminated Groundwater Using Fenton-Like Oxidation Activated with Basic Oxygen Furnace Slag

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Abstract: The industrial solvent trichloroethylene (TCE) is among the ubiquitous chlorinated organic compounds found in groundwater contamination. The objective of this study was to evaluate the potential of applying basic oxygen furnace (BOF) slag as the catalyst to enhance the Fenton-like oxidation to remediate TCE-contaminated groundwater. Results indicate that TCE oxidation via the Fenton-like process can be enhanced with the addition of BOF slag. Results from the X-ray powder diffraction analysis reveal that the major iron type of BOF slag/quartz sand media was iron oxyhydroxide (α-Fe2O3). Approximately 81% of TCE removal was observed (with initial TCE concentration of approximately 5 mg L\(^{-1}\)), with the addition of 1,000 mg L\(^{-1}\) of H\(_2\)O\(_2\) and 10 g L\(^{-1}\) of BOF slag. Results also show that TCE concentrations dropped from 5 to 1.1 mg L\(^{-1}\), and chloride concentrations increased from 0 to 2.7 mg L\(^{-1}\) after 60 min of reaction with the presence of H\(_2\)O\(_2\) and BOF slag. This indicates that the depletion of TCE corresponded with the oxidation reactions and release of chloride ions very well in this study. Results demonstrate that the BOF slag can be used to supply catalysts continuously, and it can be installed in a permeable barrier system to enhance the Fenton-like process in situ.

CE Database subject headings: Hydrogen peroxide; Groundwater pollution; TCE; Oxidation.

Author keywords: Fenton-like; Basic oxygen furnace slag; Hydrogen peroxide; Groundwater contamination; TCE.

Introduction

Groundwater at many existing and former industrial sites and disposal areas is contaminated by chlorinated organic compounds that were released into the environment (Kao et al. 2008; Lee et al. 2008; Tsai et al. 2009a). Chlorinated organic compounds [e.g., trichloroethylene (TCE)], which is characterized as dense non-aqueous-phase liquids, is one of the common pollutants in groundwater and could be a significant component of hazardous waste streams. The toxic and persistent nature of TCE poses a serious health threat to humans and ecological receptors (Kao et al. 2003; Bennett et al. 2007; Tsai et al. 2008).

In situ chemical oxidation is a promising innovative technology of degrading an extensive variety of hazardous wastes for the remediation of groundwater at waste disposal and spill sites. Chemical oxidation with hydrogen peroxide (H\(_2\)O\(_2\)) can be direct and/or involve generation of free radicals. Hydrogen peroxide is a powerful oxidizing agent, which can be delivered deep into the ground by using soil mixing techniques or injected groundwater amendments (Chen et al. 2001; Teel et al. 2001; Goi et al. 2006; Ramirez et al. 2007). There are two categories of Fenton processes. One is the standard Fenton reaction which utilizes soluble ferrous iron (Fe\(^{2+}\)) as the catalyst [Yeh et al. 2003; Georgi and Kopinke 2005; Interstate Technology and Regulatory Council (ITRC) 2005], and the other is the so-called modified Fenton or Fentonlike process, which includes the use of ferric iron (Fe\(^{3+}\)) and iron oxides (Watts et al. 1997; Yeh et al. 2003; Hanna et al. 2008; Tsai et al. 2009b).

The Fenton-like reaction reviews that H\(_2\)O\(_2\) reacts with iron oxide, which generates strong oxidizing radicals (e.g., HO\(^{•}\)) to degradation of the organics (Watts and Dilly 1996; Li 1999; Li et al. 1999; Wang 2008). Iron oxides are commonly used in the Fenton-like oxidation process as both heterogeneous and homogeneous catalysts. Heterogeneous catalysis offers significant advantages. Unlike Fenton’s reagent, the reaction of iron oxides with H\(_2\)O\(_2\) can effectively catalyze the oxidation of organic contaminants at circumneutral pH. Use of iron oxides instead of dissolved iron may be especially advantageous for in situ remediation of contaminated groundwater where pH cannot be adjusted (Pignatello et al. 2006; Matta et al. 2007).

The application of the Fenton-like oxidation process to decompose chlorinated organic compounds has attracted extensive attention due to its satisfactory success (Baciocchi et al. 2004; Yeh et al. 2008). Yeh et al. (2003) reported a 78% reduction of sorbed TCE by 3% of H\(_2\)O\(_2\) in the aquifer sand containing 2.01 g kg\(^{-1}\) of extractable iron. More than 70% of TCE removal was achieved in a sandy clay loam by the application of 1,000 mg H\(_2\)O\(_2\) per kilogram of soil and no addition of external soluble iron (Ravikumar and Gurrol 1994; Yeh et al. 2003).

The removal efficiency of contaminants by Fentonlike reaction
catalyzed by iron oxide is influenced by parameters such as types and concentrations of iron oxides, H$_2$O$_2$ concentration, the presence of other oxidant-consuming compounds, and pH (Kwak and Voelker 2003; Yeh et al. 2002, 2003; Chiu et al. 2006; Siedlecke et al. 2008). The Fentonlike reaction is observed for various types of mineral catalysts such as hematite, magnetite (e.g., FeO), ferrhydrite, goethite, lepidocrocite, mixed element oxides, and steel slag (Watts et al. 1997; Chou et al. 2001; Lee et al. 2009).

Basic oxygen furnace (BOF) slag is a final waste material in the BOF steel making process. In blast furnace iron making, limestone (as fluxes) is added to react with the gangue minerals (iron ore and coke) to form iron slag. Slag is separated from the molten iron owing to the different specific gravity of molten iron and slag. In a BOF, the molten iron is converted into steel with oxygen, which also requires some flux materials to react with gangues. The slag formed in the BOF, after being solidified, is called BOF slag (Li et al. 1999; Chou et al. 2006; Liang et al. 2007). In recent years, the management of BOF slag has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints (Li et al. 1999; Chou et al. 2006; Chiu 2007). BOF slag is heterogeneous oxide materials which are compounded by some main oxides such as Fe$_2$O$_3$, FeO, CaO, SiO$_2$, SO$_3$, Al$_2$O$_3$, and MgO due to their mass percentage. The XRD data of solid sample such as BOF slag, quartz sand, magnetite (Fe$_3$O$_4$), hematite (α-Fe$_2$O$_3$), and goethite (α-FeOOH) were collected with a Rigaku Rint-2000 (Japan) diffractometer using Ni-filtered Cu Kα radiation generated at 30 kV and 10 mA. The XRD patterns were recorded over the range 0–40° 2θ with a scanning speed of 1.0° 2θ/min (Hsu et al. 2007). The tested groundwater was sampled from a background and uncontaminated area of a TCE-contaminated site in southern Taiwan. Redox potential and pH were measured by an oxidation-reduction potential (ORP) meter (ORION Model 250 A+, Thermo, United States) and a pH meter (TES 1380, Taiwan), respectively. The analytical procedures for groundwater analyses were described in standard methods [American Public Health Association (APHA) 2001]. Table 1 shows the characteristics of tested groundwater.

### Experimental Conditions and Procedures

In this study, the oxidation potential of TCE (used as the target contaminants) by Fenton-like process activated by BOF slag was evaluated in a continuous stir bath reactor (CSBR) system (close system) composed of a 250-mL brown glass bottle with a chloride electrode (HORIBA 6560 10C, Japan) inserted into the reaction solution. The initial TCE concentrations were approximately 0.3, 1, and 5 mg L$^{-1}$ (after equilibration). The operating parameters included concentration of H$_2$O$_2$, BOF slag dosage, and concentrations of TCE. All experiments were performed in duplicates. Each CSBR system contained 200 mL of collected groundwater and 100 g of quartz sand in the bottle sealed with a thick butyl rubber septum. Preliminary results show that the groundwater pH increased after the addition of BOF slag (initial pH=12.1). The more the BOF slag added, the more the alkaline condition was observed (data not shown). In this experiment, the initial pH value (initial pH=5.4±0.2) of the CSBR system was controlled by the addition of 0.1 N of HNO$_3$/NaOH at the beginning of the experiment, and the pH value was also maintained at 5.4 throughout the experiment using 0.1 N of HNO$_3$/NaOH. The experiment was conducted at room temperature, and the water samples were collected at different time points (e.g., 0, 5, 10, 20, 40, and 60 min) for the analysis of TCE, chloride (Cl$^-$), and H$_2$O$_2$ during the reaction. The first-order decay constant (min$^{-1}$) of TCE was calculated to evaluate the effect of BOF slag addition on the Fentonlike reaction rate. The following equation was applied for the calculation of first-order TCE decay constant ($K_{obs}$, min$^{-1}$) calculation (Chu and Choy 2000; Choy and Chu 2001):

$$\frac{-d[TCE]}{dt} = K_{obs}X[TCE]$$

Concentrations of TCE were analyzed in accordance with EPA Method 601, using a Tekmer Purge and Trap Model LSC 2000 with a Varian Model 3800 gas chromatograph. A 50 m × 0.32 mm DB-624 capillary column with a 0.25 μm film (J&W
Hydrogen peroxide concentrations were determined by iodometric titration with 0.1-N sodium thiosulfate (Schumb et al. 1995). At the end of the oxidation experiment, selected samples were analyzed for the possible degradation by-products using GC/MS. The GC/MS was operated with the computer system MS ChemStation (HP) following the procedures described in Kao et al. (2004).

Results and Discussions

Characterization of Basic Oxygen Furnace Slag

Fig. 1 shows the production of Fe$^{2+}$ and Fe$^{3+}$ from BOF slag in tested groundwater (initial pH=5.4 and ORP=465 mV). Results show that Fe$^{2+}$, Fe$_{r}$, and Fe$^{3+}$ can be released from BOF slag in tested groundwater (Fig. 1). According to the pH-pE speciation diagram (Matheson and Tratnyek 1994), the dominant form of iron was Fe$^{3+}$ in the tested groundwater. Fig. 2 shows the XRD patterns of the BOF slag, quartz sand, magnetite (Fe$_3$O$_4$), hematite (α-Fe$_2$O$_3$), and goethite (α-FeOOH) before the oxidation process. On the basis of the positions of the main diffraction peaks in the XRD patterns, different crystallites in the catalysts are identified. The patterns show that the main diffraction peaks of BOF slag and quartz sand appeared at 2θ=33.2 and 35.9, which could be the characteristics of α-Fe$_2$O$_3$. Results indicate that the measured amorphous iron and extractable iron in BOF slag were approximately 14.7 and 45.2 g kg$^{-1}$, respectively. Results of this study demonstrated that BOF slag contained a significant amount of α-Fe$_2$O$_3$ (e.g., Fe$^{3+}$), which could be used to continuously supply iron catalyst to activate the Fentonlike oxidation process for the oxidation of TCE.

Experiments without Basic Oxygen Furnace Slag

Figs. 3(a and b) present the efficiencies of TCE (with initial TCE concentration of approximately 5 mg L$^{-1}$) removal versus reaction time with different initial H$_2$O$_2$ concentrations (0, 100, 500, and 1,000 mg L$^{-1}$) without BOF slag addition (initial pH=5.4). Results indicate that approximately 10, 14, 25, and 37% of TCE removal were observed for the concentrations of oxidant H$_2$O$_2$ 0, 100, 500, and 1,000 mg L$^{-1}$, respectively, after 60 min of reaction. In the experiment with 100 mg L$^{-1}$ of H$_2$O$_2$, the TCE concentrations dropped from 5 to 4.3 mg L$^{-1}$ (14% of TCE removal) after 60 min of reaction. Although H$_2$O$_2$ can be used as an oxidant alone, the oxidation reaction was not kinetically efficient enough to degrade significant amount of TCE at low H$_2$O$_2$ concentration [Interstate Technology and Regulatory Council (ITRC) 2001, 2005]. Results also indicate that TCE removal efficiency can be increased with increased H$_2$O$_2$ concentration. Results show that approximately 37% of TCE was removed in experiments with H$_2$O$_2$ concentrations of 1,000 mg L$^{-1}$ after 60 min of oxidation. This indicates that the TCE oxidation can be enhanced under conditions of higher H$_2$O$_2$ concentration.

As shown in Fig. 3(b), H$_2$O$_2$ concentration has a linear correlation (with a high correlation coefficient, $R^2=0.997$) with TCE removal efficiency. Higher H$_2$O$_2$ concentration caused a more efficient TCE degradation. However, the obtained TCE removal efficiency of α-Fe$_2$O$_3$ (e.g., Fe$^{3+}$), which could be used to continuously supply iron catalyst to activate the Fentonlike oxidation process for the oxidation of TCE.

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\text{chloride yield(%) = } \frac{\text{(moles of chloride measured)} \times 100}{\text{(moles of TCE removed)} \times \text{(number of Cl in one TCE molecule)}}
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increased BOF slag dosage would not produce more Fe$^{3+}$ concentrations; conditions: [TCE]$_0$=5 mg L$^{-1}$, BOF slag dosages=0 g L$^{-1}$, and initial pH=5.4. (b) calculated first-order decay constants for TCE oxidation with different initial H$_2$O$_2$ concentrations; conditions: [TCE]$_0$=5 mg L$^{-1}$, BOF slag dosages=0 g L$^{-1}$, and initial pH=5.4

Fig. 3. (a) Rates of TCE remaining versus reaction time with different initial H$_2$O$_2$ concentrations; conditions: [TCE]$_0$=5 mg L$^{-1}$, BOF slag dosages=0 g L$^{-1}$, and initial pH=5.4. (b) calculated first-order decay constants for TCE oxidation with different initial H$_2$O$_2$ concentrations; conditions: [TCE]$_0$=5 mg L$^{-1}$, BOF slag dosages=0 g L$^{-1}$, and initial pH=5.4.

Effect of BOF slag dosage on the Treatment Efficiency

Fig. 4(a) presents the effect of BOF slag dosage (1, 5, 10, 20, and 30 g L$^{-1}$) on the efficiency of TCE (with initial TCE concentration of approximately 5 mg L$^{-1}$) removal with the addition of 1,000 mg L$^{-1}$ of H$_2$O$_2$. Results indicate that the increased BOF slag caused the increase in the production rate of Fe$^{3+}$ and the degradation rate of TCE after 60 min of reaction. As the dosage of BOF slag increased from 1 to 10 g L$^{-1}$, the TCE removal increased from 25 to 81%. This indicates that more BOF slag addition would accelerate the removal efficiency of TCE. This produced Fe$^{3+}$ could activate the Fentonlike reaction, and generate HO$^\cdot$ for TCE oxidation. Results also reveal that TCE removal dropped from 81 to 53% when BOF slag dosage increased from 10 to 20 g L$^{-1}$, respectively. No significant Fe was generated (Fig. 1) when 20 g L$^{-1}$ of BOF slag was used. Results indicate that the inhibition for TCE oxidation could be due to the reduction of iron species. This might be due to the phenomenon that higher BOF slag dosage (>10 g L$^{-1}$ in this study) would cause the consumption of H$_2$O$_2$ for water production (Lu 2000). Thus, increased BOF slag dosage would not produce more 'OH, but causes superfluous fresh iron surfaces. The extra iron surfaces would also cause the consumption of oxidants (e.g., H$_2$O$_2$ and 'OH) rapidly and, thus, lead to significant decline of TPH removal efficiency (Zhou et al. 2008a, b).

Results also show that the percentage of TCE removal increased from 1.6 to 23% when BOF slag dosage increased from 1 to 30 g L$^{-1}$ in experiments without H$_2$O$_2$ addition [Fig. 4(a)]. Because the iron forms in BOF slag are mainly FeO (Fe$^{2+}$) and Fe$_2$O$_3$ (Fe$^{3+}$), reductive dechlorination of TCE would not occur in this system. Thus, TCE removal in experiments without H$_2$O$_2$ addition could be due to the occurrence of sorption mechanisms.

Fig. 4(b) shows the calculated first-order decay constants ($k_{obs}$) for TCE oxidation with the addition of 1,000 mg L$^{-1}$ of H$_2$O$_2$. Results indicate that the highest decay rate constant (2.7 × 10$^{-2}$ min$^{-1}$) was observed in experiment with 10 g L$^{-1}$ of BOF slag. Similar to the results observed in Fig. 4(a), higher BOF slag addition (>10 g L$^{-1}$) would cause higher amount of Fe$^{3+}$ production and also cause subsequent H$_2$O$_2$ consumption for water production. Thus, 10 g L$^{-1}$ of BOF slag was applied in the following batch experiments.

Effect of H$_2$O$_2$ Concentration on the Treatment Efficiency

Figs. 5(a and b) show the variations in the percentage of TCE remaining versus reaction time with varied initial H$_2$O$_2$ concentrations (with initial TCE concentration ≈5 mg L$^{-1}$ and BOF slag=10 g L$^{-1}$). Results indicate that higher TCE removal efficiency (81%) was observed in experiment with 1,000 mg L$^{-1}$ of H$_2$O$_2$ addition after 60 min of reaction. Moreover, decreased TCE removal efficiency was observed with decreased H$_2$O$_2$ addition. Results show that TCE removal efficiencies were 30, 56, and 81% with H$_2$O$_2$ concentrations of 100, 500, and 1,000 mg L$^{-1}$, re-
Fig. 5. (a) Variations in the percentage of TCE remaining versus reaction time with varied initial H₂O₂ concentrations; conditions: [TCE]₀=5 mg L⁻¹, BOF slag dosages=10 g L⁻¹, and initial pH =5.4; (b) calculated first-order decay constants for TCE oxidation with the addition of varied initial H₂O₂ concentrations; conditions: [TCE]₀=5 mg L⁻¹, BOF slag dosages=10 g L⁻¹, and initial pH =5.4

respectively [Fig. 5(a)]. Fig. 5(b) presents the first-order decay constants of TCE oxidation under various H₂O₂ concentrations. The first-order decay constants with the concentration of H₂O₂ of 0, 100, 500, 800, and 1,000 were 1.5×10⁻³, 5.5×10⁻³, 1.2×10⁻², 1.7×10⁻², and 2.5×10⁻² min⁻¹, respectively. As shown in Fig. 5(b), H₂O₂ concentration had a linear correlation (with a high correlation coefficient, R²=0.97) with TCE removal efficiency. Compared with the results obtained from Fig. 4(a), results imply that TCE oxidation could be significantly enhanced with the addition of reasonable amount of H₂O₂ and 10 g L⁻¹ of BOF slag.

Figs. 6(a and b) present the variations in TCE, chloride ion, and H₂O₂ concentrations versus reaction time with 1,000 mg L⁻¹ of H₂O₂ and 10 g L⁻¹ BOF slag (with initial TCE concentration of approximately 5 mg L⁻¹). The production of chloride ion, consumption of H₂O₂, and decreased TCE concentration in the batch experiment confirmed the occurrence of TCE oxidation. Results show that TCE concentrations dropped from 5 to 1.1 mg L⁻¹, and chloride concentrations increased from 0 to 2.7 mg L⁻¹ after 60 min of reaction with the presence of 10 g L⁻¹ of BOF slag. Because the molecular weight of TCE consists of 81% of chloride and the initial TCE concentration in this experiment was 5 mg L⁻¹, approximately 4.05 mg of chloride per liter during TCE oxidation would be detected in the reactor at the end of the experiments if TCE was completely oxidized to CO₂ and H₂O. Results show that 2.7 and 1.1 mg L⁻¹ of chloride and TCE concentrations were detected in the reactor. This indicates that approximately 3.2 mg L⁻¹ of chloride ion concentration was detected at the end of the experiment (data not shown). Thus, the calculated variation among the theoretical chloride concentration, observed chloride concentration, and observed chloride concentration in control experiment was 0.4 mg L⁻¹. This indicates that the depletion of TCE corresponded with the oxidation reactions and release of chloride ions very well in this study. Moreover, GC/MS was applied to determine the degradation by-products of TCE in reactors at the end of the experiments. Only slight degradation by-products (less than 0.2 mg L⁻¹) (e.g., vinyl chloride and dichloroethene) were observed in reactors at the end of the experiments (data not shown). This indicates that most of the produced by-products were also oxidized. The detected by-products also explained the variation in chloride ion concentrations between the observed and theoretical values. Results from Fig. 6 reveal that a complete depletion of H₂O₂ was observed after 40 min of reaction. The complete consumption of H₂O₂ also caused the leveling off of the TCE degradation curve after 40 min of operation.

**Effect of Initial Concentration of TCE on the Treatment Efficiency**

Fig. 7 presents the effect of initial TCE concentrations (with initial TCE concentration of approximately 0.3, 1, and 5 mg L⁻¹) on the removal efficiencies with the addition of 1,000 mg L⁻¹ of H₂O₂ concentrations and 10 g L⁻¹ of BOF slag. Fig. 7 depicted that TCE degradation rates with H₂O₂ and BOF slag addition were 88, 97, and 81%, while the first-order decay constants were found to be 3.5×10⁻², 6.2×10⁻², and 2.5×10⁻² min⁻¹ and half-life were 20, 11, and 28 min for the initial concentrations of TCE 0.3, 1, and 5 mg L⁻¹, respectively, after 60 min of reaction. Re-
results show that the experiment with initial TCE concentration of 5 mg L\(^{-1}\) had the most significant TCE removal efficiency during the first 10 min of reaction compared with the degradation trends with 0.3 and 1 mg L\(^{-1}\) of initial TCE concentrations. However, the reaction rates for the experiments with 1 and 5 mg L\(^{-1}\) of initial TCE concentrations leveled off after 40 min of reaction. This could be due to the complete consumption of H\(_2\)O\(_2\) on the removal efficiencies with the addition of H\(_2\)O\(_2\) and BOF slag dosages=10 g L\(^{-1}\). Supplements of higher H\(_2\)O\(_2\) concentrations is a necessity to remediate higher TCE-contaminated groundwater. Results from this Fenton-like oxidation experiment also imply that higher initial TCE concentration would cause higher TCE degradation rate and higher TCE removal efficiency under the condition of sufficient H\(_2\)O\(_2\) supplement.

Conclusions

The application of the BOF slag to catalyze H\(_2\)O\(_2\) to enhance Fentonlike oxidation of TCE was investigated in this study. Conclusions obtained from this study include the following:

1. Results suggest that addition of BOF slag is able to activate the Fentonlike oxidation process and improve the degradation efficiencies of TCE.
2. Results show that the optimal BOF slag concentration was around 10 g L\(^{-1}\). Higher initial TCE concentrations require higher initial H\(_2\)O\(_2\) concentrations.
3. Based on the results from XRD analysis, the major iron type in the BOF slag/quartz sand system was iron oxyhydroxide (e.g., \(\alpha\)-Fe\(_2\)O\(_3\)).
4. Results indicate that the BOF slag can be used to supply catalysts continuously for the activation Fenton-like oxidation. Thus, the BOF slag can be installed in a permeable reactive barrier system to enhance the Fenton-like process in situ.

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