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Technical Note

Remediation of TCE-contaminated groundwater using acid/BOF slag enhanced chemical oxidation

T.T. Tsai [a], C.M. Kao [b,*], J.Y. Wang [c]

[a] *Integrated Research Center for Green Living Technologies, National Chin-Yi University of Technology, Taichung, Taiwan*
[b] *Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan*
[c] *Civil & Environmental Engineering, Nanyang Technological University, Singapore*

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ABSTRACT

The objective of this study was to evaluate the potential of applying acid/H_2O_2/basic oxygen furnace slag (BOF slag) and acid/$S_2O_8^{2-}$/BOF slag systems to enhance the chemical oxidation of trichloroethylene (TCE)-contaminated groundwater. Results from the bench-scale study indicate that TCE oxidation via the Fenton-like oxidation process can be enhanced with the addition of BOF slag at low pH (pH = 2–5.2) and neutral (pH = 7.1) conditions. Because the BOF slag has iron abundant properties (14% of FeO and 6% of Fe_2O_3), it can be sustainably reused for the supplement of iron minerals during the Fenton-like or persulfate oxidation processes. Results indicate that higher TCE removal efficiency (84%) was obtained with the addition of inorganic acid for the activation of Fenton-like reaction compared with the experiments with organic acids addition (with efficiency of 10–15% lower) (BOF slag = 10 g L^{-1}; initial pH = 5.2). This could be due to the fact that organic acids would compete with TCE for available oxidants. Results also indicate that the pH value had a linear correlation with the observed first-order decay constant of TCE, and thus, lower pH caused a higher TCE oxidation rate.

1. Introduction

Chlorinated solvents such as trichloroethylene (TCE) are common groundwater contaminants at many hazardous waste sites. In Taiwan, because of the improper storage and disposal of the spent solvents, groundwater contamination by chlorinated solvents (mainly TCE) at many industrial and waste disposal sites has been discovered, and has caused serious environmental problems (ITRC, 2005; Tsai et al., 2008). The toxic and persistent nature of TCE poses a serious health threat to humans and ecological receptors. Chemical oxidation is a promising innovative technology for degrading an extensive variety of hazardous wastes for the remediation of groundwater at waste disposal and spill sites. For example, the chemical oxidants (e.g., Fenton's reagent, persulfate) could be injected directly into contaminated groundwater for TCE treatment, offering a relatively high efficiency alternative to conventional technologies (e.g., pump and treat, air sparging) (Neyens and Baeyens, 2003; Ferrarese et al., 2008; Tsai et al., 2008; Liang et al., 2009).

The Fenton's reaction utilizes soluble Fe(II) as the catalyst (ITRC, 2005; Tsai et al., 2010), and the Fenton-like reaction uses Fe(III) or iron oxides [e.g., goethite (α-FeOOH), hematite (α-Fe_2O_3), iron chelates] as catalysts for strong oxidizing radical ($\cdot$OH) generation (Watts et al., 1997; Hanna et al., 2008). Because iron usually exists in environments in the form of Fe(III), acids or chelating agents (e.g., citric acid, cyclodextrins, EDTA) can be used to increase the availability of Fe(III) to enhance the Fenton-like reaction (Seol and Javandel, 2008). Recently, a Fenton's oxidation system that combines H_2O_2 with an organic acid (e.g., HCOOH) and an iron oxide was developed (Ferraz et al., 2007). However, studies about the effects of applying organic acids for enhancing Fenton-like oxidation on the remediation of TCE-contaminated groundwater are rare.

Persulfate usually requires higher activation energy than other chemical oxidants such as permanganate. It has been postulated that persulfate anion ($S_2O_8^{2-}$) can be activated by transition metal ions such as Fe(II) to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-}\cdot$) with a redox potential of 2.4 V, which can potentially destroy chlorinated solvents (Liang et al., 2004). In a side-by-side comparison of TCE degradation in groundwater versus unbuffered reverse osmosis (RO) water, it was demonstrated that when the system pH is buffered to near neutral conditions due to the presence of natural occurring groundwater constituents, the TCE degradation rate is higher than in unbuffered RO water where the system pH dropped from 5.9 to 2.8 (Liang et al., 2007). Results from other studies suggest that in a field application of chemical oxidation, pH should be monitored and adjusted if it is necessary (Liang et al., 2009).

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* Corresponding author. Tel.: +886 7 525 4413; fax: +886 7 525 4449.
E-mail address: jkao@mail.nsysu.edu.tw (C.M. Kao).

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Basic oxygen furnace (BOF) slag is a final waste material in the basic oxygen furnace steel making process. 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, 1999; Stadler et al., 2007; Tsai and Kao, 2009). BOF slag is heterogeneous oxide materials, which are compounded by some main oxides such as Fe_2O_3, FeO, CaO, SiO_2, SO_3, Al_2O_3, and MgO due to their mass percentage (Stadler et al., 2007). There is 5–20% of FeO and 1–8% of Fe_2O_3 present in the BOF slag (Li, 1999). Furthermore, FeO and Fe_2O_3 can be dissociated to produce Fe(II) and Fe(III) in aqueous solution. The application of the Fenton-like oxidation with BOF slag process to decompose chlorinated solvents has attracted extensive attention due to its satisfactory success (Tsai et al., 2010).

Changing the solution pH is one way to control the generation of $^{\cdot}OH$ and $SO_4^{-\cdot}$. Therefore, the objectives of this bench-scale study were to (1) evaluate the effectiveness of using different types of iron minerals (e.g., magnetite, hematite, goethite, and BOF slag) to activate Fenton-like oxidation processes to remediate TCE-contaminated groundwater, (2) evaluate the potential of applying different types of acids including organic and inorganic acids (e.g., sulfuric acid, citric acid, glacial acetic acid, tartaric acid) to enhance the chemical oxidation processes, and (3) evaluate the effectiveness of using BOF slag to activate Fenton-like and persulfate oxidation processes to remediate TCE-contaminated groundwater. Results obtained from this study will be useful in developing a practical system for field application.

2. Materials and methods

2.1. Materials

All chemicals used were reagent grade [TCE (≧99.5% purity) (Fisher Scientific, USA), H_2O_2 (30%) and sodium persulfate ($Na_2S_2O_8$, minimum 99.0%) (Merck KGaA Chemicals, German)], which was used as received. Magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and goethite (α-FeOOH) were obtained from Fluka Chemical (USA). The BOF slag was obtained from China Steel, Taiwan and it was sieved with a No. 100 mesh (1 mm) sieve to remove large slag. BOF slag was washed with distilled water, dried at 200 °C in an oven, and cooled down in a desiccator before use. BOF slag was analyzed to determine the iron components [e.g., FeO, Fe_2O_3, amorphous iron, extractable iron, Fe(II), total iron (Fe_t), and Fe(III)] (Li, 1999). Amorphous iron concentration was quantified by ammonium oxalate extraction (Mckeague and Day, 1966). Extractable iron was determined using hydroxylamine chloride solution as an extract following the procedures described by Hesse (1971). The Fe(II) and Fe_t contents were colormetrically determined using a HACH DR 2400 spectrophotometer, in accordance with HACH methods 8146 and 8008, respectively (APHA, 2001). Table 1 shows the major compositions of the BOF slag applied in this study.

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 ORP meter (ORION Model 250A+, Thermo, USA) and a pH meter (TES 1380, Taiwan), respectively. The analytical procedures for groundwater analyses were described in Standard Methods (APHA, 2001). Methane was analyzed using a Shimadzu 9A GC (Shimadzu, Tokyo, Japan) via the headspace technique. The groundwater contained the following components at the specified concentrations (mg L^{-1}): nitrate, 1.8; Fe_t, 1.7; Fe(II), 0.2; sulfate, 38; sulfide, 4.9; methane, 0.03; ammonia nitrogen, 9; phosphate as P, 1.31. The initial pH and ORP values of the groundwater were 5.2 and −132 mV, respectively.

Table 1
The major compositions of BOF slag.

Compositions	Value
FeO (%)	14
Fe_2O_3 (%)	6
CaO (%)	34.8
MgO (%)	5.8
Extractable iron (g kg^{-1})	46.1
Amorphous iron (g kg^{-1})	15.9
$Fe^b{}_o/Fe^a{}_d$	0.34
pH	10.7

$^a Fe_d$: Extractable iron, $^b Fe_o$: Amorphous iron.

2.2. Experimental procedure

Each batch experiment was performed in triplicate in a continuous stir batch reactor system (close system), composed of a 250-mL brown bottle with a pH electrode inserted into the reaction solution. The initial TCE concentration was approximately 20 mg L^{-1} (after equilibration). The studied control factors that affect the TCE removal efficiency included types of iron mineral, pH, types of inorganic or organic acids, and types of oxidants (5000 mg L^{-1} of H_2O_2 and 5000 mg L^{-1} of $S_2O_8^{2-}$) as shown in Table 2. Control tests in the absence of iron mineral, and chemicals were also conducted in parallel for each experiment.

The pH of the batch reactor system was controlled by the addition of 0.1 N H_2SO_4/NaOH, 0.1 N $C_6H_8O_7$ (citric acid)/NaOH, 0.1 N CH_3COOH/NaOH, and 0.1 N HOOC–$(CHOH)_2$–COOH (tartaric acid)/NaOH at the beginning of the experiment. The initial pH values were approximately 3, 4, 5.2 7.1, and 10.7 (Table 2). Each batch reactor system contained 200-mL of collected groundwater and 10 g L^{-1} of iron mineral (e.g., magnetite, hematite, goethite, and BOF slag) (Table 2). The resulting solution was equilibrated for 5 min and a predetermined amount of chemicals based on measured initial TCE concentration was subsequently added and mixed completely. The experiment was conducted at room temperature, and water samples were collected at different time points up to 60 min for the analysis of TCE and H_2O_2 concentration during the reaction. All batch experiments were performed in triplicate. 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 GC. A 50 m × 0.32 mm DB-624 capillary column with a 0.25 μm film (J&W Sci.) was used for sample separation. Hydrogen peroxide concentrations were determined by iodometric titration with 0.1 N sodium thiosulfate (Schumb et al., 1995). The first-order decay constant (k_{obs}, min^{-1}) of TCE was calculated to evaluate the effect of iron mineral, pH, and type of chemical agent addition on the oxidation rate.

3. Results and discussion

3.1. Effects of iron mineral on TCE removal

Fig. 1 presents the effects of iron mineral types on TCE oxidation efficiency. Results show that the batch experiment with 10 g L^{-1} of magnetite had the most significant TCE removal efficiency during the first 5 min of reaction compared with the other experiments with the addition of BOF slag, hematite, and goethite (Fig. 1). Results from Fig. 1 show that the observed TCE removal efficiencies followed the order of magnetite (78%) > BOF slag (63%) > goethite (47%) > hematite (45%) during the first 10 min of operation. However, no significant further TCE removal was observed in the four experiments after 60 min of reaction. Table 3 presents the results of TCE oxidation after 60 min of operation. Results indicate that magnetite had a more significant enhancement of TCE oxidation