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Chemical oxidation of chlorinated non-aqueous phase liquid by hydrogen peroxide in natural sand systems

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Abstract

This study explored the Fenton-like oxidation of trichloroethylene (TCE) existing as dense non-aqueous phase liquid (DNAPL) in natural silica sand (iron = 0.04 g/kg) and the sand from an aquifer (iron = 2.01 g/kg). Glass bead containing no iron mineral was used as the control. Batch oxidation experiments were conducted to assess interactions between oxidant and TCE DNAPL. Column experiments were performed to evaluate dynamics of TCE and H_2O_2 during oxidation. The pH was not altered. In the batch system, a single application of 3% H_2O_2 to the aquifer sand oxidized 40% of the added TCE DNAPL in 1 h, which was four times of that by dissolution with the gas purge procedure. This demonstrated the ability of mineral-catalyzed Fenton-like reaction to directly oxidize TCE in non-aqueous liquid. In the column experiments, after passing 7 pore volumes (PVs) of 1.5 and 3% H_2O_2 solution, the residual TCE in aquifer sand column was 12.0 and 2.6% of the initial added, respectively. On the other hand, 28.4% of the added TCE still remained in the silica sand column by 7 PVs of 3% H_2O_2. The distribution of TCE in column and effluent indicated the occurring of direct oxidation of TCE DNAPL and the increased solubilization, which probably due to size reduction of DNAPL droplets, followed by water-phased TCE oxidation.

Keywords: Chemical oxidation; Groundwater remediation; Fenton-like; TCE; DNAPL

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1. Introduction

Chlorinated solvents, such as trichloroethylene (TCE), are commonly used as degreasers or dry cleaning solvents worldwide. Chlorinated solvents are carcinogenic and often recalcitrant in environment. Because of low water solubilities and higher densities than water, chlorinated solvents are often found to exist as dense non-aqueous phase liquids (DNAPLs) in aquifers of contaminated sites [1,2]. Because DNAPLs are the continuous source for the plume of dissolved and volatile contaminants, in situ degradations of DNAPLs would be desirable in order to reduce the exposures and risks to the environment and human.

Traditional pump-and-treat processes are inefficient to remove DNAPLs due to their low solubilities, high interfacial tension, and limited mass transfer in aquifers [3,4]. In situ chemical oxidation has been shown to be a promising alternative to remediate soils and aquifers contaminated by organic compounds, particularly for the zone of high concentrations [5]. One of the chemical oxidation processes is the iron-catalyzed H_2O_2 oxidation system to produce the hydroxyl radical ($HO^\bullet$), which is a very strong and non-specific oxidant. The range of oxidation rate constants of organic compounds by $HO^\bullet$ was reported to be between 10^7 and $10^9\,M^{-1}\,s^{-1}$ [6]. There are two types of iron-catalyzed H_2O_2 oxidation processes: the Fenton oxidation, which utilizes soluble iron such as Fe^{2+}, and the Fenton-like process which uses iron oxyhydroxide such as goethite (α-FeOOH). A significant portion of contaminants in soils was found to be oxidized by H_2O_2 without any addition of soluble iron [7–9], and the mineral-catalyzed Fenton-like reaction was proposed to describe the oxidation occurring in the natural soils [8]. Because soil and aquifer material usually contain considerable amounts of natural iron minerals such as iron oxyhydroxide, mineral-catalyzed Fenton-like reaction has been shown to be an effective alternative for the remediation of contaminated soil and groundwater. Ravikumar and Gurol [9] reported a 50% reduction of sorbed TCE by 1.68 mmol of H_2O_2 in the sand containing 800 mg/kg of natural iron. More than 70% of TCE removal was achieved in a sandy clay loam by the application of 1 g H_2O_2 per kg of soil and no addition of external soluble iron [10].

The mechanism of iron oxyhydroxide minerals to catalyze H_2O_2 is quite different at acidic and natural pH. The iron oxyhydroxide mineral was dissolved at acidic pH to produce Fe^{2+}, which then catalyzed H_2O_2 [11]. Because there was little dissolution of iron minerals, it was proposed that, at natural pH, the H_2O_2 was catalyzed on the surface of iron oxyhydroxide minerals (i.e. a heterogeneous catalysis) [8,12,13].

The application of iron-catalyzed H_2O_2 oxidation processes on wastewater treatment has been studied intensively [14–16]. Many studies have reported that the oxidation efficiency was influenced by parameters such as the type and concentration of iron [17], H_2O_2 concentration [10], the presence of other $HO^\bullet$-competitive organic compounds [8,18], and pH [12]. Fenton-like reaction was found to achieve similar efficiency at lower H_2O_2 dose [8,17]; however, with the addition of ferrous sulfate, a better oxidation and lower oxidant requirement was also reported [9,19].

Acidic pH was often used to optimize the efficiency of iron-catalyzed H_2O_2 oxidation [7,8,12,20]. However, acidic soil environments might cause ecological impacts. Several studies have shown that Fenton-like oxidation could be effectively carried out at both acidic and natural pH degradation [9,10,21]. The oxidation of nitrobenzene by Fenton-like oxidation was even faster at pH 7 than pH 4 due to a greater production rate of $HO^{\bullet}$ in the H_2O_2/iron oxyhydroxide system at natural pH [22].

Multiple phases of contaminants, including vapor, sorbed, dissolved and non-aqueous phases, usually co-exist in an aquifer contaminated by a large quantity of chlorinated solvent. The oxidation of dissolved-phase contaminants has been studied extensively in the past. It has been well accepted that the hydroxyl radical oxidizes organic compounds in water solution very effectively. Previously, it was believed that most compounds presented in sorbed or particulate phases could not be directly oxidized because the generated hydroxyl radicals were rapidly consumed in the aqueous phase [23]. In a photo-Fenton system, only the dissolved polychlorinated biphenyls could be oxidized by hydroxyl radicals [18]. However, by comparing the dissolution rate of hexachlorobenzene and the Fenton oxidation rate, it was concluded that the sorbed compounds might be directly oxidized at high doses of H_2O_2 [17]. Yeh et al. [24] proposed that “oxidation–desorption–oxidation” was one of the interaction mechanisms among the oxidant, soil organic matters (SOM), and the sorbed chlorophenols during iron-catalyzed H_2O_2 oxidation. The oxidation of SOM resulted in the release of sorbed chlorophenols, which were then oxidized by the excess H_2O_2.

Laboratory studies have shown effective results on the remediation of soil spiked with petroleum hydrocarbons in the form of non-aqueous liquid [25,26]. In a TCE DNAPL contaminated site, 93% of TCE DNAPL was reduced to less than 50 ppb by injecting H_2O_2, trace quantities of ferrous sulfate and acid through a patented Geo-Cleanse® process [27]. However, the interaction mechanisms between the oxidant and the contaminants existed in DNAPLs have not been well clarified. The $HO^{\bullet}$ generated from the Fenton or Fenton-like process could oxidize the NAPLs through two possible mechanisms: the “direct” attack of $HO^{\bullet}$ on the DNAPLs, and the “indirect” way through the dissolution of DNAPLs to aqueous solution, which is then oxidized by $HO^{\bullet}$.

The interactions occurred during the direct oxidation of DNAPLs in the Fenton-like oxidation at natural pH could include the catalysis of H_2O_2 at the surface of soil, and the reaction of $HO^{\bullet}$ and DNAPLs in the water–liquid interface. Thus, the amount and rate of $HO^{\bullet}$ generation and the transport of $HO^{\bullet}$ to the DNAPLs would be the rate-limiting factors for the direct oxidation of DNAPLs.

In the indirect oxidation mechanism, the dissolution of DNAPLs into water would be an additional controlling parameter in addition to the catalysis of H_2O_2 and the transport of $HO^{\bullet}$. Because DNAPLs are very insoluble in water, it is expected that the oxidation efficiency should be low through the indirect oxidation mechanism, causing an increase in the time and the cost for remediation.

Therefore, the purposes of this study are to evaluate the oxidation efficiency and the interaction mechanisms between the oxidant and the contaminants in the form of DNAPLs. Specifically, this study tried to find out whether the DNAPL-form chlorinated contaminants could be directly oxidized by the oxidant, H_2O_2, through the catalysis of natural-occurring iron mineral. Such information would help remediation engineers further expand the application of the Fenton-like process to treat the DNAPL spots in contaminated sites. For practical purpose, the experimental work was concentrated on the oxidation under natural pH.

Table 1
Characteristics of tested sands

Compositions	Glass bead (wt.%)	Silica sand (wt.%)	Aquifer sand (wt.%)
Size (mm)			
<0.417	0.0	1.0	16.7
0.417–0.589	0.0	27.4	32.8
0.589–0.833	0.0	58.3	8.1
0.833–1.0	0.0	11.0	11.3
1.0–1.168	3.0	2.1	30.7
1.168–2.0	57.1	0.3	0.3
2.0–2.4	39.9	0.0	0.0
Uniform coefficient, d_{60}/d_{10}	1.2	1.7	3.4
Organic matter (g/kg)	<1.2	<1.2	<1.2
pH	7.2	6.9	7.5
Porosity (%)	40	52	37
Extractable iron (g/kg)	ND	0.04	2.01

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (Merck, 35%, non-stabilized) and TCE (Baker, >99.98% purity) were used as received. Three types of sand, named as aquifer sand, silica sand, and glass bead, were tested. Their characteristics are shown in Table 1. The particle size of the aquifer sand was the smallest (0.4–1.0 mm) and the least uniform. The aquifer sand was sampled from approximate 5–8 m of the aquifer of an illegal dumping site located near the bank of Kao-Ping River in Pingtung County, Taiwan. The natural silica sand was frequently used as the packing material for groundwater monitoring wells in Taiwan. The aquifer sand contained 50 times of extractable iron than the silica sand. The natural silica sand was imported from Vietnam and washed with distilled water prior to use. The glass bead containing no iron mineral was used as the control. These sands were low in soil organic contents; therefore, sorption of TCE would be negligible.

2.2. H_2O_2 decay experiment

The capability of the aquifer sand and natural silica sand to catalyze the Fenton-like decay of H_2O_2 was evaluated in batch and column systems. In batch experiments, 100 g of sand was first added to a BOD bottle wrapped with aluminum foil to prevent the photo decay of H_2O_2. After the addition of 200 ml of 3% H_2O_2 solution, the bottle was capped and hand-shaken for approximately 10–20 s every 20 min. A water sample of 0.5 ml was taken, diluted to 10 ml, and analyzed for H_2O_2 at 30 s, 1, 2, 4, 6, and 8 h, respectively.

Column experiments were performed to observe the distribution of H_2O_2 over the sand column during the passing of 3% H_2O_2. The column was made of glass, which was 3.2 cm in diameter and 90 cm in length with sampling port located 10 cm apart (Fig. 1). The total depth of the sand bed was 30 cm. A layer of glass bead (1 mm in diameter) was placed between

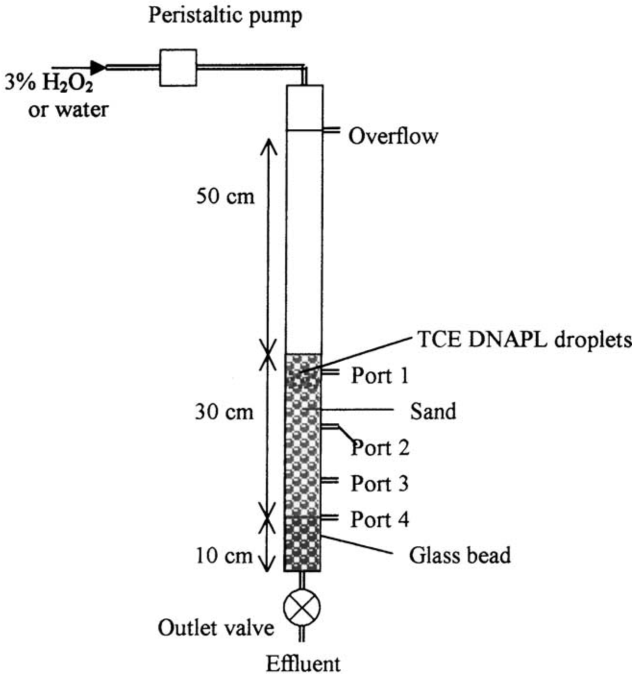


Fig. 1. The set-up for column study (no TCE in the H_2O_2 decay tests).

the sand bed and the outlet to prevent the washout of sand. The sand was constantly tapped and vibrated during every 10-cm increment of packing. In each increment, 25 ml of water was first added to the column and then the pre-soaked sand was delivered into the column through a glass tube extended down to the bottom. Then, 3% of H_2O_2 solution was pumped through the column in a downflow mode. An outlet valve controlled the flow rate through the column. The initial Darcy flow velocity in the column was set at 2.04 m per day (8.5 cm/h), which was within the expected range of velocities in aquifers under natural and remediation conditions [28,29]. Water samples from the sampling ports and effluent from the bottom were collected for H_2O_2 measurement after passing each pore volume (PV) of H_2O_2 solution.

2.3. Oxidation mechanism of TCE DNAPL

If the oxidation of DNAPLs only occurred in the water solution (i.e. the indirect interaction of $HO^\bullet$ and DNAPLs), the oxidation would be limited by the dissolution of the DNAPL. Therefore, the maximum oxidation rate would be equal to or less than the maximal dissolution rate of TCE. On the other hand, a higher oxidation rate than the dissolution rate of DNAPLs would indicate the capability of $HO^\bullet$ to directly oxidize the contaminants in the form of DNAPLs (i.e. the direct interaction mechanism).

Therefore, the oxidation of TCE DNAPL was conducted in a batch system and the results were compared to the dissolution of TCE DNAPL. The experimental procedure of TCE

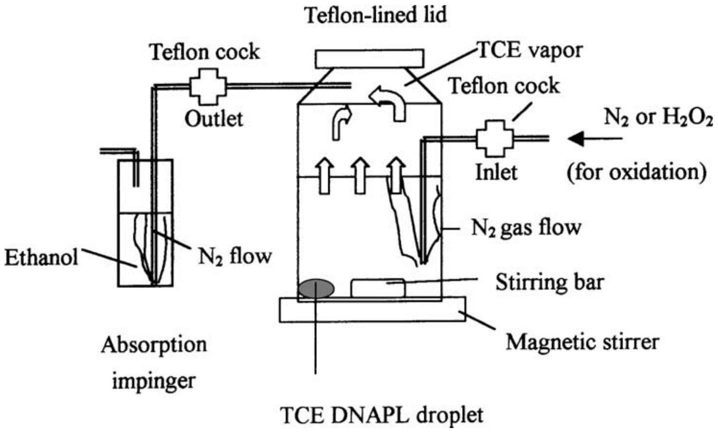


Fig. 2. Experimental set-up for batch tests. Inlet: N_2 flow for gas purge procedure; H_2O_2 for oxidation experiments. Outlet: no ethanol absorption for oxidation tests.

DNAPL dissolution, using a gas purge procedure, was modified from the steps described by Brusseau et al. [30] and Watts et al. [17]. The theory of gas purge procedure is that the dissolution rate of a solid or a liquid is a function of the concentration in water phase; thus, the rate of TCE dissolution would remain maximally when the dissolved-phase TCE is volatilized by gas purging and the aqueous concentration of TCE is maintained near zero. The dissolution test was performed in 250 ml borosilicate wide-mouth bottles with Teflon-lined screw caps (Fig. 2). An aqueous solution containing 1% of TCE DNAPL was prepared by adding 1 ml (1.46 g) of TCE liquid through pipette to the bottle containing 100 ml of distilled water. The tip of pipette was inserted to the bottom of the bottle to minimize the volatilization loss. Three different N_2 flows (90, 180, and 1200 ml/min) were used to purge the TCE as soon as it was dissolved. Because the rate of dissolution is inversely proportional to the droplet size of a non-aqueous liquid, special cares as the followings were taken. The inlet of purging gas was approximately 1 cm above the bottom of the bottle and the speed of stirring bar was set at 180 rpm in order to avoid the breakage of the TCE droplet by mixing and purging. Visual inspection during the experiment confirmed that the TCE droplet was able to maintain in one piece. The off gas containing TCE was then sorbed in the 165 ml gas impinger filled with 50 ml of ethanol. The TCE in the gas impinger was sampled and analyzed for TCE every 5 min. After the experiment ended, 100 ml of ethanol was added to the bottle to dissolve the remaining TCE DNAPL, and 2 μl of sample was taken and analyzed by a GC. The calculation of mass recovery of the TCE sorbed in gas impinger and that remained in the bottle after gas purging was within 95–105%.

The Fenton-like oxidation of TCE DNAPL was conducted with the procedures similar to the TCE DNAPL solubility tests described earlier, except that the system contained 75 g of sand and no N_2 purging was used. Immediately after the addition of TCE droplet, the bottle was capped and H_2O_2 was added to produce the Fenton-like reaction. The initial H_2O_2 was 3% (0.88 M). After 10, 30 and 60 min of reaction, 100 ml of ethanol was injected to scavenge the remaining $HO^{\bullet}$ and to dissolve the un-reacted TCE DNAPL.

Table 2
Operational conditions of column experiments

Run	H_2O_2 concentration	Pore volumes
Glass bead-run 1–3	0	0, 3, 6
Glass bead-run 4, 5	3%	4, 7
Silica sand-run 1–3	0	0, 3, 6
Silica sand-run 4, 5	3%	3, 7
Aquifer sand-run 1–3	0	0, 3, 7
Aquifer sand-run 4, 5	1.5%	4, 7
Aquifer sand-run 6, 7	3%	3, 7

2.4. *Column oxidation experiments*

A total of 17 column oxidation experiments were performed to investigate the dynamics of TCE removal during oxidation. The experimental conditions are summarized in Table 2. The column set-up was identical to that used in the H_2O_2 column decay test. After the packing with sand, the column was filled to the top with distilled water; TCE droplets were injected, using a microsyringe, through the sampling port 1 (1 cm below the top of sand bed) into the sand column. The total volume of injected TCE DNAPL was 1.0 ml (1.46 g), which led to the initial TCE concentration being approximately 3.0 g/kg of sand in the column. After the injection of TCE, the column was sealed for 3 days to allow the TCE to redistribute in the column.

Each sand column was flushed with various pore volumes of H_2O_2 solution that was pumped through the column. At the end of each pore volume, 0.5 ml of solution was withdrawed from each sampling port for H_2O_2 measurement. The effluent was collected in a Teflon tedlar bag for volume measurement, and TCE, H_2O_2 and Cl^- analyses. Distilled water was applied to the control column to observe the movement of TCE DNAPL.

The distribution of residual TCE in various depths of sand bed after the passing of 3% H_2O_2 solution was determined by methanol extraction. The reason for using methanol as an extractant was that TCE is miscible in methanol. Methanol is also soluble in water and low in viscosity. Therefore, it would not form a separate phase in any water-containing micropores and could be drained freely in columns. At the end of oxidation, the pump was stopped. The water above sand bed was first withdrawn from the sampling port 1. The water in the sand column was then drained slowly from the outlet valve at the bottom of the column. These aqueous samples were analyzed for TCE, H_2O_2 and Cl^-. After drainage, 45 ml of methanol (Merck, 99.9%) was injected into sampling port 4 to fill the pores of sand in the 25–40 cm depth of column. The sand was then soaked in methanol for 30 min to allow the residual TCE in this region to be dissolved. Thereafter, the outlet valve was opened to collect the methanol containing the extracted TCE. The steps were repeated three times and all the methanol samples collected were combined and analyzed. Similar steps were performed to extract the TCE in sand column every 5-cm increment with pre-calculated amount of methanol equivalent to the pore volume of each section. The overall mass recovery of TCE in the control tests using such a procedure was 89–104%.

The residual TCE in each depth of column was calculated as follows:

$$\text{TCE in column}(\%) = 100 \times \frac{(\text{concentration of TCE in methanol}) \times (\text{volume of methanol})}{\text{weight of injected TCE}}$$

The breakage of Cl–carbon bonds and the release of chloride ion by chemical oxidation is an index of toxic reduction of chlorinated organic compounds [10]. The percentage of Cl^- released was calculated as follows:

$$\text{chloride yield } (\%) = \frac{(\text{moles of chloride measured}) \times 100}{(\text{moles of TCE removed}) \times (\text{number of Cl in one TCE molecule})}$$

2.5. Analysis

Particle size distribution was determined by the standard sieve. The Walkley–Black wet oxidation method was used to measure the organic carbon in soil [31]. The residual H_2O_2 was titrated with iodometric method [32]. Chloride ion was determined by the mercuric nitrate method [33]. Extractable Fe determination, using hydroxylamine chloride solution as an extract, followed the procedures described by Hesse [34].

TCE in aqueous samples and methanol extract was analyzed by a Hewlett-Packard 5890 series II Gas chromatography equipped with a TD-2 purge and trap system (Scientific Instrument Services Inc., Ringoes, NJ, USA). The column was a 1.8 m × 2.0 mm i.d. stainless steel column packed with 1% SP-1000 on 60/80 mesh Carbopack B. The carrier gas was N_2, detector FID temperature was 200 °C, and the injector temperature was 200 °C. The oven temperature program was 45 °C for 5 min, then increased to 200 °C at 5 °C/min.

3. Results and discussion

3.1. Decomposition of H_2O_2 in sand

As shown in Fig. 3, more than 88% of the added H_2O_2 was decomposed in the natural aquifer sand at near-natural pH, as compared to little decrease in glass sand and the control of no sand. Even though, the silica sand contained only 0.4 mg/kg of extractable iron, the data also shows approximately 50% of the added H_2O_2 was catalyzed within 1 h of reaction time. Thus, the occurrence of H_2O_2 decomposition only in sands containing iron led us to conclude that the added H_2O_2 has been catalyzed through mineral-catalyzed Fenton-like reaction, as was reported in many researches [9,10,19]. It should be noted that the decrease of H_2O_2 in silica sand was rapid but ceased after 1 h of reaction. A second dose of 3% H_2O_2 was added to the same silica sand, and it was found that the decomposition of the second dose of H_2O_2 in silica sand followed the similar pattern to that in the first dose. The phenomena indicated that the capability of the silica sand to catalyze H_2O_2 was repeatable but somehow inefficient, probably due to the low iron content of silica sand.

The distribution of H_2O_2 in the sand column during the continuous passing of 3% H_2O_2 solution is shown in Fig. 4. Upon contacting with the aquifer sand, H_2O_2 rapidly decreased

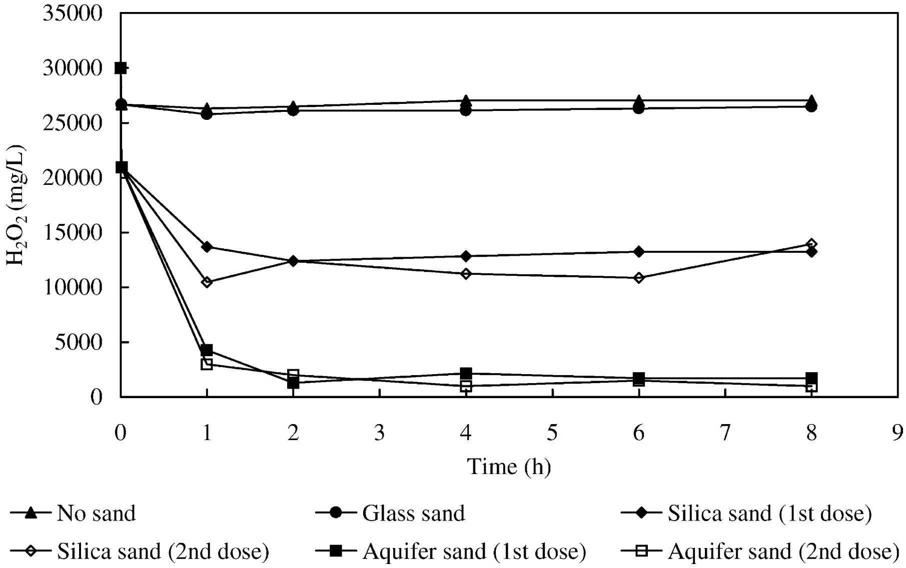


Fig. 3. Decay of H_2O_2 in various sands.

to about 5000 mg/l, and reduced to less than 100 mg/l in the column below 10 cm of depth. In the case of silica sand, which contained much less extractable iron than the aquifer sand, the H_2O_2 concentration progressively decreased along the depth of the column. The H_2O_2 concentration during the initial pore volumes of H_2O_2 circulation was only 30–60% of the added quantity, probably due to the dilution. It increased and then reached steadiness after passing 6 pore volumes of 3% H_2O_2 solution. This was in accordance with the results in the batch study of H_2O_2 decay. A much less iron content of the silica sand resulted in an inefficient catalysis capability. Therefore, a significant portion of the added H_2O_2 was still detected in the column.

3.2. Interaction mechanism between TCE DNAPL and the oxidant

Fig. 5 presents the comparison of accumulative TCE removal over a 1-h period by Fenton-like oxidation with that by the gas purge procedure. Even though, the dissolution rates of TCE DNAPL increased slightly with higher purging flow of N_2 gas (1200 ml/min), the decrease of TCE DNAPL by dissolution was far less than that in the case of mixing H_2O_2 with aquifer sand. When H_2O_2 was added, the decrease of TCE DNAPL in the aquifer sand reached 40% in 1 h. On the other hand, the amount of continuous dissolution with the highest purging flow was approximately 10%. The results also showed that the decrease of TCE by oxidation in natural silica sand was more than that in the glass bead system, but was only slightly higher than that in the dissolution system.

Based on the data presented in Fig. 5, it could be interpreted that the decrease of TCE in the presence of sand and H_2O_2 apparently resulted from Fenton-like reaction by the

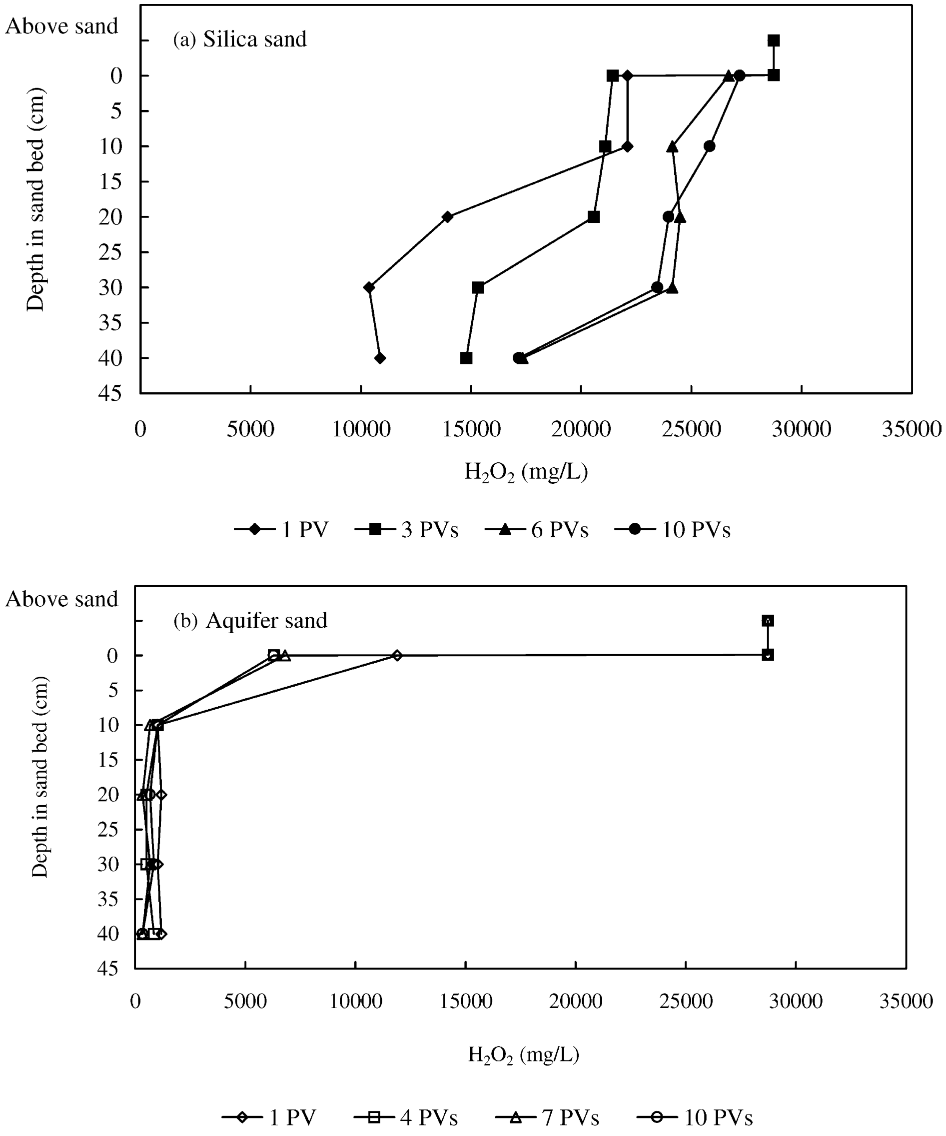


Fig. 4. Decay of H_2O_2 in sand columns.

iron content of the sands, not the oxidation by H_2O_2. Otherwise, the TCE reduction in two iron-containing sands should have been be the same as that in the glass bead system at the same H_2O_2 dosage. Furthermore, because the oxidation of soluble phase contaminant by hydroxyl radicals is usually very fast [6,35], the decrease of TCE DNAPL would be a dissolution-controlled procedure if the oxidation was through the dissolution and then oxidation. In other words, the oxidation rate of TCE DNAPL would be equal to or less

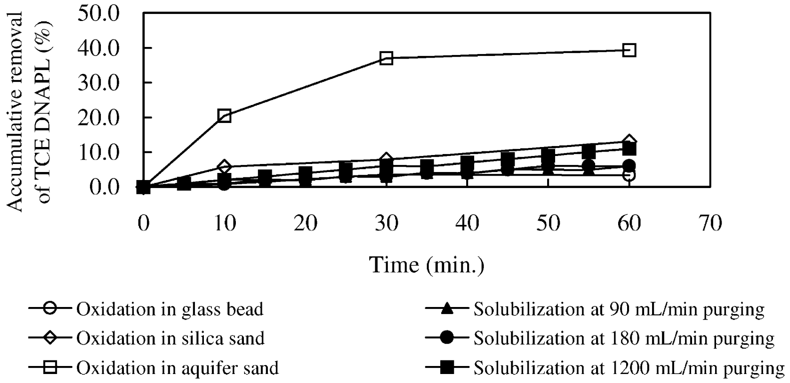


Fig. 5. Comparison of TCE DNAPL removed by Fenton-like oxidation and solubilization.

than the maximum dissolution rate. However, in this study the decreasing rate of TCE has much exceeded its maximum dissolution rate, which would imply the occurrence of direct reaction. Therefore, the data provided a strong evidence of the direct chemical oxidation of TCE DNAPL by mineral-catalyzed Fenton-like reaction.

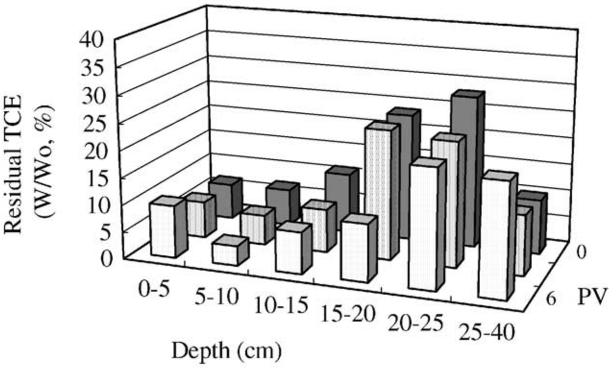
The slight increase of TCE reduction by Fenton-like oxidation in silica sand system could be interpreted by the low oxidation power of the system. Because there was not enough $HO^{\bullet}$ due to low iron content, the little amount of $HO^{\bullet}$ must have already been consumed during the oxidation of the dissolved TCE; leaving no more $HO^{\bullet}$ available to attack the TCE DNAPL. As the mixing intensity in the batch oxidation experiment was not as vigorous as that in the gas purge system, the actual dissolution rate of TCE DNAPL during oxidation in the silica sand system was lower than that measured in the gas purge system. Thus, the occurrence of direct oxidation of TCE DNAPL in the silica sand system could not be completely ruled out. But if it did occur, it would be in a much less extent than that in the aquifer sand system.

3.3. *Oxidation of TCE DNAPL in sand column*

The data obtained from the glass bead column containing TCE DNAPL also show no significant H_2O_2 decay and TCE oxidation (Figs. 6–8). The TCE remained in glass bead column after passing H_2O_2 solution did not significantly decrease (Fig. 6b), as compared to that treated with water (Fig. 6a). The accumulated residual TCE remained in the entire 40-cm-deep glass bead column was 80% after passing 6 PVs of water, and 73% after passing 7 PVs of 3% H_2O_2. The difference among various treatments of pore volume was probably caused by the variation in packing and the non-homogenous distribution of glass bead in column.

The TCE concentrations in the effluent of the glass bead column during passing of water and H_2O_2 solution were in the range of 150–800 mg/l, as shown in Fig. 7. This indicated that the decrease of residual TCE in the column was more likely due to TCE dissolution. After 3 days of contact in column, the TCE in the effluent of the first pore volume from the

(a) Water



(b) 3% H_2O_2

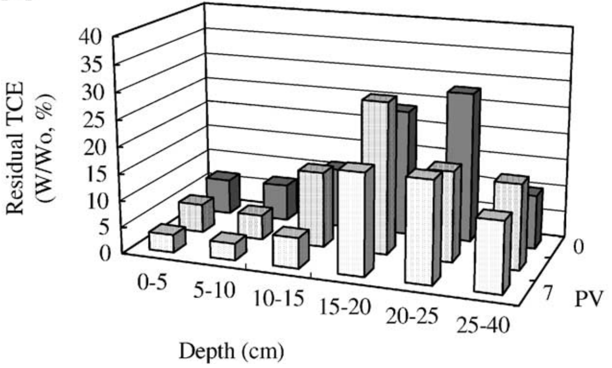


Fig. 6. Distribution of TCE in glass bead column treated with various pore volumes of (a) water (b) 3% H_2O_2.

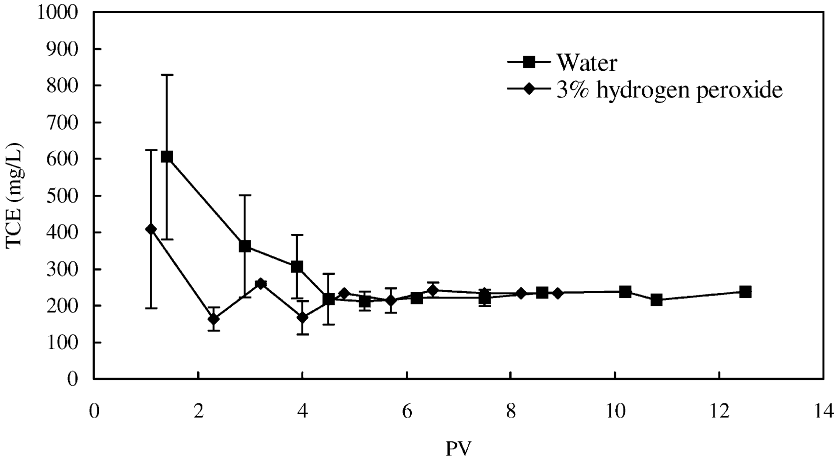


Fig. 7. Variation of TCE in the effluent of glass bead column.

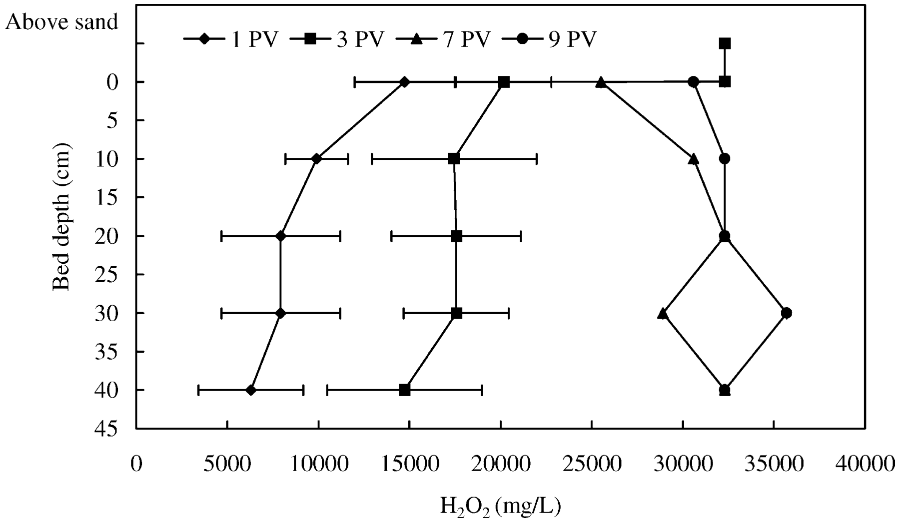


Fig. 8. Progressive decrease of H_2O_2 in glass bead column during passing of 3% H_2O_2.

glass bead column was 600 ± 200 mg/l. Then, the TCE quickly decreased to 250 ± 50 mg/l as more solution passing though, suggesting a non-equilibrium dissolution during the flow of water. The concentration of H_2O_2, as presented in Fig. 8, increased to almost the same as the added concentration as the flow passed through the column, reflecting no sign of Fenton-like catalysis in glass bead column.

The results in Fig. 9 elucidate the occurrence of continuous Fenton-like oxidation of TCE in natural silica sand column. A significant disappearance of TCE was observed after passing 3 PVs of 3% H_2O_2 solution, compared to that of passing 3 PVs of water. The accumulated residual TCE in the entire 40-cm-deep bed was 28.4% after passing 5 PVs of 3% H_2O_2 solution. This was much lower than that treated with water (91%). Consistent with the decrease of TCE in column, the concentration of H_2O_2 as presented in Fig. 10, decreased from 30,000 to 20,000 mg/l, supporting the occurrence of Fenton-like catalysis.

Similar to the results in Fig. 7, a part of the decreased TCE in the column showed up in the effluent, as presented in Fig. 11. However, The TCE concentrations in the effluent of columns treated with H_2O_2 solution were higher than those treated with water only. In addition, the elution of TCE in silica sand column exhibited several “increase and then decrease” patterns, particularly in the run of 7 PVs. It is likely that the oxidation of TCE in either DNAPL or dissolved form would result in a gradual decrease in the size of DNAPL droplets in silica sand column. Because the dissolution rate of a solid or a liquid is affected by its size and contact area, the decrease in the size of TCE droplets would enhance the dissolution rate in column. Furthermore, because of the inefficient catalytical ability of the silica sand, a portion of the dissolved TCE was not oxidized and consequently eluted out in the effluent. In other words, the data implied that the decrease of TCE in the sand column probably included direct oxidation of TCE DNAPL and enhanced dissolution.

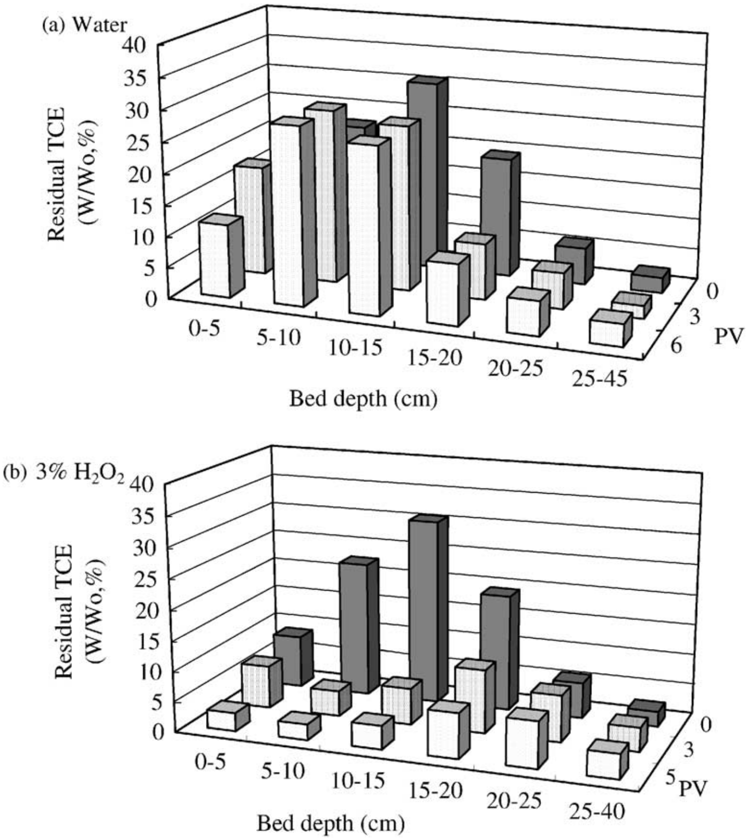


Fig. 9. Distribution of TCE in silica sand column treated with various pore volumes of (a) water (b) 3% H_2O_2.

Fig. 12 presents the TCE remained in aquifer sand columns. Fig. 13 exhibits the TCE concentration in the effluent during the passing of various PV of water, 1.5 and 3.0% H_2O_2 solution. It should be noted that considerable TCE was removed in the aquifer sand column and appeared in the effluent by just passing 8 and 10 PVs of water (Figs. 12a and 13a). In addition, the effluent TCE concentration in water-flow column remained steadily high and close to 1000 mg/l (the water saturated value of TCE), indicating the possibility of washout of TCE DNAPL. Such phenomena could be due to the use of the smallest granular size and the least uniform of the aquifer sand, resulting in significant channeling of flow, and increased flow rates in aquifer sand column.

Nevertheless, results in Fig. 12b and c shows that TCE remained in the aquifer sand column after passing of H_2O_2 was the lowest of the three tested media. They demonstrated that the aquifer sand containing more iron have a better oxidation efficiency. Similar to that in the silica sand column, the effluent TCE in the aquifer sand column increased and then decreased during the Fenton-like oxidation (Fig. 13). In particular, in the aquifer sand columns treated with 3% H_2O_2 solution, TCE in the effluent was lower than that treated with

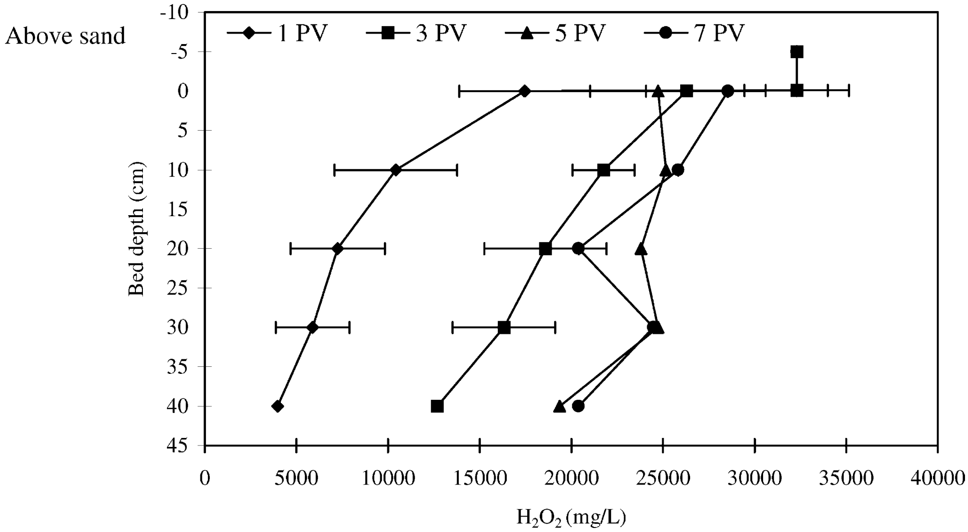


Fig. 10. Progressive decrease of H_2O_2 in silica sand column during passing of 3% H_2O_2.

water and 1.5% H_2O_2. It finally decreased to below 30 mg/l. It is more likely that abundant iron minerals and higher doses of H_2O_2 have produced sufficient $HO^{\bullet}$, resulting in the decrease of both dissolved and DNAPL forms of TCE. As well, the TCE concentration was the lowest in the effluent of aquifer sand columns treated with 3% H_2O_2. The very low H_2O_2 in the aquifer sand column again indicated the occurrence of Fenton-like reaction (Fig. 14).

The elution of TCE in aquifer sand column also exhibited a significant “increase and then decrease” pattern. This is possibly also caused by the decrease of DNAPL size and the increase of dissolution rate. In a system containing both soluble and undissolved form

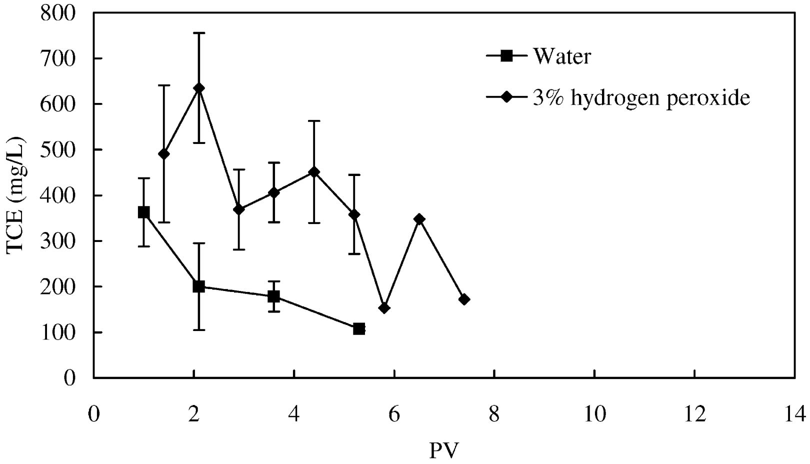
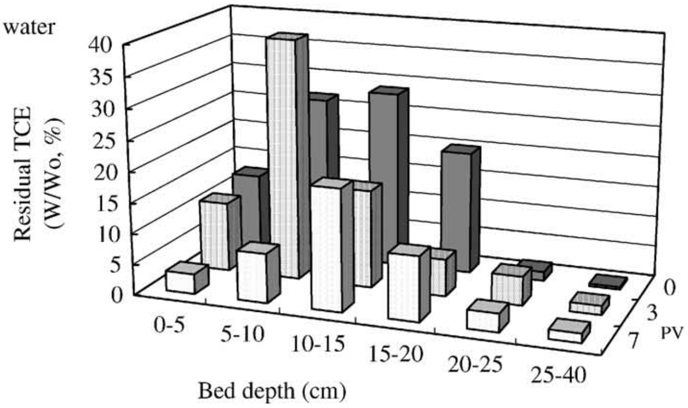
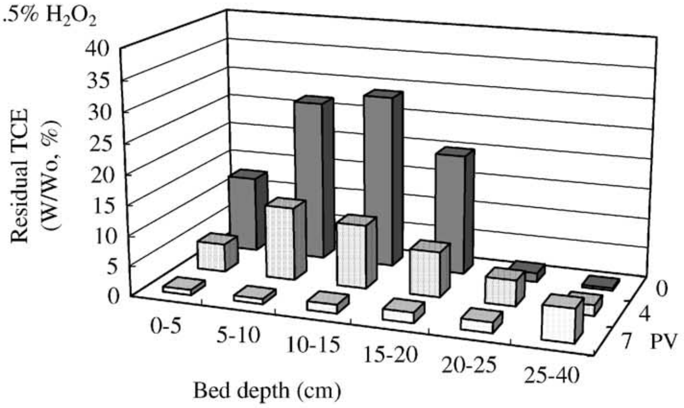


Fig. 11. TCE concentration in the effluent of silica sand column.

(a) water



(b) 1.5% H_2O_2



(c) 3% H_2O_2

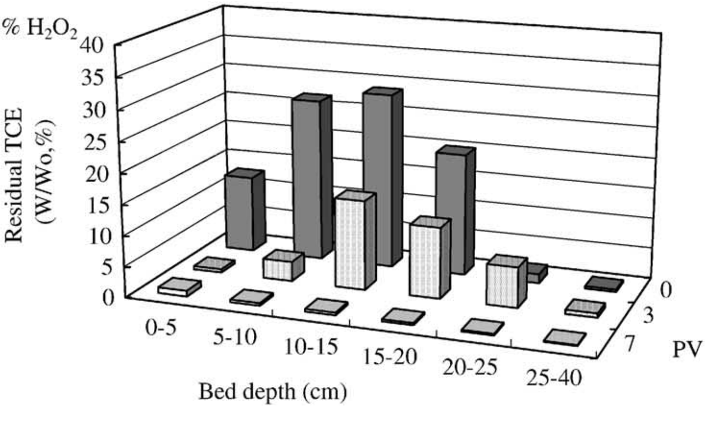


Fig. 12. Distribution of TCE in aquifer sand column treated with various pore volumes of (a) water (b) 1.5% H_2O_2 (c) 3% H_2O_2.

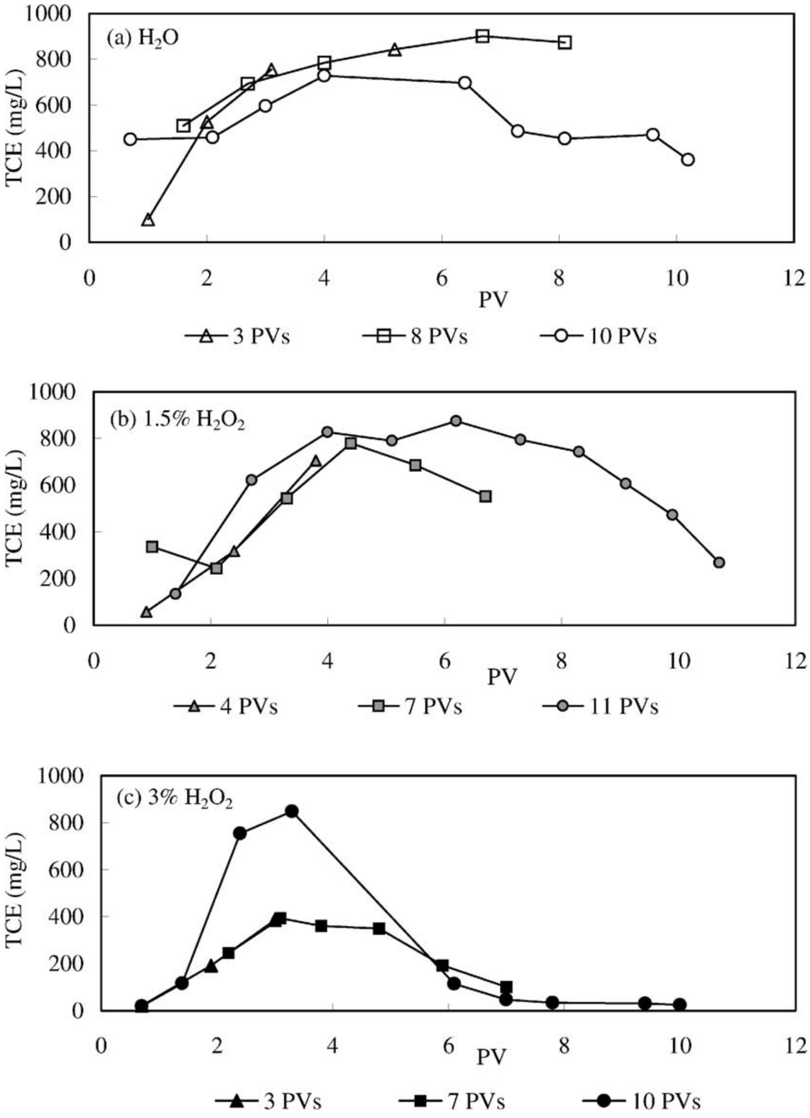


Fig. 13. Variation of TCE in the effluent of aquifer sand column.

of TCE, the change in dissolved TCE concentration during Fenton-like oxidation can be expressed as:

$$\frac{M_{\text{net}}}{T} = \frac{M_{\text{dissolved}}}{T} - \frac{M_{\text{oxidized}}}{T}$$

where M_{net}/T is the TCE concentration in the effluent. M_{oxidized}/T is the oxidation rate of dissolved TCE and is a function of H_2O_2 and iron mineral. $M_{\text{dissolved}}/T$ is the dissolution rate

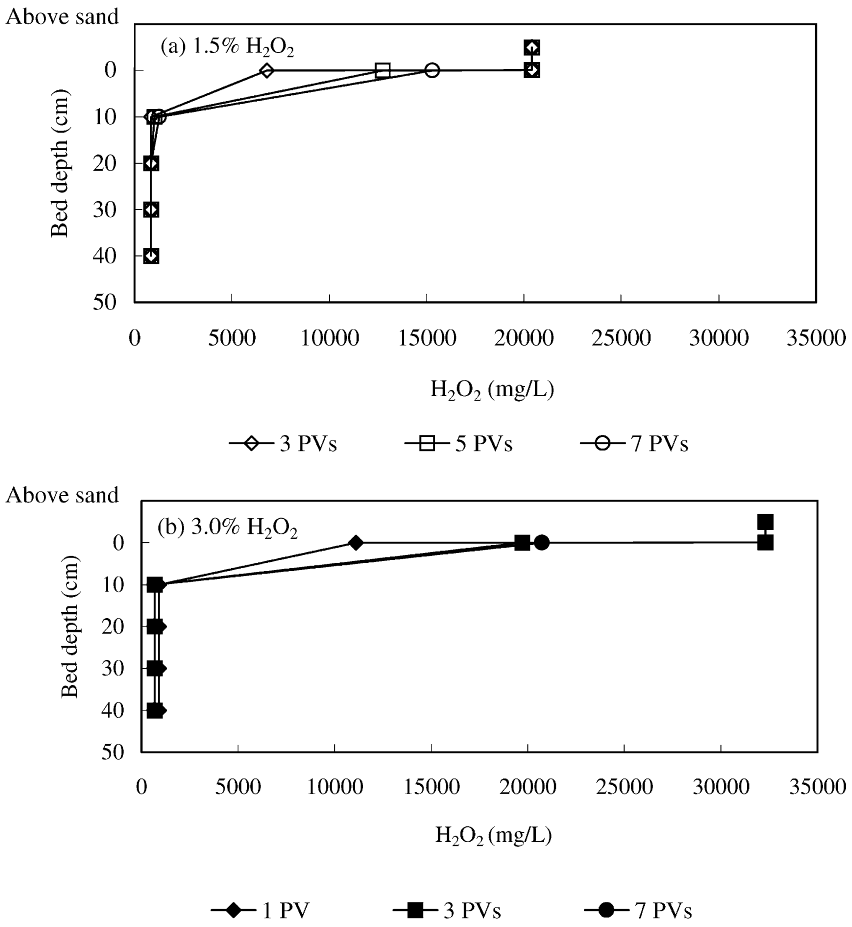


Fig. 14. Rapid decrease of H_2O_2 in aquifer sand column during passing of 1.5 and 3% H_2O_2.

of TCE DNAPL, which is influenced by the size and contact area of TCE DNAPL. Because TCE DNAPL was directly oxidized in the aquifer sand system, as indicted in the batch tests, it is likely that during the direct oxidation of TCE DNAPL, the size of DNAPL decreased and the solubilization rate increased. Accordingly, an increased concentration of dissolved TCE (i.e. a positive M_{net}/T) was observed. In a strong oxidation and complete-mixing system, a positive M_{net}/T is unlikely to occur, because the dissolved TCE is expected to be immediately oxidized. However, the sand column more likely presented a plug flow system of weak (silica sand) or moderate (aquifer sand) oxidation power. In addition, the highest concentration of TCE DNAPL and the strongest oxidation would occur in the top region of the columns. Thus, it appeared that the increase in effluent TCE, particularly those shown in the early PVs (Fig. 13b with 1.5% H_2O_2 and aquifer sand) could be the results of increased solubilization rate due to direct oxidation and size reduction of TCE DNAPL. As more H_2O_2 was circulated or the concentration of H_2O_2 increased, the period of increased

Table 3
Percentage of TCE remained in column and effluent, overall TCE oxidation, and Cl^- production after passing 7 PVs of water or H_2O_2

	Glass bead (%)		Silica sand (%)		Aquifer sand (%)		
	Water	3% H_2O_2	Water	3% H_2O_2	Water	1.5% H_2O_2	3% H_2O_2
TCE in column[a]	74.5	63.1	85.4	28.4	45.9	12.0	2.6
TCE in effluent[a]	25.8	26.8	14.6	29.8	54.1	38.6	19.3
Overall TCE							
Removal	–	10.1	–	41.8	–	49.4	78.1
Cl^- yield	–	<1.0	–	36.4	–	70.9	85.9

[a] TCE mass after treatment/ TCE mass of added ($W/W_0 \times 100$).

effluent TCE became shorter (Fig. 13c). This could be due to the continuous oxidation of the dissolved TCE under stronger oxidation condition.

Table 3 is the comparison of Fenton-like oxidation of TCE DNAPL in three sand systems after passing 7 PVs of water or H_2O_2 solution. It appeared that the iron mineral content and H_2O_2 dosage both affected the oxidation efficiency of TCE DNAPL and chloride yield. H_2O_2 catalysis, TCE degradation, and chloride yield in the aquifer sand containing 2.01 g/kg of extractable iron were the highest, followed by the natural silica sand. After passing 7 PVs of H_2O_2 solution, the TCE remained in the aquifer sand columns was significantly reduced to 12 and 2.6% of the initially added for 1.5% H_2O_2 and 3.0% H_2O_2, respectively. With respect to the silica sand, a poorer efficiency was expected because of less iron content. The application of 1.5% H_2O_2 solution yielded an overall 49% reduction of TCE DNAPL in aquifer sand, whereas, a 3% H_2O_2 was required for the silica sand to achieve a similar efficiency. This indicated that less H_2O_2 solution was required for the sand containing more iron. It was also found that, unlike the increased effluent TCE mass in the silica sand, the overall TCE eluted out from the aquifer sand during Fenton-like oxidation was less than that in the water system. The content of iron mineral and H_2O_2 dosage also influenced the chloride yield of oxidation. The data in Table 3 indicates that the chloride yield could be enhanced by increased H_2O_2 concentration and more natural iron mineral. Thus, the high toxicity associated with the TCE DNAPL could be greatly reduced by the breakage of Cl–carbon bonds.

In terms of concentration, the remaining TCE after passing 7 PVs of H_2O_2 solution in all columns could still be higher than stringent remediation goal. For example, 2.6% of TCE remained in aquifer sand column was equivalent to 127 mg/kg. In addition, a part of TCE removed from column was presented in the effluent as a result of enhanced solubilization. Thus, it is suggested that in order to meet stringent remediation goals, Fenton-like oxidation of TCE DNAPL should be utilized in combination with other remediation technologies. The chemical oxidation process is more advantageous in reducing contaminants in extremely high concentrations that are difficult to be treated by other moderate processes. Therefore, it would be more cost-effective to use Fenton-like oxidation of DNAPL spots followed by other remediation technologies such as bioremediation. Increasing pore volumes of H_2O_2 circulation is also feasible to further reduce the TCE in column. An above ground treatment of TCE in the effluent pumped out from an aquifer, which is a common practice, would take care of the dissolved TCE during in situ Fenton-like oxidation.

One of the key issues in the field application of Fenton or Fenton-like oxidation was the transport of H_2O_2 to the contaminants. Because H_2O_2 was catalyzed rapidly, the $HO^\bullet$ would be consumed near the injection port and became unavailable to the contaminants located downstream. Therefore, stabilizers such as phosphate salts were proposed to slow down the release of $HO^\bullet$ [12,36]. In this study, all the experimental results have shown that H_2O_2 remained very low throughout the aquifer sand bed. However, it was noted that after passing the H_2O_2 solution, the TCE DNAPL existing in the deeper zone of the aquifer sand column was significantly decreased. For example, data points in Fig. 12a 7 PVs and in Fig. 12c 7 PVs showed that the residual TCE in the 10–20 cm region below the sand bed was approximately 30% less than that of the control set. Similarly, data in various H_2O_2 concentrations and pore volumes also showed more reductions of residual TCE in columns. These results indicated the oxidation of TCE DNAPL in the deeper zone of the sand bed. Previous results have shown that TCE could only be oxidized by $HO^\bullet$ released from H_2O_2. Because $HO^\bullet$ is very unstable, it is likely that the decrease of TCE in the 10–20 cm of the aquifer sand columns was due to the generation of $HO^\bullet$ in that region. This indicated the possibility of H_2O_2 available in the deeper zone. The rate of H_2O_2 decomposition is a function of iron content in both Fenton and Fenton-like reaction [17,19]. Even though, the iron content of the aquifer sand was the highest among the tested media in this study, it was still lower than those reported in some researches (e.g. 30 g/kg of Fe [36], 4.4 g/kg of Fe [17]). The iron content in most soils is usually greater than 1% [37]. It is likely that the rate of H_2O_2 canalization by the iron mineral in the aquifer sand was not fast enough and incomplete; therefore, there could be H_2O_2 available in the deeper zone of the column. In addition, Kalarla and Watts [12] reported that considerable amounts of stabilized H_2O_2 were decomposed in the top zone of low permeable soils due to long contact time. Unlike the sands used in other studies, which were smaller in size or containing more fine materials, the size of the sand tested in this study was relatively coarse, leading to a faster flow rates. This would also enable the transfer of H_2O_2 to the deeper zone of the column. The H_2O_2, transported to the deeper zone, was then catalyzed to release $HO^\bullet$, and TCE DNAPL existing in the deeper zone of the column was oxidized.

4. Conclusions

Mineral-catalyzed Fenton-like oxidation, which utilizes natural-occurring iron minerals to catalyze H_2O_2 and produce $HO^\bullet$, is effective in oxidizing soluble and sorbed contaminants in soil and groundwater. This study explored the Fenton-like oxidation of TCE existing as DNAPL form in natural sands of various iron content. The results of this study would help remediation engineers further expand the application of the Fenton-like process to treat DNAPL spots in contaminated sites. For practical applications in the field, the pH was not altered.

Based on the results of laboratory investigations, the following conclusions were reached.

The batch oxidation study has demonstrated the ability of mineral-catalyzed Fenton-like reaction to directly oxidize TCE in the form of non-aqueous liquid. The decomposition of H_2O_2 was more rapid in the aquifer sand, containing 2.01 g/kg of iron, than in silica sand containing 0.04 g iron/kg sand. With a single application of 3% of H_2O_2 to the aquifer sand, 40% of TCE DNAPL was oxidized in 1 h, which was four times of that by dissolution.

The results from column studies showed that both iron content and H_2O_2 dosage enhanced the reduction of TCE remained in columns, increased chloride yield, and reduced TCE in the effluent. After passing 7 PVs of H_2O_2 solution, TCE remained in aquifer sand columns was significantly reduced to 12 and 2.6% of that initially added for 1.5 and 3.0% H_2O_2, respectively.

By comparing the dynamic of TCE concentrations in columns and in effluent, it appeared that the interaction between the oxidant and TCE DNAPL included direct oxidation. The direct oxidation resulted in size reduction of TCE DNAPL, which in turn, led to enhanced dissolution. In the aquifer sand system in which the oxidation capability was stronger, the dissolved TCE was then oxidized and exhibited a quicker “increase and decrease” pattern in the effluent. When the oxidation was weak (the silica sand system), a repeated “increase and decrease” pattern was found.

The results also showed that the TCE exiting in the 10–20 cm region below the surface of sand beds was significantly reduced, suggesting that fewer problems in the delivery of H_2O_2 to the deeper zone in coarse sand system.

Based on the experimental results, it is recommended that Fenton-like oxidation could be utilized to directly oxidize the TCE DNAPL spots of a contaminated site. The residual TCE dissolved in the effluent could be further degraded by other remediation technologies such as bioremediation and/or above ground treatment.

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