Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes

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Abstract

The contaminants present as nonaqueous phase liquids (NAPLs) in the subsurface are long-term sources for groundwater pollution. Fenton-like reaction catalyzed by natural iron oxides such as goethite in soils is one of the feasible in situ chemical reactions used to remediate contaminated sites. This research evaluated the Fenton-like reaction of five chlorinated ethylenes and three aromatic hydrocarbons using goethite as the catalyst. The reaction efficiencies and rate constants of these compounds in NAPL and dissolved forms were compared. The content of goethite used in batch experiments was in the range similar to those found in subsurfaces. Low H_2O_2 concentrations (0.05 and 0.1%) were tested in order to represent the low oxidant concentration in the outer region of treatment zone. The results showed that at the tested goethite and H_2O_2 ranges, the majority of contaminants were removed in the first 120 s. When aromatics and chloroethylenes were present as NAPLs, their removal efficiencies and reaction constants decreased. The removal efficiencies of 0.02 mmol NAPL contaminants were 26–70% less than those of the dissolved. The measured rate constants were in the order of $10^9\,\text{M}^{-1}\,\text{s}^{-1}$ for dissolved chlorinated ethylenes and aromatic hydrocarbons, but were 25–60% less for their NAPL forms. The initial dosage of H_2O_2 and NAPL surface areas (18.4–38.2 mm^2) did not significantly affect reaction efficiencies and rate constants of chlorinated NAPLs. Instead, they were related to the octanol–water partition coefficient of compounds. For both dissolved and NAPL forms, aromatic hydrocarbons were more reactive than chlorinated ethylenes in Fenton-like reaction. These results indicated that the decrease in reaction efficiencies and rate constants of NAPL-form contaminants would pose more negative impacts on the less reactive compounds such as benzene and cis 1,2-DCE during goethite-catalyzed Fenton-like reaction.
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1. Introduction

After serious spills, leakages or improper disposal of petrochemicals, nonaqueous phase liquids (NAPLs) of pollutants often distribute at the contaminated site. The NAPLs, present as droplets, pools and/or even free-moving layers in the subsurface, will slowly dissolve and become long-term sources to groundwater contamination [1]. NAPL remediation is a tough challenge. Technologies that can effectively remove NAPLs are favored to reduce health risks and save time and cost of remediation. In situ chemical oxidation (ISCO) processes have been used increasingly for remediation of contaminated sites [2]. The Fenton

technology, one type of ISCO processes, uses iron compounds to catalyze H_2O_2 and produce free radicals to react with contaminants. There are two categories of Fenton processes. One is the standard Fenton reaction which utilizes soluble Fe(II) as the catalyst, and the other is the so-called modified Fenton or Fenton-like process, which includes the use of Fe(III), iron oxides such as goethite (α-FeOOH) and iron chelates [3,4]. Recently, pyrolusite (β-MnO$_2$) was found to catalyze a similar Fenton-like reaction [5]. Hydroxyl free radical (HO$^\bullet$) is considered to be the key oxidant species in the Fenton reaction [6]. The reaction rate constants ($k_{\text{HO}^\bullet}$) of many hazardous organic compounds with HO$^\bullet$/O$^{\bullet-}$ were reported to range between 10^8 and $10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$ [7–9]. Even thought HO$^\bullet$ is a strong and non-specific oxidant for many contaminants, the $k_{\text{HO}^\bullet}$ values of chloroaliphatic organics such as carbon tetrachloride (CT) and chloroform are less than $10^7\,\text{M}^{-1}\,\text{s}^{-1}$, thus the oxidation of CT and chloroform by HO$^\bullet$

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is ineffective. Recent studies have reported that other nonhydroxyl radicals such as perhydroxyl radicals ($HO_2^\bullet$), superoxide radical anions ($O_2(^-)$), hydroperoxide anions (HO_2^-) produced during the propagation of Fenton-like reaction provided feasible reductive removals for chloroaliphatic compounds [5,10].

The best efficiency of standard Fenton reaction usually takes place at low pH, which could cause negative environmental impacts [11,12]. On the other hand, modified Fenton process has the advantage of high efficiencies at natural pH ranges [13]. The goethite-catalyzed Fenton-like process at natural pH is a heterogeneous process [3,14]. It was found that the H_2O_2/iron oxide reaction was even faster at pH 7 than pH 4 due to a greater production rate of $HO^\bullet$ at the natural pH [15]. Fenton-like reaction can also achieve a better efficiency at lower H_2O_2 doses, meaning less H_2O_2 requirement in field application [16].

Soils and aquifer materials usually contain considerable amounts of natural iron oxides [17]; therefore, natural Fenton-like reaction will occur when H_2O_2 is injected into the subsurface. A 50% removal of sorbed TCE was achieved by adding 1.68 mmol of H_2O_2 to the sand containing 800 mg/kg of natural iron [13]. Similarly, the addition of 1 g H_2O_2 per kg of soil without external soluble iron removed more than 70% of TCE in a sandy clay loam soil [18]. Gasoline-related compounds such as MTBE [19,20] and BTEX [21] were also reported to be significantly degraded by Fenton processes in soil systems.

The removal efficiency of contaminants by iron oxide catalyzed Fenton-like reaction is influenced by parameters such as types and concentrations of iron oxides [22], H_2O_2 concentration [18], the presence of other oxidant-consuming compounds [23] and pH [12]. Although many researchers have reported the effects of these parameters on the contaminant removal, consistent observations have not yet been developed and further studies are required. For example, it was reported that goethite exhibited a better surface reactivity than semicrystalline iron oxide [24]. However, the second-order rate constants of H_2O_2 catalysis by goethite and ferrihydrite were observed to be in the same range of 0.02–0.06 L/M^{-1} s^{-1} [25]. In one of our previous works, we compared the catalysis of H_2O_2 by ferrihydrite, goethite and an aquifer sand containing natural iron oxides, and found no difference in the amount of $HO^\bullet$ produced at higher H_2O_2 doses [26]. With respect to the effect of H_2O_2 doses, the removal of trichloroethylene (TCE) by Fenton-like reaction in natural soils increased with H_2O_2 doses [16]. However, the reaction efficiency of octachlorodibenzo-*p*-dioxin in a natural soil was found to be irrelevant to the dosage of H_2O_2, probably due to the strong sorption characteristics of contaminants [27].

It has been well accepted that Fenton and Fenton-like processes effectively degrade the dissolved phase contaminants. Early studies believed that diffusion limitation of hydroxyl radicals will prevent the compounds in sorbed or particulate phases from being directly oxidized [28]. However, by comparing dissolution rate and Fenton reaction rate, several studies revealed that radicals produced during Fenton reaction were likely to directly react with sorbed hexadecane [29] and chlorobenzene [22]. Results from field applications also reported the ability of Fenton and Fenton-like processes to remove substantial mass from NAPLs [30]. In a contaminated site, more than 90% removal

of PCE and TCE NAPLs was achieved by a patented Fenton process [31]. The NAPL of petroleum hydrocarbons could also be effectively oxidized by a Fenton-like process [29]. One of our previous studies found that with a single application of 3% H_2O_2, 40% of TCE DNAPL was decomposed within 1 h, which was four times of that by dissolution [32]. These results strongly indicated that in addition to the "dissolution and reaction" mechanism, the direct interaction between Fenton radicals and NAPLs is possible.

The decrease of organic concentrations by $HO^\bullet$ reaction is related to concentrations of radicals and organic compounds. A second order rate law was proposed for $HO^\bullet$ reaction with an organic compound [9]:

$$-\frac{d[P]}{dt} = k_{HO\cdot}[P][HO\cdot] \tag{1}$$

in which $k_{HO^\bullet}$ is the rate constant of $HO^\bullet$ with organic compound P (M^{-1} s^{-1}). The [P] and [$HO^\bullet$] are the concentrations of compound and hydroxyl radical, respectively. Reaction kinetics is fundamental for remediation engineers to evaluate and design an ISCO process. Several reports have provided extensive lists of $HO^\bullet$ rate constants for toxic compounds [7–9]. The order of rate constants can be used for comparing Fenton reaction potential among compounds. However, most rate constants were obtained from the reaction system of completely dissolved substrates; and their application to the NAPL system needs to be further developed.

Therefore, this study compared the reaction efficiencies and rate constants for goethite-catalyzed Fenton-like reaction of five chlorinated ethylenes and three aromatic hydrocarbons in NAPL and dissolved forms. To simulate the Fenton-like reaction catalyzed by natural iron oxides in soils, the content of goethite used in batch Fenton experiments was in the range similar to those found in subsurfaces. Low H_2O_2 concentrations (0.05 and 0.1%) were tested in order to focus on the low oxidant conditions in the outer region of treatment zone. The reaction rates of NAPLs were compared to their dissolution rates to explore whether the radical was reactive to NAPLs. The effects of NAPL surface areas, H_2O_2 doses and the chemical characteristics of pollutants were also evaluated.

2. Materials and methods

2.1. Chemicals

Synthetic goethite was purchased from Fluka Chemical Co. The total iron oxide containing in goethite, as measured in our previous study [26], was 367.8 g/kg as Fe. Hydrogen peroxide (~35%, w/w) was purchased from Nihon Shiyaku Industries. The chlorinated ethylenes tested included PCE (J.T. Baker, 99.7%), TCE (J.T. Baker, 99.8%), cis 1,2-DCE (Fluka, 97%), trans 1,2-DCE (Tokyo Kasei Kygyo, 98%) and 1,1 DCE (Aldrich, 99%). Benzene (Merck, 97.7%), toluene (J.T. Baker, 99.8%) and ethyl benzene (Allied Signal, 99.7%) were selected to represent the gasoline hydrocarbons because their high water solubilities usually result in large plumes in the subsurface. All the tested compounds are highly reactive to $HO^\bullet$, with the $k_{HO^\bullet}$

values in the order of $10^9 \, M^{-1} \, s^{-1}$ [7]. All the chemicals were used as received without further purification.

2.2. Measurement of NAPL dissolution

The maximum dissolution rates of NAPLs were measured using a gas purge technology; and the results were compared to reaction rates of NAPLs. The gas purge procedure was designed to measure the maximum dissolution rates of volatile o rganic liquids in water solution with vigorously gas purging to maintain the dissolved concentrations in solution near zero [10]. The apparatuses and experimental procedures of chlorinated NAPL dissolution were the same as those used in our previous work [26]. Immediately after the injection of NAPL pure liquid, the gas purging (1200 mL/min) started and continued for 5 min (the same reaction time for the Fenton reaction test). The purged volatile compound in the gas stream was sorbed with methanol and analyzed.

Because the Fenton reaction efficiency changes with the organic concentration (Eq. (1)), the initial amount of dissolved or NAPL contaminants in the system was the same (0.02 mmol) for all tested compounds to avoid the effects caused by substrate concentration [P]. Using cis 1,2-DCE (MW = 96.9, density = 1.28 g/cm^3) as an example to describe the preparation of solution containing 0.02 mmol NAPL. Take 1.5 µL of pure DCE (with a microsyringe) and inject into to a serum bottle containing 20 mL DI water and goethite. Thus, the mass of DCE NAPL in 20 mL water is $1.5 \times 1.28/96.9 = 0.02$ mmol. To study the effect of contact surface areas (droplet sizes) of chlorinated NAPLs, the 0.02 mmol NAPL was injected as 1, 3 and 5 droplets within mini circular fences (1 cm in diameter, Teflon) at the bottom of reactors. The mini circular fences were used to keep each NAPL droplet separated from contacting each other during mixing.

Because the densities of aromatic hydrocarbons are less than 1 g/cm^3, instead of sinking to the bottom, their NAPLs float on top of water and volatilize quickly to the headspace. Therefore, the dissolution experiment of aromatic hydrocarbons was conducted in a different system which utilized sealed 250-mL borosilicate wide-mouth bottles with hollow screw caps and Teflon-lined septa. The bottles were filled with water first to have zero headspace. The liquid of aromatic hydrocarbons was injected into the bottle, and then the bottle was turned up side down and hand-shaken vigorously for 5 min. The water sample was withdrawn carefully with a syringe penetrating through the septa and analyzed for dissolved aromatic hydrocarbons.

2.3. Fenton reaction of dissolved-form compounds

The Fenton-like reaction of chlorinated ethylenes was performed in 250-mL borosilicate wide-mouth bottles with Teflon-lined screw caps (Fig. 1). Because earlier studies [13,25] have shown that the amount of iron oxide is a major factor in the catalytic decomposition of H_2O_2, the concentration of goethite tested in this study was in the same range of aquifer sands to simulate the natural Fenton-like reaction catalyzed by
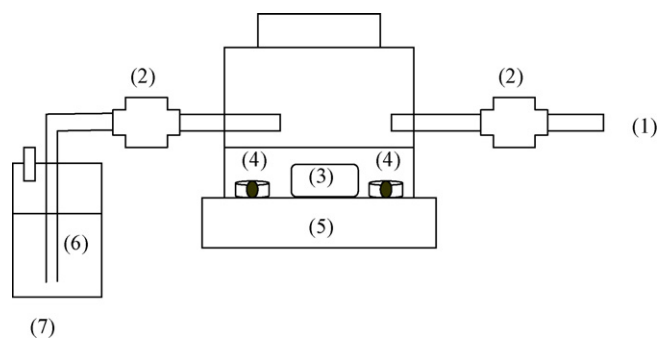

Fig. 1. The experimental set-up for Fenton-like reaction. (1) Injection port of H_2O_2 and methanol. (2) Cocks. (3) Magnetic bar. (4) DNAPL droplets inside circular fences (for DNAPL tests). (5) Stirrer. (6) Methanol. (7) Absorption impinger.

soil iron oxides in the subsurface. After adding 10 mL deionized water and 0.22 g goethite (equivalent to iron oxide content of 4 g/L as Fe), the solution was magnetically stirred and suspended for 1 h to reach equilibrium. Then, 10 mL of 2.0 mM dissolved organic compounds was added to the bottle followed by injection of H_2O_2. The initial concentration for dissolved organic compounds and H_2O_2 was 1.0 mM, and 0.01 and 0.5%, respectively. We tested low H_2O_2 concentration in order to represent the situation of low oxidant concentration in the outer region of treatment zone. When applied to the subsurface, the Fenton procedure often faces the limitation of H_2O_2 transport, because H_2O_2 decays very fast. Thus, in the outer region of effective radius, the H_2O_2 concentration decreases dramatically. The test of low H_2O_2 doses would help to understand the reaction efficiency when H_2O_2 transports for a distance and decreases.

Our previous studies have shown that at low H_2O_2 doses, most of the added H_2O_2 decomposed and the contaminant concentrations stopped decreasing within 2–3 min [26]. Thus, the reaction time was set at 5 min in this study. After 5 min, the inlet and outlet of reaction bottle were opened and methanol was added to fill to the top of bottle. The large quantity of methanol scavenged immediately any remaining free radicals, and no further reaction occurred. In the NAPL system, the added methanol also helped the dissolution and measurement of the un-reacted NAPLs in solutions. The aliquot in the bottle and gas sorption impinger was mixed and then centrifuged at 4500 rpm (i.e., 1500 g) for 10 min, and analyzed for the remaining organic concentration. All experiments were performed in triplicate at room temperature (25 ± 3 °C).

2.4. Fenton reaction of NAPL-form compound

The reaction procedures used for chlorinated NAPLs were identical to those described in Section 2.3, except that chlorinated NAPL droplets (0.02 mmol) were placed within mini circular Teflon fences on the bottom of bottles. The circular fence was used to keep each droplet from sticking to each other during mixing. As soon as NAPL droplets were injected to the reactor, H_2O_2 was added and Fenton-like process started. Thus, there was little dissolution of the added NAPL before H_2O_2 addition, and the reaction between the dissolved phase and free

radicals was minimized. To avoid quick volatilization, the reaction of aromatic NAPL compounds was performed in a 500-mL Tedlar bag containing goethite slurry and no headspace. The injection and withdrawal of solution was through the two-way injection/withdrawal port of the bag.

The removal percentages of dissolved and NAPL compounds (%) were calculated as follow.

$$\text{Mass removal percentages}\,(\%) = (C_o V_o - C_f V_f) \times \frac{100}{C_o V_o} \qquad (2)$$

where C_o is the initial mmol of tested compound per liter of water, V_o the volume of solution in reactor before the reaction, C_f the final compound concentration of mixed solution in reactor and impinger and V_f is the combined volume of the solution in reactor and impinger.

2.5. Measurement of rate constants

We modified the competitive kinetic method to measure and calculate the rate constants. The competitive kinetics was commonly used to measure and calculate the HO$^\bullet$ reaction rate constants [7]. The target and reference compounds were mixed and reacted in the same solution; and their concentrations before and after reaction were measured. This method excluded the influence of any radical scavengers, assuming that such effects are the same for target and reference compounds [33]. Thus, the $k_{\text{HO}^\bullet}$ values of compounds can be compared. However, we have found that the reported $k_{\text{HO}^\bullet}$ value for a compound could be different if the tested conditions (e.g., substrate concentration or reference compounds) were varied. Such an inconsistency was also pointed out by Buxton et al. [7] and Fartahazis and Ross [34]. For example, the $k_{\text{HO}^\bullet}$ values of 2.2 and $3.4 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$ were documented for 0.02 and 0.014 mM hexachlorocycleopentadiene, respectively, using the same reference compounds [8]. Similarly, a wide range of $k_{\text{HO}^\bullet}$ values for phenol ($6.2–18 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$) tested with different reference compounds were reported [7,34], which indicating that the reactivity of a compound toward the free radical was affected by the reference compound present in the same solution.

Therefore, this study used a modified competitive kinetics in which the target and reference compounds were tested separately, under the assumption that when the test condition for target and reference compounds was identical, the effects of radical scavengers and the amount of radicals available for target and reference compounds should be the same, even though they were tested separately. From Eq. (1), when the available [HO$^\bullet$] is the same for target and reference compound systems, the following equations can be derived:

$$[\text{HO}\cdot] = \frac{-d[P]}{k_{\text{HO}\cdot P}[P]\,dt} = \frac{-d[R]}{k_{\text{HO}\cdot R}[R]\,dt} \qquad (3)$$

and then

$$k_{\text{HO}\cdot P} = k_{\text{HO}\cdot R}\left\{\ln\left[P_f/P_0\right]\,/\ln\left[R_f/R_0\right]\right\} \qquad (4)$$

in which the subscripts of 0 and f denote the initial and final concentrations of reference compound (R) and target pollutants (P). Eq. (4) is identical to that used in the competitive kinetics method for calculating rate constants [9], but is different in that the target and reference compounds are reacted separately.

In this study, nitrobenzene (Kanto Chemicals, 99.8%) was used as the reference compound to quantify the $k_{\text{HO}^\bullet}$ values of aromatics and chloroethylenes during the Fenton-like reactions. The known second-order rate constant of HO$^\bullet$ for nitrobenzene is $3.9 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$ [7].

2.6. Analysis

The concentrations of compounds before and after Fenton reaction were analyzed with a Hitachi 1200 HPLC equipped with a 25 cm × 4.6 mm i.d., 5-μm particles Supelcosil LC8-DB column. The moving phase for nitrobenzene was the mixture of methanol/1% acetic acid (A) and water/1% acetic acid (B). The gradient program was 65% A + 35% B at 0–5 min, and increased to 82.5% A + 17.5% B in the next 10 min. The UV wavelength was 267 nm. The analytical condition for chlorinated ethylenes was 75% methanol + 25% water at 0–8 min, and then increased to 95% methanol + 5% water for 8 min. The flow rate was 1.0 mL/min. The UV wavelength was 210 nm. An isocratic elution solution of 65% methanol and 35% water was used for aromatic hydrocarbon analysis. The flow rate was 1.5 mL/min and the UV wavelength was 254 nm.

3. Results and discussion

3.1. Reaction of NAPL and dissolved forms

The degradation curves for dissolved and NAPL PCE and cis 1,2-DCE indicated that the majority of decrease in concentrations occurred within 120 s after H$_2$O$_2$ addition (Fig. 2). Fenton process produces both hydroxyl and nonhydroxyl radicals [7,36]. However, the dominant radical species and reactions occurring in a Fenton system depend on many factors, including compound reactivity with radicals, H$_2$O$_2$ doses, catalysts, pH, etc. The reactivity of nonhydroxyl radicals with contaminants is relatively weak [37]. Therefore, the reaction curve of substrates with highly reactive hydroxyl radicals usually exhibits a significant and quick drop of concentrations within minutes [20,35]. On the contrary, the less reactive nonhydroxyl radicals tend to last longer and substrate concentrations usually decrease slowly but continuously for hours [10]. Furthermore, the nonhydroxyl radicals are favorably formed at high H$_2$O$_2$ dose (e.g., >1%) [37] or alkali pH (e.g., >11) [10]. The reaction pattern shown in Fig. 2 resembles the one with hydroxyl radicals (i.e., a rapid decrease in a short period). In addition, low H$_2$O$_2$ doses (0.01 and 0.5%) and neutral pH range in this study did not favor the generation of nonhydroxyl radicals. Thus, in this study it is likely that the removal of contaminants within 5 min was primary due to hydroxyl radicals.

The reaction rates and percentages of NAPLs by goethite-catalyzed Fenton reaction were lower than those of the dissolved phase. On the other hands, the removal percentages of NAPL form were much higher than the mass percentages released from NAPL dissolution in the experiment. As shown in Fig. 2(a), 23% of added PCE droplet was destructed in 5 min by one application
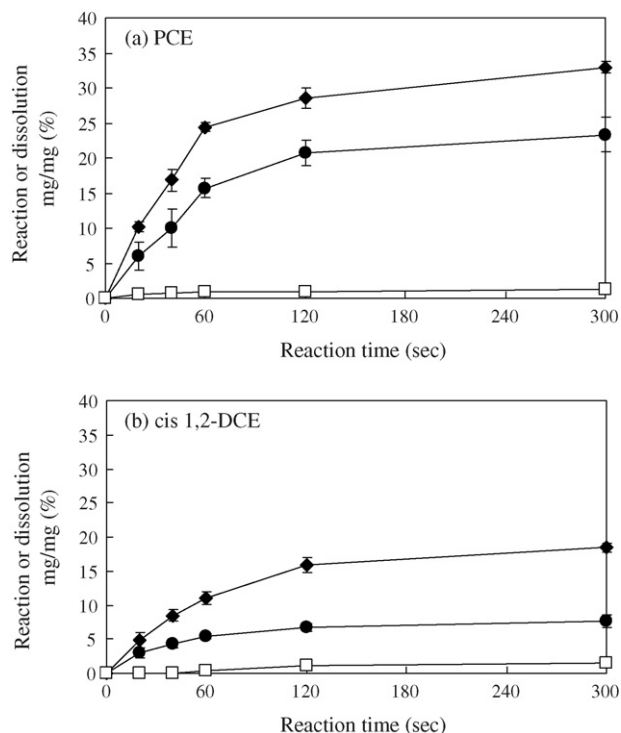
Fig. 3. Reaction efficiency for chlorinated NAPL droplets with various surface areas. (□) cis 1,2-DCE, $H_2O_2 = 0.01\%$. (■) cis 1,2-DCE, $H_2O_2 = 0.5\%$. (△) Trans 1,2-DCE, $H_2O_2 = 0.01\%$. (▲) Trans 1,2-DCE, $H_2O_2 = 0.5\%$. (○) PCE, $H_2O_2 = 0.01\%$. (●) PCE, $H_2O_2 = 0.5\%$.

Fig. 2. (a and b) Comparison of solubilization to Fenton-like reaction of NAPL and soluble chlorinated ethylenes (H_2O_2 dose = 0.5 %, one NAPL droplet). (♦) Reaction of dissolved form. (●) Reaction of NAPL form. (□) Solubilization of NAPL.

of 0.5% H_2O_2. This amount of reacted PCE NAPL was approximately 10% less than that of the completely dissolved form. In the meantime, only little PCE (1.5%) dissolved over the same period. The difference in PCE NAPL mass removed by Fenton reaction and by dissolution was 22% over 5 min of monitoring period; and in the first 60 s, PCE DNAL was degraded at 15 times the rate of gas purge dissolution. The reaction of cis 1,2-DCE exhibited a similar pattern (Fig. 2b). The total mass loss of DCE NAPL by Fenton-like reaction was 11% less than the dissolved form, but 6% more than that by gas purge dissolution. These data again revealed that the occurrence of NAPL and radical interaction in the Fenton-like reaction, as reported in other studies [5,10,26,29].

During the movement of NAPLs in the subsurface, the bulk flow of liquids can be trapped in soil pores as many small droplets. This study assessed the effects of such a NAPL distribution on Fenton reaction efficiency. Fig. 3 compared the Fenton-like destruction of 0.02 mmol chlorinated NAPLs existed as 1, 3 and 5 droplets. As can be seen from the figure, an 80% increase of total surface area (i.e., five smaller droplets instead of a single and large one) only resulted in additional 0.9–2.2% and 0.5–3.3% removals for the H_2O_2 doses of 0.01 and 0.5%, respectively. Thus, it appears that at the same amount of DNAPL, the surface area of liquid droplets or H_2O_2 doses do not significantly influence Fenton reaction of NAPLs.

Similar results were observed for the reaction of aromatic NAPLs (Fig. 4). The removal of NAPL-form aromatic hydrocarbons was 9.1–11.2% less than the dissolved. There were
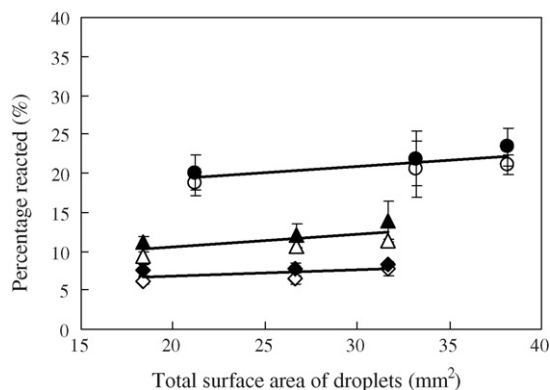
more NAPLs reacted than dissolved at the same reaction period. Increasing the H_2O_2 dose by 50-folds only resulted in additional 5–10% reaction efficiencies, indicating that H_2O_2 dose was not a major factor for the reaction.

3.2. Effects of chemical characteristics

It appears that the compounds with higher water solubilities tended to display lower removal percentages. From Fig. 2, the reaction of cis 1,2-DCE (water solubility = 3500 mg/L), either in dissolved or NAPL form, was 15% less than that of PCE (water solubility = 150 mg/L). Among the aromatic compounds tested, ethyl benzene had the highest amount of removal, followed by toluene and benzene (Fig. 4). Fig. 5 shows a good correlation between the amount of reaction and octanol–water
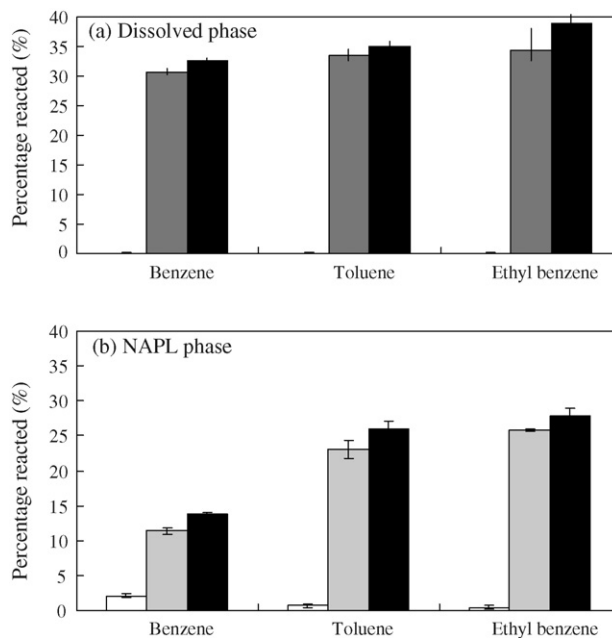

Fig. 4. Comparison of the dissolution and reaction of dissolved and NAPL aromatics. (□) Dissolution after 300 s. (▨) Reaction: 0.01% hydrogen peroxide. (■) Reaction: 0.5% hydrogen peroxide.
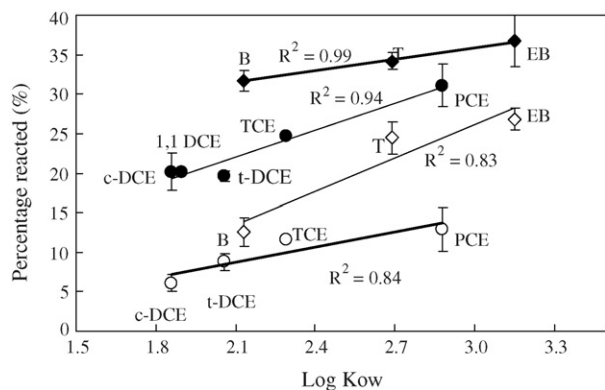
Fig. 5. Correlation between the K_{ow} values and reaction efficiency for various organic compounds. (♦) Dissolved aromatic compounds. (◊) Aromatic NAPLs. (●) Dissolved chlorinated compounds. (○) Chlorinated NAPLs

Fig. 6. Plots of rate constants against Log K_{ow}. (■) Dissolved chlorinated compounds. (●) Dissolved Aromatic compounds. (□) Chlorinated NAPLs. (○) Aromatic NAPLs.

partition coefficient (log K_{ow}) for chlorinated ethylenes, and so did for aromatics. The compounds of more Cl and C atoms in chemical structure tend to be more hydrophobic (i.e., lower water solubility) and have higher K_{ow} values. Therefore, it leads to conclude that compounds with more chlorine atom or methyl groups were more reactive in the goethite-catalyzed Fenton-like reaction. In Fig. 5, however, it should be noted that the prediction of reaction potentials based on the K_{ow} values can only be applied for compounds with similar structures. For example, the log K_{ow} value of benzene (2.13) is smaller than that of PCE (2.88), but their Fenton reaction efficiencies were similar (31.2 and 31.1%, respectively). In Fenton reaction with organic compounds, $HO^\bullet$ plays as an electrophile and attacks perferentially on the unsaturated bonds rather than H-atom abstraction [7,8]. Leung et al. [11] found that dichloroacetic acid was an intermediate of PCE oxidation in Fenton reaction. Accordingly, the aromatic hydrocarbons, having three double bonds in their chemical structures, would be more reactive with the radicals than chlorinated ethylenes, which contain only one double bond. As a result, more aromatic hydrocarbons were reacted than chlorinated ethylenes for the same Fenton reaction conditions.

The calculated rate constants are presented in Table 1, together with previously reported values [7]. Reports of various $k_{HO^\bullet}$ values of compounds were found among systems using different reference compounds, initial substrate concentrations, pH and methods of $HO^\bullet$ generation [7,8,34]. Therefore, comparison of the rate constant obtained from different Fenton conditions needs to be careful. The rate constants from this study were compared to those reported in the literature; and it is not surprising that because of using different test method, our $k_{HO^\bullet}$ values were not the same as those reported by Buxton et al. [7]. Our values are lower, but the order ($10^9 \, M^{-1} \, s^{-1}$) is the same as others. Nevertheless, in our study, all the Fenton-like reactions were performed at the same conditions, thus, the $k_{HO^\bullet}$ values of compounds in dissolved and non-dissolved form are comparable to each other. Furthermore, the present rate constant values are in good agreement to the previous reports, which found linear relations between Hammett constants and $k_{HO^\bullet}$ values. Hammett constants are widely used to predict the structure activity and reactivity of substituted compounds. Well correlation equa-
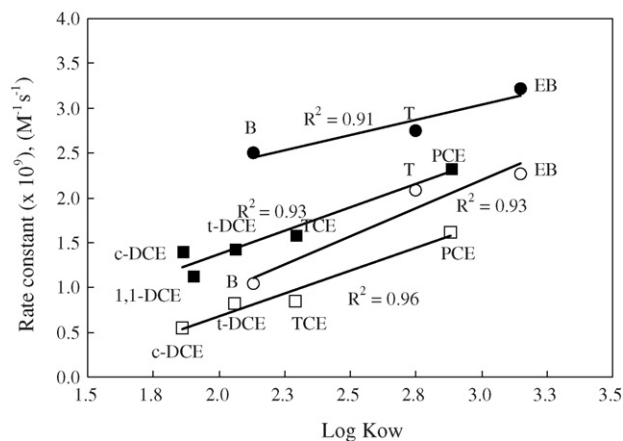
tions of $k_{HO^\bullet}$ values for aromatics [8] and chlorinated phenols [33] based on Hammett constants have been developed. This means that the $k_{HO^\bullet}$ values for the same family of organic compounds are related to their chemical characteristics. Fig. 6 shows that in this study, the rate constants of the same family of organic compounds were also well correlated to their K_{ow} values. Such relations indicate that the K_{ow} can be used to quickly compare the reaction rate of compounds of family in field remediation works.

3.3. Impacts on remediation

The data have shown that when the compounds existed as NAPLs, their Fenton reactivities decreased. The reaction percentage of NAPL form was 10–19% less than that of the dissolved for all the tested compounds. At first glance, such an extent of reduction does not appear to seriously affect the reaction efficiency. However, the Reaction$_{(NAPL)}$/Reaction$_{(dissolved)}$ ratios reveal that such a decrease (10–19%) in NAPL reaction efficiency would have more impacts on the compounds with lower Fenton reactivities. Taking aromatic hydrocarbons as an example, one can find that the reaction percentage for benzene dropped from 31.7% for the dissolved form (Reaction$_{(dissolved)}$) to 12.6% for the NAPL(Reaction$_{(NAPL)}$), and the calculated Reaction$_{(NAPL)}$/Reaction$_{(dissolved)}$ value was 40%. In other words, when benzene is present as a NAPL in the subsurface, the removal of benzene NAPL by Fenton reaction will be more difficult and needs a much longer time because the NAPL reaction efficiency is only 40% of its dissolved form. On the other hand, the reaction efficiency of ethyl benzene NAPL was 73% of its dissolved form. Thus, only a minor difference in remediation results are expected between the removal of dissolved and NAPL ethyl benzene. Similarly, cis 1,2-DCE exhibited the most significant reduction in reactivity (−70%) among the chlorinated ethylenes when the phase changed to NAPL. The rate constant also exhibited the same phenomenon (Table 1). The most significant impact of decrease in rate constants occurred for those compounds having lower rate constants. The rate constant values of cis 1,2-DCE and ben-

Table 1
$k_{HO\bullet}$ values (all are $\times 10^9 \, M^{-1} \, s^{-1}$)

Compound	This study (modified C.K. method)[a]			Reference[b]
	Dissolved form	NAPL form	$k_{HO\bullet \, (NAPL)}/k_{HO\bullet \, (dissolved)}$	Dissolved form
1,1-DCE	1.13	–	–	*
Cis 1,2-DCE	1.41	0.54	39%	*
Trans 1,2-DCE	1.43	0.82	57%	7.3 (C.K.)[c]
				5.0 (P.b.k.)[d]
TCE	1.59	0.85	53%	*
PCE	2.33	1.62	69%	2.3 (C.K.)
				2.8 (P.b.k.)
Benzene	2.50	1.04	41%	7.5 (C.K.)
				8.2 (C.K.)
Toluene	2.75	2.08	76%	3.0 (C.K.)
Ethyl benzene	3.22	2.26	70%	7.5 (no details)

(–): Not measured; (*): no reported data.
[a] Target and reference separated.
[b] Source: [7].
[c] Competitive kinetics, target and reference mixed.
[d] Product buildup kinetics.

zene were only 38.3 and 41.6%, respectively, of their dissolved forms.

Compounds with lower K_{ow} values usually are highly soluble in water and poorly sorbed to the soils. It appears that these low K_{ow} compounds also exhibited less Fenton reaction efficiencies and rate constants. To make matters worse, when these compounds are present as NAPLs, their Fenton reactivities further decreased. Benzene, a compound of high health risk, is particularly worth concerning about. Benzene transports faster in the aquifer and is stringently regulated, but its removal by Fenton-like reaction is more difficult than other aromatic compounds.

4. Conclusions

For the tested aromatics and chloroethylenes, their reaction efficiencies and rate constants of dissolved and NAPL forms were well correlated to their K_{ow} values and chemical characteristics of family compounds. The compounds with smaller K_{ow} values tend to exhibit lower reactivity during goethite-catalyzed Fenton-like reaction. Aromatic hydrocarbons, having three double bonds in the aromatic rings, were found to react more effectively than chlorinated ethylenes. When the contaminants were present as NAPL form, their reaction rate constants and reaction efficiencies decreased significantly, particularly for the compounds with low Fenton reactivity. The parameters of liquid droplet surface area and H_2O_2 dose did not significantly affect the reaction efficiency of 1 mmol/L NAPLs. The reaction efficiencies of cis 1,2-DCE and benzene NAPLs decreased to 30 and 40% of their dissolved forms, respectively. The $k_{HO\bullet \, (NAPL)}/k_{HO\bullet \, (dissolved)}$ ratio for cis 1,2-DCE was only 38% and was 42% for benzene. Thus, the significant decrease in reaction efficiencies and rate constants of NAPL form for the compounds with lower K_{ow} values meant that more remediation time and effort will be required during Fenton-like removal of NAPLs.

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