Application of in situ chemical oxidation to remediate sulfolane-contaminated groundwater: batch and pilot-scale studies

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ABSTRACT

To investigate the feasibility and effectiveness of applying in situ chemical oxidation (ISCO) on the remediation of sulfolane-contaminated groundwater, batch and pilot-scale studies were conducted in this study. The kinetics of sulfolane oxidation by Fenton and Fenton-like processes and optimal operational conditions were evaluated. The major control factors in the ISCO study included H_2O_2 concentrations, ratio of H_2O_2 to ferrous iron (mol/mol), molar ratios of oxidant to sulfolane, and catalyst effect. Results show that the Fenton reaction could obtain a complete sulfolane oxidation with the following operational conditions: 3% of H_2O_2, molar ratio of H_2O_2 to ferrous iron = 1:0.5, and initial sulfolane concentration = 72 mg/L. The calculated pseudo-first-order decay rate constants (k') were 1.32×10^{-1} and 6.69×10^{-2} min^{-1} for sulfolane degradation under Fenton and Fenton-like oxidation reaction processes with 3% of H_2O_2 concentration, respectively. However, the sequential Fenton-like operational pattern could be an alternate option to obtain a complete sulfolane removal efficiency. Results from the soil oxidant demand test show that approximately 25%–35% of supplied H_2O_2 (3%) was consumed by soil organic matter, and thus, higher oxidant concentration would be required for field application. Sulfolane oxidation would result in sulfuric acid production, which caused the decrease in solution pH, and this would be beneficial to Fenton reaction. A sulfolane-contaminated groundwater site was selected for the pilot-scale study and Fenton oxidation process was applied for sulfolane degradation. Approximately, 600 L of H_2O_2 solution (5%) [molar ratio of $[H_2O_2]$:$[Fe^{2+}]$ = 1:0.5] was injected into the injection well (IW) to oxidize sulfolane in situ. Up to 97% and 88% of sulfolane could be removed (initial sulfolane concentration = 68 mg/L) in the IW and a downgradient monitor well (located 5 m downgradient of the IW). Results from the batch and pilot-scale studies demonstrate that the Fenton reaction could be an applicable remedial option to oxidize sulfolane and cleanup sulfolane-contaminated groundwater.

Keywords: Fenton reaction; Fenton-like reaction; Groundwater contamination; In situ chemical oxidation; Sulfolane

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1. Introduction

Sulfolane (tetrahydrothiophene 1,1-dioxide, $C_4H_8O_2S$) is a widely used solvent in petrochemical industry for liquid–liquid aromatic extraction from petroleum, and it can be also used for the removal of carbon dioxide, hydrogen sulfide, and organic sulfides from natural gasses [1,2]. Sulfolane has a high polarity due to its double bond between sulfur and oxygen atom [3]. Because of this chemical structure, sulfolane is a compound with stable and recalcitrant properties, including high solubility (1.266 g/L at 20°C), low Henry's law constant (8.95×10^{-10} atm-m³/mol at 25°C), low octanol–water partition coefficient (log K_{ow} = −0.77 at 25°C), and high thermal stability (boiling point = 285°C) [4]. Moreover, sulfolane would influence the central nervous system in mammals [5], and thus, it becomes an organic pollutant if spills from petrochemical industries occur. Sulfolane release would pose a significant risk to human health and ecosystem once it contaminates the groundwater aquifers and surface water bodies [6].

Biological processes on sulfolane degradation have been studied [7]. Kasanke and Leigh [1] reported that sulfolane could be biodegraded by mixed bacterial cultures, and results from Yang et al. [7] demonstrated that a complete sulfolane removal (initial sulfolane concentration = 100–120 mg/L) could be obtained within 11 d through the addition of trace elements and specific sulfolane degrading bacterium (*C. plantarum* Y9). In addition, results from a batch experiment conducted by Saint-Fort [3] showed that the sulfolane in soils (initial sulfolane concentration = 875 mg/kg) was degraded completely within 52 d with the addition of ammonia nitrogen. Thus, sulfolane can be biodegraded in situ under either biostimulation or bioaugmentation processes. Eq. (1) presents the stoichiometric equation of the aerobic biodegradation of sulfolane [8]. However, a longer treatment time is required to complete the removal process of sulfolane, and thus, the emergency response and immediate risk reduction cannot be achieved when in situ bioremediation is selected as the remedial option [8].

$$C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO_4^{2-} \qquad (1)$$

Recently, increased interests in applying chemical oxidation methods for sulfolane degradation have been noticed [9,10]. Yu et al. [11] reported that sulfolane could be degraded by either H_2O_2 or O_3 under ultraviolet (UV) C irradiation, but it could not be removed when UVC or UVA irradiation was only applied. Izadifard et al. [10] demonstrated that persulfate along with UVC and UVC/O_3 could efficiently degrade sulfolane in water. Brandão et al. [12] showed that sulfolane could be removed from soils using water as the washing agent, and 99% of the sulfolane could be removed from sulfolane-contained water treated by H_2O_2/UV within 1 h. Besides these oxidation methods, Ye et al. [13,14] also used nanocomposites to possess advisable stability performance for organic compounds removal in contaminated river water. Although the oxidation method has been shown to be a feasible option for sulfolane degradation, researches and field studies using in situ chemical oxidation (ISCO) for sulfolane-contaminated groundwater remediation are rare.

ISCO is an effective technology for the remediation of organic-pollutant contaminated groundwater [15,16]. During the ISCO processes, oxidants (e.g., H_2O_2, $Na_2S_2O_8$, O_3, $KMnO_4$) are injected into the subsurface to degrade or destruct organic pollutants, and the treatment efficiency can be improved with the increased oxidant concentrations and supplement of catalysts [15–17]. Fenton and Fenton-like oxidation processes have been wildly applied to effectively remediate organic-compound polluted subsurface using the generated hydroxyl radical ($HO^{\bullet}$) (E^0 = 2.8 V) with the supplement of catalysts [ferrous iron (Fe^{2+}) or ferric iron (Fe^{3+})] (Eq. (2)) [18,19]. The produced free radicals can react with organic compounds resulting in degradation (Eq. (3)). The organic radical (R) can reduce Fe^{3+} to Fe^{2+} when Fe^{3+} is excess in the reaction system (Eq. (4)) [20–22].

Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^-$$
$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$$
$$H_2O_2 + HO_2^{\bullet} \rightarrow H_2O + O_2$$
$$Fe^{2+} + HO^{\bullet} \rightarrow OH^- + Fe^{3+}; \qquad E^0 = 2.8 \text{ V} \qquad (2)$$
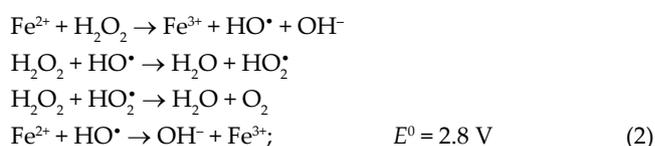
Organic compound reacting with hydroxyl radical:

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \qquad (3)$$

Reaction with Fe^{3+}:

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + \text{product}$$
$$RO^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + \text{product} \qquad (4)$$

In the field experiments, the effective oxidant distribution in the subsurface is one of the most important issues. The delivery of oxidants to the subsurface is affected by several factors, including permeability and heterogeneity of soils, oxidant persistence, and oxidant stabilization. Moreover, soil oxidant demand (SOD) plays an important role in ISCO application because it consumes the oxidant dosage during the practical application [23,24]. Thus, the influences of SOD need to be evaluated before the field application. In this study, the feasibility and effectiveness of applying Fenton and Fenton-like oxidation processes on the remediation of sulfolane-contaminated groundwater was evaluated. The principal objectives were to: (1) conduct the laboratory batch experiments to determine the performance and optimal operational conditions of Fenton and Fenton-like processes on sulfolane oxidation, (2) evaluate the SOD effects on sulfolane oxidation efficiency, (3) determine the kinetics of sulfolane oxidation using Fenton and Fenton-like oxidation processes, and (4) operate a pilot-scale system at a sulfolane-contaminated groundwater site to determine the effectiveness and operational conditions of the ISCO application on sulfolane removal.

2. Materials and methods

2.1. Materials

Sulfolane (99% purity) (Formosa Petrochemical Co., Taiwan), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, minimum 99.5%,

Riedel-de Haen, Germany), and liquid hydrogen peroxide (30% by weight) (Ferak Laborat GMBH Co., Germany) were used as the target contaminant, oxidant, and activator, respectively. Chemicals used in this study were analytical and pharma grades.

2.2. Batch experiments

Four groups of batch experiments were conducted to determine the performance and optimal operational conditions of Fenton and Fenton-like processes on sulfolane oxidation. Groundwater and soils used in the batch experiments were collected from a sulfolane-contaminated site. Table 1 shows the characteristics of soils and groundwater used in this study. The concentrations of sulfolane and ferrous iron in collected groundwater were 72 and 1.1 mg/L, respectively. The concentrations of total iron and soil organic matter (SOM) in soils were 26.8 mg/kg and 1.2%, respectively.

Table 2 presents the operational conditions and components of four groups of batch experiments. In Group 1 experiment, four different Fenton-like tests (Tests 1–4) were conducted without extra ferrous iron addition. Each test was conducted in a 2.5-L serum bottle (reactor), which was covered with aluminum foil and capped with a Teflon-lined rubber septum to prevent the photolysis effect. 1 L of sulfolane-polluted groundwater (SPG), 1 L of H_2O_2 solution, and 200 g of soils were added in each bottle. In Tests 1–4, H_2O_2 concentrations were 0 (control), 0.5%, 1%, and 3%, respectively. Water samples were determined for sulfolane concentrations to evaluate the sulfolane oxidation efficiency.

In Group 2 experiment, 0.5 L of H_2O_2 solution was re-injected into the bottle to further enhance the sulfolane oxidation process. The H_2O_2 concentration was the same with the concentration used in each test described in Group 1 experiment. Water samples were determined for sulfolane concentrations after 20 and 40 min after the re-injection.

Group 3 experiment was performed to determine the effect of Fenton reaction on sulfolane oxidation. In this experiment, three different Fenton oxidation tests (Tests 1–3) were conducted. Each test was conducted in a

2.5-L serum bottle (reactor), which was covered with aluminum foil and capped with a Teflon-lined rubber septum to prevent the photolysis effect. 1 L of SPG, 1 L of H_2O_2 solution, 200 g of soils, and 0.5 L of $FeSO_4$ solution were added in each bottle. In Tests 1–3, H_2O_2 concentrations were 0.5%, 1%, and 3%, respectively. The molar ratio of $[H_2O_2]$ to $[Fe^{2+}]$ was 0.01 (mol/mol). Collected water samples from the bottles were analyzed for sulfolane concentrations frequently during the 160-min operational period.

Effects of ferrous iron concentrations on sulfolane oxidation during the Fenton reaction was evaluated in the Group 4 experiment. In this experiment, three different tests (Tests 1–3) were conducted with the $[H_2O_2]$ to $[Fe^{2+}]$ molar ratios of 1:0.005, 1:0.01, and 1:0.5 with a fixed H_2O_2 dosage of 0.5%, respectively. The experimental procedures were the same with those described in Group 3. Again, water samples from the bottle were analyzed for sulfolane concentrations to determine the oxidation efficiency.

Table 1
Characteristics of the groundwater and soils collected from the studied site

Media	Parameter	Value
Groundwater	pH	7.70
	Oxidation reduction potential (mV)	208
	Electronic capacity (µS/cm)	868
	Total organic carbon (mg/L)	54.1
	Sulfate (mg SO_4^{2-}/L)	57.3
	Ferrous iron (mg Fe^{2+}/L)	1.12
	Total iron (mg Fe/L)	4.2
	Sulfolane (mg/L)	72
Soil	pH	7.95
	Soil organic matter (%)	1.2
	Total iron (mg/kg)	26.8
	Sand (%)	55.3
	Silt (%)	37.4
	Clay (%)	7.3

Table 2
Control factors and operational conditions of batch oxidation experiments

Group	Oxidation type	Control factor	Components
1	Fenton-like	[sulfolane] = 72 mg/L $[H_2O_2]$ = 0%, 0.5%, 1%, and 3%	1 L of SPG + 1 L H_2O_2 + 200 g of soils
2		[sulfolane] = 72 mg/L $[H_2O_2]$ = 0.5%, 1%, and 3%	1 L of SPG + 500 mL H_2O_2 (first injection) + 500 mL H_2O_2 (second injection) + 200 g of soils
3	Fenton	[sulfolane] = 72 mg/L $[H_2O_2]$ = 0.5%, 1%, and 3% $[H_2O_2]:[Fe^{2+}]$ = 1:0.01	1 L of SPG + 1 L H_2O_2 + 500 mL $FeSO_4$ + 200 g of soils
4		[sulfolane] = 72 mg/L $[H_2O_2]$ = 0.5% $[H_2O_2]:[Fe^{2+}]$ = 1:0.0067; 1:0.01; 1:0.5	1 L of SPG + 1 L H_2O_2 + 500 mL $FeSO_4$ + 200 g of soils

SPG, sulfolane-polluted groundwater.

2.3. Soil oxidant demand test

Each SOD test was conducted in a 200-mL serum bottle, which was covered with aluminum foil and capped with a Teflon-lined rubber septum. Each bottle contained 5 g of soils and 50 mL of H_2O_2 solution (H_2O_2 concentration = 0.5%). All bottles were shaken for 1 h and water samples were collected and analyzed for the remaining concentrations of H_2O_2. Soils collected from different subsurface depths [1–2, 3–4, and 5–6 m below land surface (bls)] were applied in the SOD tests. The percentages of silt plus clay in three different soil samples were 45.1% (1–2 bls), 42.3% (3–4 bls), and 47.6% (5–6 bls), respectively.

2.4. Pilot-scale study

A SPG site located in the central Taiwan area was used for the pilot-scale study. Sulfolane leakage from a wastewater treatment tank resulted in the groundwater pollution by sulfolane. Within the test area, the average sulfolane concentrations in groundwater were in the range from 55.7 to 65.8 mg/L. The hydraulic conductivity and groundwater flow velocity of the aquifer were 6.19×10^{-5} and 1.02×10^{-7} m/s, respectively.

In this study, one injection well (IW) was installed in the upgradient area for oxidant and ferrous iron injection and groundwater monitoring. Three monitor wells (labeled as MW1, MW2, and MW3) were installed for groundwater quality monitoring. MW1 was located approximately 5 m southeast downgradient of IW and MW2 was located 6 m southeast downgradient of MW1. MW3 was located 5 m southwest downgradient of IW. In IW, 600 L of Fenton reagent (H_2O_2 concentration = 5%, molar ratio of $[H_2O_2]:[Fe^{2+}] = 1:0.5$) was injected into IW with an injection flow rate of 2 L/min.

Fig. 1 is the site map showing the locations of IW, monitor wells, and groundwater flow direction. Groundwater was collected and analyzed for water quality indicators [oxidation-reduction potential (ORP), electric conductivity (EC), dissolved oxygen (DO), and pH] and
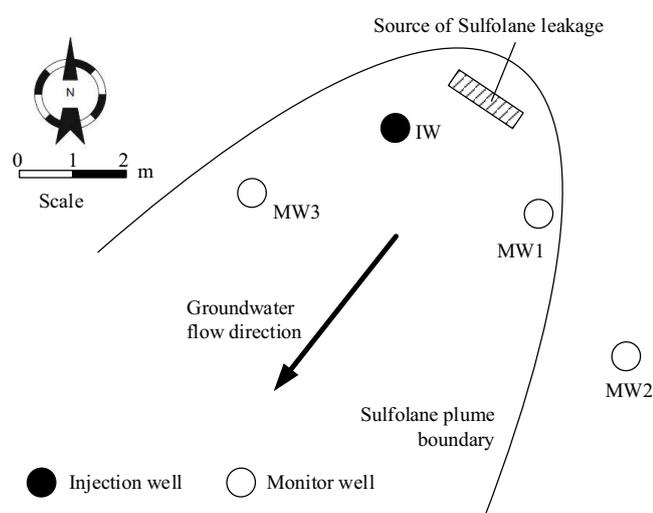
Fig. 1. Schematic diagram showing the injection and monitor wells at the sulfolane-contaminated groundwater site.

concentrations of sulfolane, H_2O_2, total iron, and ferrous iron during the operational period.

2.5. Sample analysis

Groundwater samples were extracted by dichloromethane for sulfolane concentration determination. The extract was analyzed by an Agilent 6850 Gas Chromatograph (GC) equipped with a mass spectrometry (GC-MS) and a DB-1 HT capillary column following the procedures described in Brandão et al. [12] and NIEA [25]. The pH and ORP values of the groundwater samples were measured using a pH/ORP meter (Metter MP120, Mettler-Toledo International Inc., India). DO was analyzed by an Orion DO meter (Model 840, USA). H_2O_2 concentrations were measured by iodometric titration with 0.1 N sodium thiosulfate [26]. Ferrous ion and total iron concentrations were measured using a Hach test kit and a spectrophotometer (Hach Co., USA). EC was measured by a conductivity meter (Model C-120, Suntex Instruments Co., Taiwan).

3. Results and discussion

3.1. Sulfolane degradation by Fenton-like oxidation

Fig. 2 presents the sulfolane (initial concentration = 72 mg/L) degradation efficiencies (remaining sulfolane) with different H_2O_2 dosages (0.5%, 1%, and 3%). Results show that similar sulfolane removal trends were observed for three different tests although different H_2O_2 dosages were applied. Results indicate that sulfolane degradation efficiency increased with the increased dosage of H_2O_2. Sulfolane concentrations decreased rapidly from 0 to 20 min and the degradation trends levelled off after 20 min. After 20 min of oxidation, approximately 42.7%, 38.6%, and 26.1% of sulfolane remained in the solution in tests with 0.5%, 1%, and 3% of H_2O_2 addition, respectively. Results indicate that intrinsic irons in water and soils could serve as the catalysts and activate the Fenton-like oxidation process resulting in the decrease in sulfolane concentrations [20,21,23].

The decreased sulfolane oxidation rates after 20 min of reaction could be due to the following causes: (1) The concentrations of ferrous iron and total iron in groundwater were 1.12 and 4.2 mg/L, respectively. Thus, the total iron in the water phase was not significant enough to catalyze H_2O_2 for hydroxyl radical generation; (2) The total iron concentration in soils was around 26.8 mg/kg. Most of the irons in soils were in the solid phase, which might not be available to H_2O_2 for the Fenton-like oxidation process; and (3) Although Fenton-like oxidation reaction could occur under neutral conditions, more efficient reaction would occur under acidic conditions [27,28]. Thus, the sulfolane oxidation efficiency would not be significant because the batch system was operated under neutral conditions.

No significant sulfolane removal was observed in the control test (without H_2O_2 addition). This indicates that the intrinsic oxidation efficiency was low if oxidant was not provided. Moreover, sulfolane has a high solubility (1.266 g/L at 20°C), a low Henry's law constant (8.95×10^{-10} atm-m³/mol at 25°C), and a low vapor pressure (0.0062 mmHg at 27.6°C), and thus, the volatilization effect

of sulfolane was not significant under natural conditions [3]. Up to 74% of sulfolane could be removed in test with 3% of H_2O_2 addition. Compared with the results from the control group, results reveal that the Fenton-like oxidation reaction could still result in a significant amount of sulfolane degradation with a higher oxidant concentration.

3.2. Sequential Fenton-like oxidation test

To improve the Fenton-like oxidation efficiency, the same dosage of H_2O_2 was further added to the reactor after 20 min of the first round of reaction. Fig. 3 presents the remaining concentrations of sulfolane versus reaction time. Results show that the sulfolane concentrations dropped rapidly within 20 min, and more than 75% of sulfolane was removed before 20 min of reaction after the first round of H_2O_2 addition at the beginning of the test.

Results show that the second round of H_2O_2 addition at 20 min could result in a complete sulfolane removal after
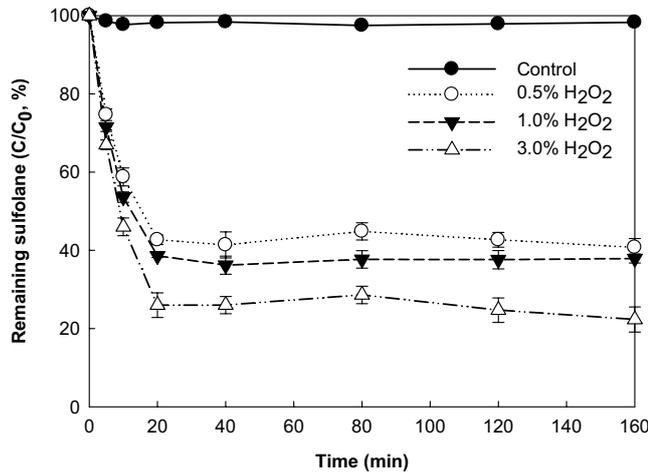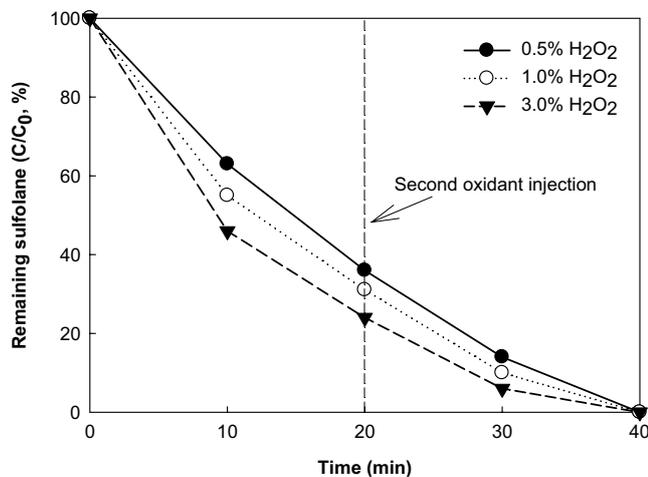
40 min of reaction. The residual sulfolane after the first round of oxidation process could be further oxidized by the second stage of Fenton-like oxidation process. Similar sulfolane removal trends were observed in three different tests with different H_2O_2 dosages. The results indicate that a sequential oxidation process could effectively improve the sulfolane removal efficiency with a high (3%) or low (0.5%) H_2O_2 dosage.

The results confirmed that the sequential Fenton-like operational pattern could be a feasible option to remediate sulfolane-contaminated groundwater [17,20,29]. Sulfolane oxidation mainly relies on the hydroxyl radicals produced by Fenton-like processes [30,31]. According to Eq. (5), the concentration of H_2O_2 plays a critical role in the amount of hydroxyl radical production [18]. These results confirmed that the Fenton-like process could be used to treat sulfolane-contaminated groundwater.

$$C_4H_8O_2S + 13H_2O_2 \rightarrow 4CO_2 + H_2SO_4 + 16H_2O \qquad (5)$$

3.3. Sulfolane degradation by Fenton oxidation

Researchers reported that efficiencies of organic pollutants oxidation by Fenton reaction could be facilitated using higher H_2O_2 concentrations [32,33]. This is because more hydroxyl radicals could be formed when high concentrations of H_2O_2 are applied. According to Eq. (2), using the ferrous iron catalyst can result in increased hydroxyl radical generation. Thus, addition of ferrous iron could obtain a higher sulfolane degradation rate. Fig. 4 presents the efficiencies of sulfolane degradation (remaining sulfolane) by Fenton reaction.

When 3% of H_2O_2 was applied, a complete sulfolane removal was observed after 20 min of reaction (initial sulfolane concentration = 72 mg/L). Approximately, 87% and 93% of sulfolane removal efficiencies were observed in experiments with H_2O_2 concentrations of 0.5% and 1%, respectively. Compared to the sulfolane oxidation efficiencies obtained from Fenton-like reaction tests, results indicate that Fenton reaction could achieve a much higher

Fig. 2. Variations in percentages of remaining sulfolane after Fenton-like reaction with varied concentrations of H_2O_2.

Fig. 3. Variations in percentages of remaining sulfolane after the second round of H_2O_2 injection in Fenton-like reaction experiment with varied concentrations of H_2O_2.
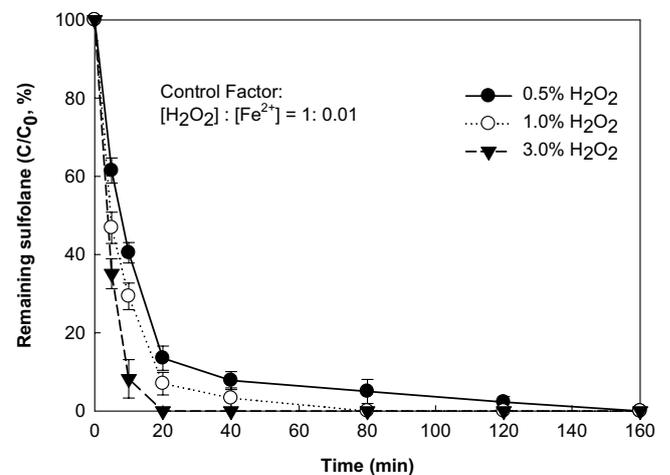
Fig. 4. Variations in percentages of remaining sulfolane after Fenton reaction with varied concentrations of H_2O_2.

sulfolane oxidation rate with the addition of ferrous iron as the catalyst, and approximately 26%–31% increases in sulfolane degradation efficiencies were observed. Two possible causes of the increased sulfolane degradation efficiencies were as follows: (1) ferrous iron addition resulted in the increased hydroxyl radical generation, which caused increased sulfolane oxidation rates [34]; and (2) increased sulfolane oxidation rate would result in increased sulfuric acid production during the sulfolane oxidation process (Eq. (5)), which caused the decrease in solution pH, and this would be beneficial to Fenton reaction [35]. Thus, a higher sulfolane removal rate could be obtained with the application of Fenton reaction process. Results suggest that Fenton reaction could be applied in the field for sulfolane removal from sulfolane-polluted sites.

Similar trends of organic contaminant oxidation by Fenton reaction have been reported [36]. However, a very high H_2O_2 concentration may have scavenging effects of $^{\cdot}OH$ by excess H_2O_2 and consequent formation of the less reactive $HO_2^{\cdot}$ by the chain reactions (Eq. (2)) [18]. Thus, an optimal dosage of H_2O_2 and operational conditions need to be maintained to achieve an acceptable organic contaminant removal rate.

3.4. Effects of ferrous iron addition on Fenton reaction

In this experiment, different molar ratios of $[H_2O_2]$ to $[Fe^{2+}]$ were selected to evaluate the effects of ferrous iron addition on sulfolane oxidation efficiency with a fixed H_2O_2 concentration (0.5%). Fig. 5 presents the sulfolane degradation efficiencies (percentage of remaining sulfolane) via Fenton oxidation process with the application of three different molar ratios of $[H_2O_2]$ to $[Fe^{2+}]$ ($[H_2O_2]/[Fe^{2+}]$ = 1:0.005, 1:0.01, and 1:0.5).

Results show that increased sulfolane removal efficiency was observed with increased ferrous iron concentrations. Sulfolane concentrations dropped rapidly from 100% to 8% within 5 min of reaction when $[H_2O_2]$ to $[Fe^{2+}]$ ratio was 1:0.5. The results matched with the findings from other studies indicating that ferrous iron played
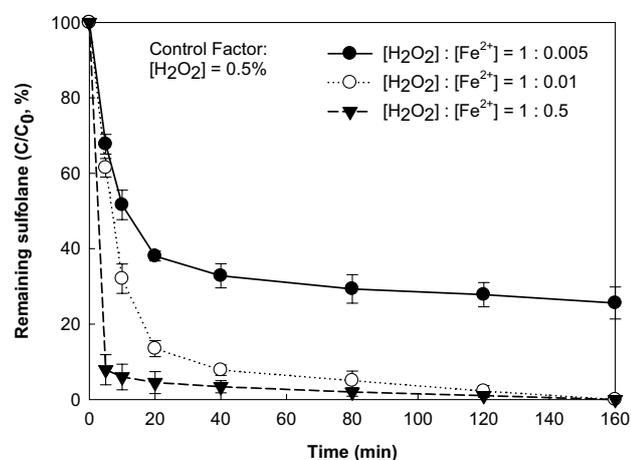
an important role in the enhancement of Fenton reaction efficiency (Eqs. (2) and (3)) [37]. Ferrous iron could enhance the catalysis of H_2O_2 and more hydroxyl radicals could be generated for organic pollutant oxidation [22].

Fig. 6 shows the variations in H_2O_2 and ferrous iron concentrations in the batch system ($[H_2O_2]$ to $[Fe^{2+}]$ ratio = 1:0.5, H_2O_2 concentration = 0.5%). Results indicate that ferrous iron decreased rapidly to 12% within 5 min of oxidation and a complete ferrous iron consumption was observed after 10 min of reaction. Results also indicate that H_2O_2 concentration decreased to 67% within 5 min of reaction. No significant change of H_2O_2 concentration was observed after the depletion of ferrous iron and sulfolane. This indicates that the consumption rate of H_2O_2 would decrease if Fenton reaction was not enhanced. Compared to hydroxyl radical, H_2O_2 was more stable and the consumption rate of H_2O_2 would decrease if Fenton reaction was not enhanced. However, for the field application, more H_2O_2 addition (higher than the theoretical value calculated from the stoichiometric equation) is required due to the existence of SOM, which would consume oxidants and produced hydroxyl radicals.

3.5. Reaction kinetics of sulfolane oxidation

Kinetics of sulfolane oxidation was studied using the pseudo-first-order kinetic model [38] (Eq. (6)):

$$\ln\left(\frac{C}{C_0}\right) = -k't \tag{6}$$

where C_0 and C are concentrations of sulfolane at the beginning of the oxidation and a certain reaction time (t), respectively. k' is the pseudo-first-order rate constant [38].

Table 3 presents the calculated oxidation rate constants of sulfolane oxidation for Fenton-like and Fenton oxidation reactions based on Eqs. (2) and (3), respectively. The calculated pseudo-first-order rate constants

Fig. 5. Variations in percentages of remaining sulfolane after Fenton reaction with varied ratios of $[H_2O_2]/[Fe^{2+}]$.
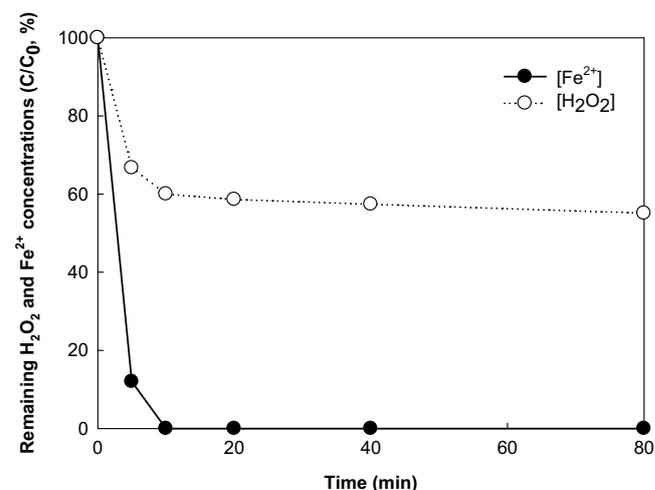
Fig. 6. Variations in remaining concentrations of H_2O_2 and ferrous iron after Fenton reaction ($[H_2O_2]$ = 0.5%; $[H_2O_2]:[Fe^{2+}]$ = 1:0.5).

Table 3
The calculated pseudo-first-order decay rate constants for Fenton-like and Fenton reactions

Oxidant concentration	Fenton-like reaction			Fenton reaction[1]		
	k' (min^{-1})	$t_{1/2}$ (min)	R^2	k' (min^{-1})	$t_{1/2}$ (min)	R^2
0.5%	4.18×10^{-2}	17	0.9775	4.38×10^{-2}	16	0.9472
1%	4.68×10^{-2}	15	0.9674	1.01×10^{-1}	7	0.9934
3%	6.69×10^{-2}	10	0.9922	1.32×10^{-1}	5	0.6239

[1]Fenton reaction: $[H_2O_2]/[Fe^{2+}]$ = 1:0.5, retention time = 20 min.

(k') of Fenton-like reaction for sulfolane degradation were 4.18×10^{-2}, 4.68×10^{-2}, and 6.69×10^{-2} min^{-1} when 0.5%, 1%, and 3% of H_2O_2 were applied, respectively. Results show that the calculated rate constant value increased with an increased oxidant concentration. This was because the increased reactive hydrogen radicals were generated with higher dosage of H_2O_2, which could expedite the oxidation of sulfolane. The half-life values of Fenton-like reaction were 17, 15, and 10 min when 0.5%, 1%, and 3% of H_2O_2 were applied, respectively. This indicates that higher oxidant dosages are required to reduce the treatment time and achieve a higher oxidation efficiency.

Table 3 also presents the k' values of Fenton reaction for sulfolane degradation. The calculated rates were 4.38×10^{-2}, 1.01×10^{-1}, and 1.32×10^{-1} min^{-1} when 0.5%, 1%, and 3% of H_2O_2 were applied, respectively. The half-life values of Fenton reaction were 16, 7, and 5 min when 0.5%, 1%, and 3% of H_2O_2 were applied, respectively. Results show that the rate constant values of sulfolane oxidation with Fenton process were approximately two times higher than those for Fenton-like reaction when higher H_2O_2 dosages (H_2O_2 > 1%) were used. However, results show that there were no significant differences for the calculated rate constants between Fenton-like and Fenton reactions when a low H_2O_2 dosage was applied (H_2O_2 = 0.5%). The results imply that less hydroxyl radicals were generated when a lower H_2O_2 concentration was provided during the Fenton or Fenton-like reaction. Thus, higher H_2O_2 dosage is required to achieve a higher rate constant and a higher contaminant oxidation efficiency.

3.6. Soil oxidant demand analysis

The presence of SOM can consume a significant amount of oxidants and hereby reducing the available oxidants for the oxidation of organic compounds. SOM can be oxidized by H_2O_2, and co-oxidized together with the organic contaminants due to the non-selective nature of hydroxyl radical produced by Fenton or Fenton-like reactions [21]. Fig. 7 shows the variations in residual H_2O_2 concentrations after the Fenton oxidation using soil samples collected from different soil sampling depths (1–2, 3–4, and 5–6 m bls) (H_2O_2 concentration = 0.5%). Results indicate that H_2O_2 concentrations dropped to 68.3%, 76.1%, and 66.8% for SOD tests with soils from depths of 1–2, 3–4, and 5–6 m bls, respectively, after 1 h of operation. Because soil sample from 5 to 6 m bls contained higher percentages of silt and clay (47.6%) (Section 2.3), higher organic matters would exist in this soil sample. Thus, higher H_2O_2 consumption was observed. Approximately, 25%–35% of H_2O_2 was
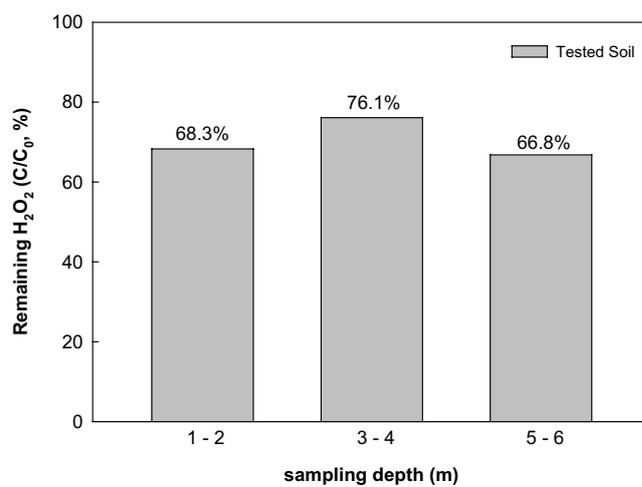
Fig. 7. Variations in remaining H_2O_2 concentrations after Fenton reaction ($[H_2O_2]$ = 0.5%; $[H_2O_2]:[Fe^{2+}]$ = 1:0.5) of tested soil.

consumed after the 1-h SOD test. The measured average SOD value was 19 ± 3 mg H_2O_2/g soil when 0.5% of H_2O_2 was applied for the tests.

Researchers reported that high concentrations of H_2O_2 (generally above 294 mM) were required for site application because various organic matters in soils would quench some of the supplied H_2O_2 [39]. Organic contaminants may exist in soils as particulates or sorb onto soil particles, and thus, a strong oxidizing condition is required to solubilize and desorb contaminants from soil particles to obtain an effective oxidation rate. In a field application, a sequential addition of high concentration of H_2O_2 can be applied to provide a stronger and continuous oxidizing power for organic contaminant oxidation.

3.7. Field-scale study

To improve the sulfolane oxidation efficiency, to overcome the SOD effect, and to reduce the treatment time, 5% of the H_2O_2 concentration was applied in the pilot-scale study. Fig. 8 presents the variations in sulfolane concentrations in IW, MW1, MW2, and MW3 after the supplement of Fenton reagent. Fig. 9 shows the variation in pH, ORP, H_2O_2, and ferrous iron measurements in IW and monitor wells (MW1, MW2, and MW3) after the supplement of Fenton reagent. A rapid decrease in sulfolane concentrations was detected in IW after the Fenton reagent injection. In IW, sulfolane concentrations dropped from an
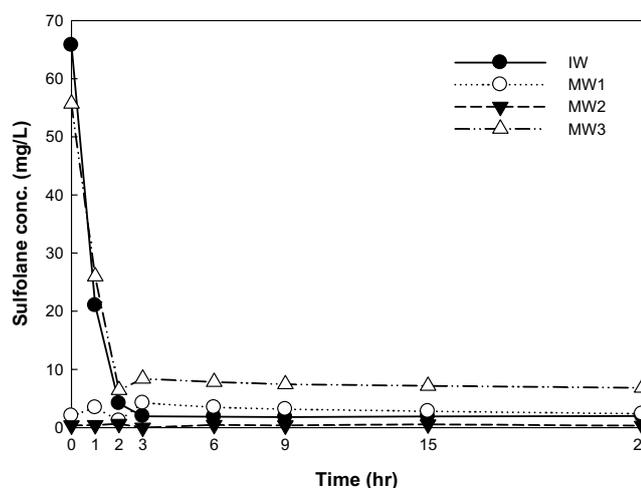
Fig. 8. Variations in sulfolane concentrations after Fenton oxidation in IW and three monitor wells (MW1, MW2, and MW3).

initial concentration of 65.8 mg/L to 21.3, 5, and 2 mg/L after 1, 2, and 3 h of operation, respectively. Results from Fig. 9 show that the H_2O_2 concentrations in IW increased from 0 to 177, 406, and 1,315 mg/L after 1, 2, and 3 h of operation, respectively. Ferrous iron concentrations in IW increased from 0 mg/L before the Fenton reagent injection to 16 and 41 mg/L after 1 and 2 h of operation, respectively. However, ferrous iron concentrations dropped to 2 mg/L after 3 h of operation in IW. The significant decrease in ferrous iron concentration caused the decreased sulfolane degradation rate after 3 h of operation. Results from Fig. 9 show that H_2O_2 concentrations were high (1,315 mg/L) after 3 h of operation, and thus, ferrous iron oxidation would be significant due to the increased ORP stage in IW. The decreased ferrous iron concentrations in IW also caused the declined sulfolane degradation rate after 3 h of operation in IW and downgradient monitor well MW3. Thus, the remaining sulfolane concentrations in IW and MW3 were around 2 and 8 mg/L, respectively, after 3 h of operation. Results also demonstrate that Fenton oxidation could result in a significant and immediate sulfolane degradation and plume control, and the environmental risks caused by sulfolane contamination could be reduced.

In MW1, sulfolane concentrations varied between 1.17 and 4.22 mg/L during the operational period indicating that MW1 was located near the edge of the plume, and the radius of influence of the Fenton reagent injection would be less than 3 m. Because MW2 was just located outside of the plume, sulfolane concentrations were less than 0.1 mg/L during the operational period.

In MW3, sulfolane concentrations decreased from 55.7 to 26.5 and 6.4 mg/L after 1 and 2 h of operation, respectively. The trend of sulfolane degradation in MW3 was similar to IW. This indicates that the injected Fenton reagent migrated to the downgradient area causing the decrease in sulfolane concentrations in MW3. Because H_2O_2 could react with the organics in the subsurface (including sulfolane and SOM), continuous H_2O_2 decay would occur along the groundwater flow path after its injection, and thus, relatively lower H_2O_2 concentrations were observed in MW3 during the operational period.

Increased ORP measurements were observed in IW and MW3 indicating that the Fenton reagent injection shifted the oxidation-reduction stage from a reduced to an oxidized stage. Moreover, sulfolane oxidation resulted in the production of sulfuric acid, which caused the significant drop of pH value in IW (Eq. (5)) (Fig. 9). Again, the pH reduction would be beneficial to the enhancement of Fenton oxidation. Thus, groundwater acidification for the enhancement of Fenton reaction would not be a necessity during the sulfolane oxidation using Fenton reagent as the oxidant. Because the groundwater and soils usually have their buffering systems, the produced acids would be neutralized before they are transported to the downgradient area. Thus, the pH drop would be limited to the ISCO treatment zone, and significant adverse effects due to the acid production would not occur in the field.

The evidences of the occurrence of sulfolane oxidation via the Fenton oxidation reaction in IW and the downgradient monitor well MW3 included the following: (1) increased ORP values, (2) decreased pH values in IW, (3) decreased ferrous iron and H_2O_2 concentrations in IW after Fenton reagent injection, and (4) decreased sulfolane concentrations in IW and MW3.

Results from the pilot-scale study show that up to 97% and 88% of sulfolane removal were observed in IW and MW3 after the operation of Fenton oxidation, respectively. Results indicate that in situ Fenton oxidation could be a potential remedial option to cleanup sulfolane-contaminated groundwater sites.

4. Conclusion

The effectiveness of ISCO treatment on the remediation and plume control of sulfolane-contaminated groundwater was evaluated. In the batch-scale study, the feasibility and operational conditions of using Fenton and Fenton-like reaction processes for sulfolane oxidation were evaluated. In the pilot-scale study, the effectiveness of using Fenton oxidation on sulfolane-contaminated groundwater remediation was assessed. Main conclusions are as follows:

• Fenton-like process could remove 74% of sulfolane (initial concentration = 72 mg/L) within 20 min of reaction with H_2O_2 concentration of 3%. H_2O_2 concentration played an important role in sulfolane oxidation, and higher sulfolane removal efficiency could be obtained with a higher H_2O_2 concentration applied.
• Compared to Fenton-like reaction, Fenton reaction resulted in a much higher sulfolane degradation rate. Fenton reaction could achieve a complete sulfolane oxidation with 3% of H_2O_2 (molar ratio of H_2O_2 to ferrous iron = 1:0.5). The calculated pseudo-first-order decay rate constants (k') were 1.32×10^{-1} and 6.69×10^{-2} min^{-1} for sulfolane degradation when Fenton and Fenton-like oxidation reaction processes were applied, respectively. Two possible causes of the increased sulfolane degradation efficiencies with the application of Fenton reaction process included the following: (1) ferrous iron addition resulted in the increased hydroxyl radical
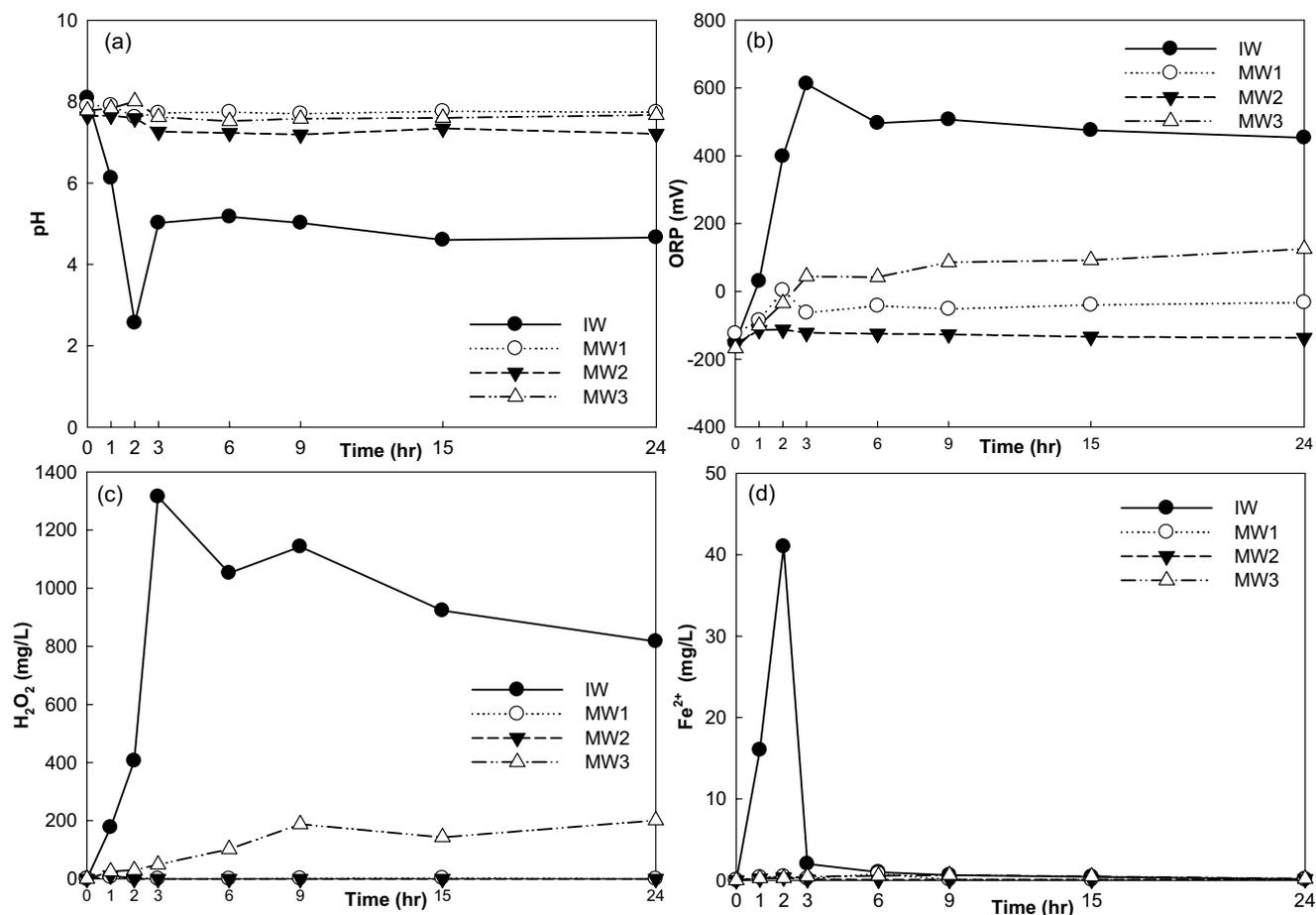
Fig. 9. Variations in (a) pH, (b) ORP, (c) H_2O_2, and (d) ferrous iron in IW and three (B1) monitor wells (MW1, MW2, and MW3).

generation, which caused increased sulfolane oxidation rates; and (2) increased sulfolane oxidation rate would result in increased sulfuric acid production during the sulfolane oxidation process, and this would be beneficial to Fenton reaction.

- Approximately, 25%–35% of H_2O_2 was consumed after the 1-h SOD test. The measured average SOD value was 19 ± 3 mg H_2O_2/g soil when 0.5% of H_2O_2 was applied for the tests. A stronger oxidizing condition is a necessity to desorb contaminants from soil particles to obtain an effective oxidation rate. In a field application, a sequential oxidation pattern can be used to supply a continuous and stronger oxidizing power.
- The evidences of the occurrence of sulfolane oxidation via the Fenton oxidation reaction in the reaction zone included the following: increased ORP values, decreased pH values in IW, decreased ferrous iron and H_2O_2 concentrations in IW after Fenton reagent injection, and decreased sulfolane concentrations in IW and MW3.
- Results from the pilot-scale study show that up to 97% of sulfolane removal was observed in IW after the operation of Fenton oxidation. Results indicate that in situ Fenton oxidation could be a potential remedial option to remediate sulfolane-contaminated groundwater sites.

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