



Application of surfactant enhanced permanganate oxidation and biodegradation of trichloroethylene in groundwater

T.T. Tsai^a, C.M. Kao^a, T.Y. Yeh^{b,*}, S.H. Liang^a, H.Y. Chien^a

^a Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan

^b Department of Civil and Environmental Engineering, National University of Kaohsiung, Kaohsiung, Taiwan

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ABSTRACT

The industrial solvent trichloroethylene (TCE) is among the most ubiquitous chlorinated solvents found in groundwater contamination. The main objectives of this study were to evaluate the feasibility of using non-ionic surfactant Simple Green™ (SG) to enhance the oxidative dechlorination of TCE by potassium permanganate (KMnO₄) employing a continuous stir batch reactor system (CSBR) and column experiments. The effect of using surfactant SG to enhance the biodegradation of TCE via aerobic cometabolism was also examined. Results from CSBR experiments revealed that combination of KMnO₄ with surfactant SG significantly enhanced contaminant removal, particularly when the surfactant SG concentrated at its CMC. TCE degradation rates ranged from 74.1% to 85.7% without addition of surfactant SG while TCE degradation rates increased to ranging from 83.8% to 96.3% with presence of 0.1 wt% SG. Furthermore, results from column experiments showed that TCE was degraded from 38.1 μM to 6.2 μM in equivalent to 83.7% of TCE oxidation during first 560 min reaction. This study has also demonstrated that the addition of surfactant SG is a feasible method to enhance bioremediation efficiency for TCE contaminated groundwater. The complete TCE degradation was detected after 75 days of incubation with both 0.01 and 0.1 wt% of surfactant SG addition. Results revealed that surfactant enhanced chemical oxidation and bioremediation technology is one of feasible approaches to clean up TCE contaminated groundwater.

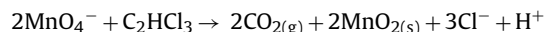
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1. Introduction

The spill of chlorinated solvents trichloroethylene (TCE) has drawn public attention in Taiwan recently. TCE is carcinogenic and may pose a threat to the public health. At many TCE spilled sites, residual TCE persists in a pure liquid phase (dense non-aqueous phase liquids, DNAPLs). Various studies have been conducted to investigate in situ chemical oxidation to remediate chlorinated solvents within the source zone in subsurface environment. In situ chemical oxidation schemes using potassium permanganate (KMnO₄) have been demonstrated as an effective approach to degrade chlorinated solvents via an oxidative dechlorination process in contaminated groundwater [1,2].

There is increasing interest in in situ treatment of chlorinated solvents to utilize oxidant KMnO₄ as the oxidant might migrate by diffusion and degrade chlorinated solvents within a low permeability media. Oxidant KMnO₄ has been well studied for the treatment of water and wastewater and it has been investigated under laboratory and field conditions to determine its potential for in situ remediation of chlorinated solvents [3–5].

A promising alternative for the remediation of sites contaminated by TCE is the injection of a KMnO₄ solution into the subsurface to chemically transform TCE into harmless compounds. This treatment concept has been intensely evaluated in many studies over the past decade. Laboratory batch studies have demonstrated that KMnO₄ can completely mineralize TCE, based on the complete recovery of chlorine atoms liberated from TCE. The study results indicated that the degradation rate of TCE by KMnO₄ was influenced predominately by reactant concentrations and temperature, and was independent of both ionic strength and pH [6]. The reaction between TCE and KMnO₄ is a complex reaction involving several steps, and the overall reaction has been reported as [7–9]:



The production rate of chloride was equal to the degradation rate of TCE for pH ranging from 3 to 10 while its production was correlated to the consumption of KMnO₄. Previous results showed that TCE degradation was pseudo-first-ordered with respect to both [TCE] and [MnO₄⁻], and an overall second order reaction [10]. If the TCE dissolution rate is faster than its degradation rate plus its volatilization rate, the TCE solution concentration can be viewed as a constant. The overall second order reaction can be approximated as a pseudo-first-order reaction where the square brackets denote

* Corresponding author. Tel.: +886 7 591 9536; fax: +886 7 591 9376.
E-mail address: tyyeh@nuk.edu.tw (T.Y. Yeh).

concentrations and reaction rate constants (k_{obs}) are the observed pseudo-first-order reaction rate constant.

$$\frac{1}{3} \frac{d[\text{Cl}^-]}{dt} = -\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-]$$

Chlorinated solvents commonly present in the subsurface and remain as a continuous source for groundwater contamination. A common practice to remove chlorinated solvents is by surfactant flushing studies [11]. Surfactant molecules consist of a hydrophilic head and a hydrophobic tail. In dilute solutions, surfactants exist as free monomers. When the concentration of a surfactant is above a critical micelle concentration (CMC), the hydrophobic tails tend to cluster together to avoid contact with water molecules, while their hydrophilic heads remain toward the solution. As a result, a micelle structure is formed. When the surfactant is injected into groundwater, the insoluble organic contaminants (e.g., TCE) will be trapped into the hydrophobic centre of the micelle structure formed by the surfactants, and thus the solubility of the organic compounds will be increased [12].

The ability of surfactant to enhance dissolution and desorption of organic compounds is well known. Surfactant-enhanced solubility has led to the development and use of surfactant flushing as a chlorinated solvents source remediation technology. However, contaminants are not destroyed during flushing, thus requiring in situ chemical oxidation (e.g., KMnO_4). The merits of surfactant addition during the remediation of chlorinated solvents contaminated groundwater might include enhancing KMnO_4 mass transfer, augmenting oxidation efficiency, and preventing MnO_2 clogging problem [13–15].

To combine surfactant enhanced solubilization of chlorinated solvents with KMnO_4 oxidation in a single step to achieve synchronized pump-while-treat contrast to common pump-then-treat was investigated. The main objectives of this study are: (1) to determine the optimal oxidation conditions, (2) to evaluate the feasibility of using non-ionic surfactant to enhance the oxidative dechlorination of TCE by KMnO_4 , and (3) to study the approach of using non-ionic surfactant to enhance the cometabolism of TCE and the effect of surfactant addition on biodegradation.

2. Materials and methods

2.1. Surface tension test

This study employed a biodegradable non-ionic surfactant, Simple Green™ (SG) (manufactured by Sunshine Makers, Inc., USA), which has an average molecular weight of 106 and a molecular formula as $\text{HOCH}_2\text{H}_2\text{O}-(\text{CH}_2)_3\text{CH}_3$. The CMC of surfactant SG was measured using the surface tension technique. Samples with different surfactant SG levels were first mixed for 24 h in a rotary shaker. After centrifugation at 4000 rpm for 30 min, the surface tension of the supernatant was measured by the tensiometer (Fisher Surface Tensiometer Model 21) consisting of a Du Nouy platinum-iridium ring suspended in the surfactant solution by a torsion balance [16]. All of the samples were measured in duplicate.

2.2. Batch experiments

A continuous stir batch reactor system (CSBR) that composed of a 200 mL brown bottle with a chloride electrode and a pH electrode was used to conduct batch experiments. Groundwater and soil samples were collected from a TCE contaminated site. Table 1 shows the physical-chemical characteristics of tested soil and groundwater.

In the batch experiments, different concentrations of KMnO_4 (e.g., 12, 48, and 96 mg L^{-1}) were added to tested soil/groundwater in the presence of surfactant SG. TCE degradation rates were investi-

Table 1
Physical-chemical characteristics of tested soil and groundwater

Parameters	Value
Soil sample	
Sand content (%)	60
Silt content (%)	35
Clay content (%)	5
Organic matter content (%)	0.8
Soil pH (1:5 H_2O)	5.6
CEC (meq/100 g)	8.6
ORP (mV)	245
Groundwater sample	
NO_2^- (mg L^{-1})	8.6×10^{-4}
NO_3^- (mg L^{-1})	5.31
SO_4^{2-} (mg L^{-1})	25.5
PO_4^{3-} (mg L^{-1})	0.14
TOC (mg L^{-1})	1.19
Total heterotrophic bacterial (CFU/100 mL)	4.29×10^{-4}
TCE (mg L^{-1})	ND

gated within the CSBR. Initial TCE concentrations were maintained ranged from 38.1 μM (5 mg L^{-1}) and 152.4 μM (20 mg L^{-1}) within this study. The effects of surfactant SG concentrations on TCE degradation rate were evaluated at surfactant SG concentrations of 0.01, 0.05, and 0.1 wt% corresponding to 0.1, 0.5, and 1 times of its CMC, respectively. All batch experiments were performed in triplicates within the CSBR to test the reaction rate. Groundwater samples were collected periodically (e.g., 0, 20, 40, 80, 120, 200, 250, and 300 min). Samples were placed in a Hettich-Zentrifugen EBA 21 Centrifuge for 30 min at 5000 rpm. The centrifuged samples were then stored in the dark at 10 °C for the analysis of TCE, KMnO_4 and chloride. TCE was analyzed in accordance with EPA Method 601, using a Tekmer Purge-and Trap Model LSC 2000 with a Varian Model 3800 Gas Chromatograph. A 50 m \times 0.32 mm DB-624 capillary column with a 0.25 μm film (J&W Sci.) was used for sample separation. Potassium permanganate concentrations were analysed by UV-vis spectrometer (ATI Unicomp) at 526.5 nm. Chloride concentrations were measured by chloride electrode (HORIBA 6560 10C, Japan).

2.3. Column experiment

The column experiment was conducted to assess the potential of different treatment schemes to degrade TCE. Oxidant KMnO_4 containing surfactant SG was applied to oxidize free product of TCE in the column via the surfactant-enhanced oxidation. Glass columns were constructed of a Plexiglas cylinder with a wall thickness of 0.30 cm, length of 30 cm, and an inner diameter of 7 cm. A schematic of the column apparatus is shown in Fig. 1. Washed and sterilized quartz sand (0.2 mm diameter) obtained by sieving tested soil was packed at each end (2–3 cm depth) to provide uniform flow distribution of the groundwater. A nylon mesh of 8 μm pore size on top of a wire mesh provided a barrier between the quartz sand and tested soil. The tested soil was uniformly placed in the middle layer in small increments and packed down using a 450 g weight. Plexiglas plates on either end of the cylinders were secured using threaded rods.

One pore volumes of tested groundwater were first pumped into the bottom of the soil column at a flow rate of 0.5 mL/min to ensure that the soil was completely saturated. 38.1 μM TCE was then pumped into the bottom of the column at 0.2 mL/min using a syringe pump to saturate the soil with TCE. After this pretreatment, the column was injected one pore volume of water containing 96 mg L^{-1} KMnO_4 and 0.1 wt% SG was circulated up-flow through the columns at a flow rate of 12 \pm 2 mL/min using a peristaltic pump. 10 mL of effluent samples was collected from the top of the column

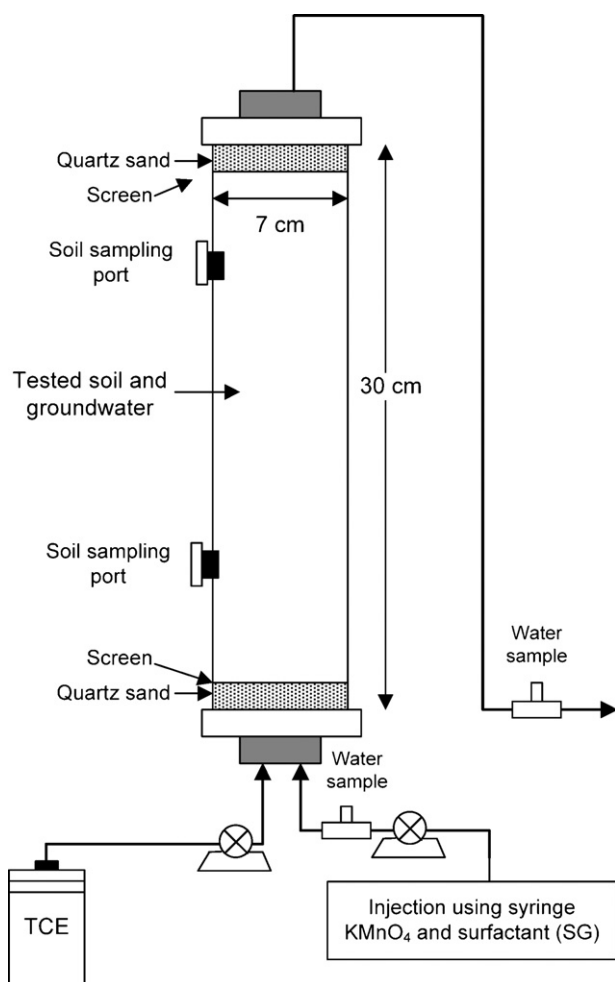


Fig. 1. Schematic of the column apparatus.

each time. Samples were analyzed for variables of TCE, its degradation by-products, KMnO_4 , chloride, and pH [17]. The degradation by-products might include 1,1-DCE, *trans*-DCE, *cis*-DCE, VC, and chloride. Because *cis*-DCE is the dominant by-product among DCE isomers during the TCE biodegradation process, only *cis*-DCE was analyzed in this study. Column experiment analytical methods for TCE, degradation by-products, KMnO_4 , and chloride are described in the previous section.

2.4. Effect of surfactant on contaminant biodegradation

Aerobic microcosm experiments were conducted to examine the feasibility of TCE biodegradation using surfactant SG as the primary substrate under aerobic cometabolic conditions. The inocula used in this microcosm study included un-contaminated groundwater and tested soil from a TCE-spill site. The aerobic activated sludge was collected from an industrial wastewater treatment plant with influent wastewater containing aliphatic chlorinated compounds (e.g., tetrachloroethene, dichloroethene, dichloroethane) and phenol. Each microcosm was constructed with 30 mL groundwater (mineral medium), 15 mL of inocula (aerobic activated sludge), 5 mL TCE solution, and surfactant (0.01 wt% and 0.1 wt% SG) in a 70-mL bottle sealed with Teflon-lined rubber septa [18]. The initial TCE concentrations in microcosm bottles were approximately $7.62 \mu\text{M}$ (1 mg L^{-1}) (after equilibration).

Four groups (control, sludge, sludge + 0.01 wt% SG, and sludge + 0.1 wt% SG) of microcosms were constructed. Control

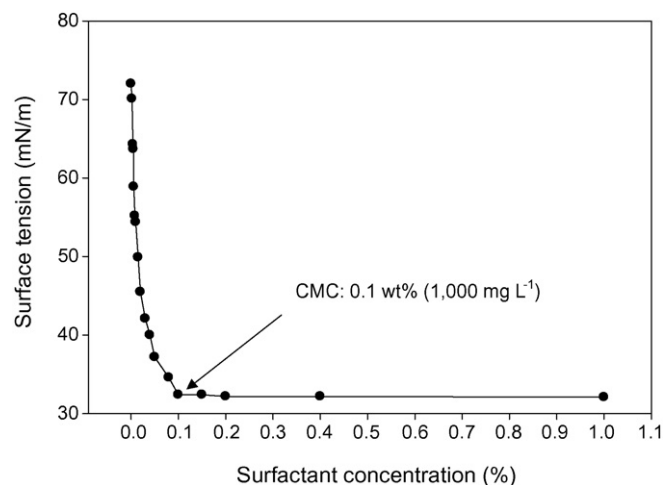


Fig. 2. Properties of surfactant SG solution as surface tension analyses.

experiments was carried out using groundwater and TCE with soil only, and control bottles contained $250 \text{ mg L}^{-1} \text{ HgCl}_2$ and $500 \text{ mg L}^{-1} \text{ NaNO}_3$, and inocula used for the control groups were autoclaved before use. Aerobic conditions were maintained by purging the reaction mixture with pure oxygen gas during the preparation, using a $0.2 \mu\text{m}$ filter and a syringe. A colorimetric redox indicator (resazurin, 0.0002%) was also added to the reactions to verify maintenance of aerobic conditions during incubation. Duplicate microcosms were scarified at each time point (e.g., 0, 3, 5, 8, 13, 18, 20, 30, 40, 50, 60, 70, 75, and 80 days) during the analysis. TCE analyses were described in the above section.

3. Results and discussion

3.1. Batch experiments

The results of surface tension investigation to test the property of surfactant SG are shown in Fig. 2. The surface tension of the solution decreased as the surfactant SG concentration increased before reaching its CMC. The CMC value of surfactant SG was 1000 mg L^{-1} (0.1 wt%) that was comparatively higher than those of commonly used non-ionic surfactants, namely Tween and Triton.

The results of oxidant KMnO_4 and surfactant SG addition on TCE degradation are shown in Fig. 3. Fig. 3(a) depicted that TCE degradation rates without surfactant SG addition are 85.7, 76.0, and 74.1% for the concentrations of oxidant KMnO_4 96, 48, and 12 mg L^{-1} , respectively after 300 min of reaction. On the other hand, TCE degradation rates with 0.1 wt% surfactant SG additions are 96.3, 84.9, and 83.8% for the concentration of oxidant KMnO_4 96, 48, and 12 mg L^{-1} , respectively. These results indicated that effect of surfactant SG to enhance TCE degradation was significant regardless the KMnO_4 concentration. In addition, the amounts of TCE degraded by KMnO_4 were significantly enhanced, particularly when the surfactant SG concentration was around its CMC (Fig. 3(b) and (c)).

The overall reaction between TCE and KMnO_4 can be written as a pseudo-first-order reaction if the TCE dissolution rate is faster than its degradation rate. The production rate of chloride was equal to the degradation rate of TCE where k_{obs} is the reaction rate constant of the pseudo-first-order reaction. In addition, the amounts of chloride generation can be quantitatively correlated to the consumption of KMnO_4 . The degradation rates, reaction rate constants, and half-life values of TCE that employed various concentrations of oxidant KMnO_4 and surfactant SG are shown in Table 2. In the presence of 0.1 wt% SG, the k_{obs} values were found to be 4.8×10^{-3} , 8.5×10^{-3} ,

Table 2
The degradation rates, reaction rate constants, and half-life values of TCE oxidation employed various KMnO_4 and surfactant SG concentrations

Initial KMnO_4 concentration (mg L^{-1})	Initial SG concentration (wt%)	Initial TCE concentration (μM)	Time (min)	k_{obs} (min^{-1})	Half-life (min)	Degradation rate (C/C_0 , %)
12	0	38.1	300	3.9×10^{-3}	178	74.1
48	0	38.1	300	5.0×10^{-3}	139	76.0
96	0	38.1	300	5.3×10^{-3}	131	85.7
12	0.1	38.1	300	4.8×10^{-3}	144	83.8
48	0.1	38.1	300	8.5×10^{-3}	82	84.9
96	0.1	38.1	300	1.36×10^{-2}	51	96.3
12	0.01	38.1	300	2.8×10^{-3}	248	70.3
12	0.05	38.1	300	3.6×10^{-3}	193	75.2
12	0.1	38.1	300	4.8×10^{-3}	144	83.8
48	0	152.4	300	5.6×10^{-3}	124	83.2
48	0.01	152.4	300	5.1×10^{-3}	136	84.6
48	0.05	152.4	300	8.2×10^{-3}	85	94.1
48	0.1	152.4	300	8.8×10^{-3}	79	94.9

and $1.36 \times 10^{-2} \text{ min}^{-1}$, and half-life were 144, 82, and 51 min, as the initial KMnO_4 concentrations of 12, 48, and 96 mg L^{-1} , respectively. On the other hand, the k_{obs} values were 3.9×10^{-3} , 5.0×10^{-3} , and $5.3 \times 10^{-3} \text{ min}^{-1}$, and half-life were 178, 139, and 131 min, without addition of surfactant SG for three KMnO_4 concentrations. The reaction rate constant k_{obs} increased as both the oxidant concentration increased and the surfactant concentration addition increased. The significantly increased of k_{obs} might be induced by the enhanced solubilization of TCE by surfactant SG. TCE degradation rates ranged from 74.1% to 85.7% without addition of surfactant SG while the TCE degradation rate increased to ranging from 83.8% to 96.3% with presence of 0.1 wt% surfactant SG.

The oxidation of TCE by KMnO_4 was investigated under different concentrations of surfactant SG. With 38.1 μM TCE and 12 mg L^{-1} KMnO_4 initial concentration, TCE degradation rates were 83.8, 75.2, and 70.3% for the dosage of surfactant SG as 0.1, 0.05, and 0.01 wt%, respectively. With the increase TCE (152.4 μM) and KMnO_4 (48 mg L^{-1}) concentration, TCE degradation rates were increased as 94.9, 94.1, and 84.6% for the conditions of 0.1, 0.05, and 0.01 wt% SG addition. These results revealed that surfactant SG has significantly increased the degradation rates of TCE by oxidant KMnO_4 . The generation of chloride and the consumption of KMnO_4 were further tested to confirm these results under the feasible testing condition as 96 mg L^{-1} of oxidant KMnO_4 and 0.1 wt% surfactant SG.

Fig. 4 presents the effect of surfactant SG addition on the KMnO_4 consumption rates while the initial KMnO_4 concentration was 96 mg L^{-1} and TCE concentration was 38.1 μM . The consumption rate of KMnO_4 was lower in the test without presence of surfactant SG. The reaction rate constants were 4.1×10^{-3} and

$5.2 \times 10^{-3} \text{ min}^{-1}$ while the half-life values of KMnO_4 were 169 and 133 min for the conditions without presence and with 0.1 wt% of surfactant SG, respectively. TCE oxidation by KMnO_4 could be enhanced in the presence of surfactant SG, particularly when the surfactant SG concentration at its CMC. The reason might be attributed to that TCE dissolution was significantly increased due to solubilization mechanism by surfactant micelles.

The amounts of chloride generated due to the reaction of TCE with 96 mg L^{-1} KMnO_4 in the absence and presence of 0.1 wt% SG are shown in Fig. 5(a) and (b). The oxidative dechlorination of TCE was demonstrated with the increase of chloride production with and without surfactant SG addition. The generation rate of chloride production was greater in the presence of 0.1 wt% SG compared to without addition of surfactant SG. Without surfactant SG addition, TCE concentration reduced from 38.1 μM to 5.5 μM while the chloride concentration increased from 0 μM to 8.5 μM . On the other hand, TCE was reduced from 38.1 μM to 1.45 μM , and chloride concentration was increased from 0 μM to 10.1 μM with addition of 0.1 wt% SG. The overall TCE removal was around 85.7% within 300 min of reaction time. TCE can be further reduced to 96.3% with 0.1 wt% of surfactant SG addition. Both the chloride production rate and the KMnO_4 consumption rate constant increased as the addition of 0.1 wt% SG.

The generation rate of chloride is proportional to the consumption rate of KMnO_4 and can be used as an indicator for the oxidation efficiency under TCE dechlorination process. The generation of chloride was lower under the condition of without surfactant SG addition compared to that added 0.1 wt% SG. In addition, the amounts of chloride generation under both conditions were below 114.1 μM (4.1 mg L^{-1}). This chloride concentration value was cal-

Table 3
The concentrations of TCE degradation by-products, chloride generation, oxidant KMnO_4 monitored at the column outlet during two oxidation stages

Time (min)	TCE (μM)	<i>cis</i> -DCE (μM)	VC (μM)	Cl^- (μM)	TCE (Control) (μM)	KMnO_4 (mg L^{-1})	$[\text{TCE}]/[\text{MnO}_4^-]$	pH	Mass balance ^a
0	38.1	0.0	0.0	0.0	38.9	0	0.00	7.82	1.00
10	34.2	1.4	0.5	1.0	37.3	20.53	0.26	8.07	0.97
20	20.6	5.3	4.2	2.0	35.3	34.08	0.10	8.17	0.85
40	17.2	12.2	4.9	3.5	35.5	88.64	0.03	8.03	0.99
80	19.4	7.0	6.1	2.3	35.1	53.07	0.06	8.04	0.91
120	15.2	8.7	4.0	1.5	35.3	31.62	0.08	8.02	0.77
200	13.1	6.6	11.1	7.2	34.0	24.73	0.08	7.93	1.00
300	11.9	8.7	7.1	8.5	34.3	16.03	0.12	7.83	0.95
KMnO ₄ addition (48 mg L ⁻¹ KMnO ₄ + 0.1 wt% SG)									
310	13.7	6.9	6.2	10.1	33.6	26.33	0.08	7.54	0.97
320	11.5	11.2	5.4	9.6	32.2	41.59	0.04	7.61	0.99
380	7.7	3.2	1.9	15.9	32.7	45.92	0.03	7.95	0.76
440	6.6	2.5	1.3	16.7	32.0	34.94	0.03	7.91	0.71
560	6.2	2.2	1.5	27.0	32.5	23.71	0.04	7.47	0.97

^a Mass balance = $[(\text{TCE} + \text{cis-DCE} + \text{VC} + \text{Cl}^-) / \text{TCE} (\text{control})] \times 100\%$.

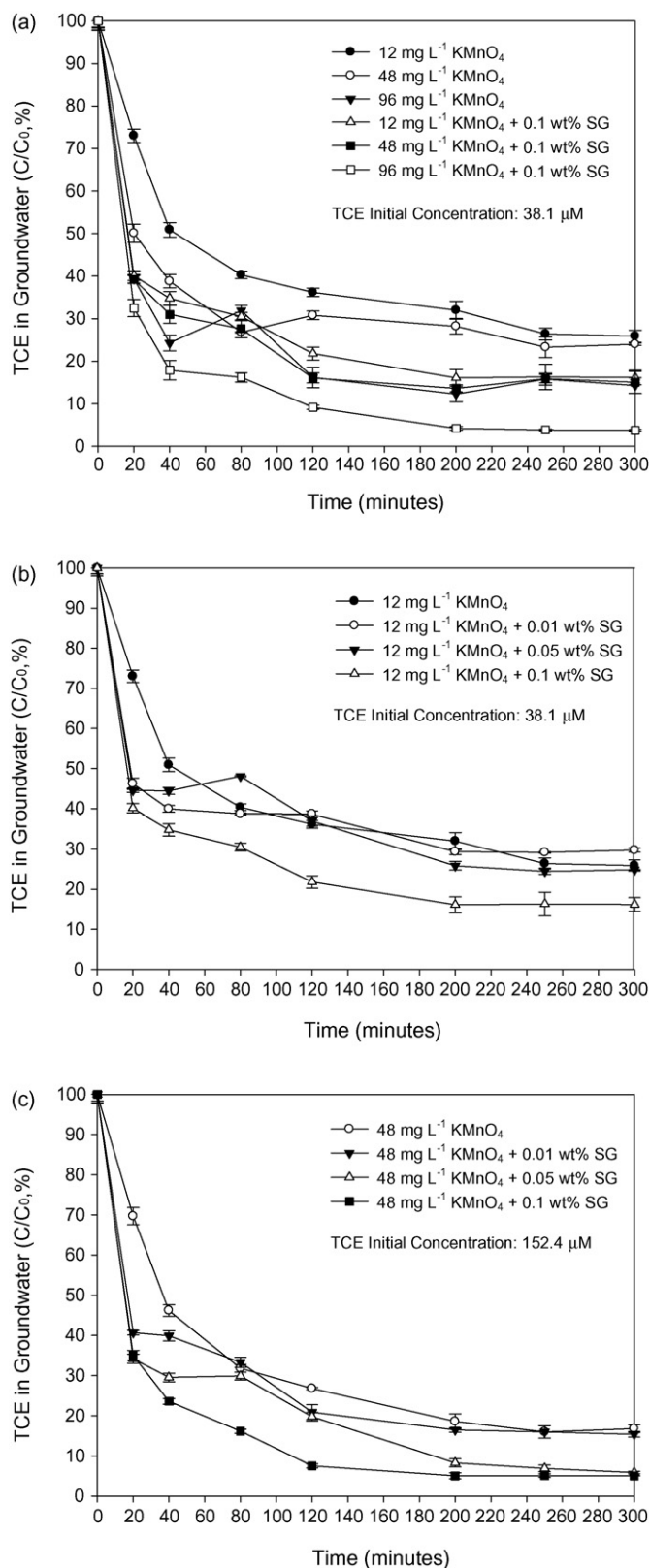


Fig. 3. Effect of $[\text{KMnO}_4]$ on the oxidation of TCE: (a) different KMnO_4 and surfactant SG concentrations; (b) $12 \text{ mg L}^{-1} \text{ KMnO}_4$ + different surfactant SG concentrations; (c) $48 \text{ mg L}^{-1} \text{ KMnO}_4$ + different surfactant SG concentrations (error bars show standard deviation in duplicate samples).

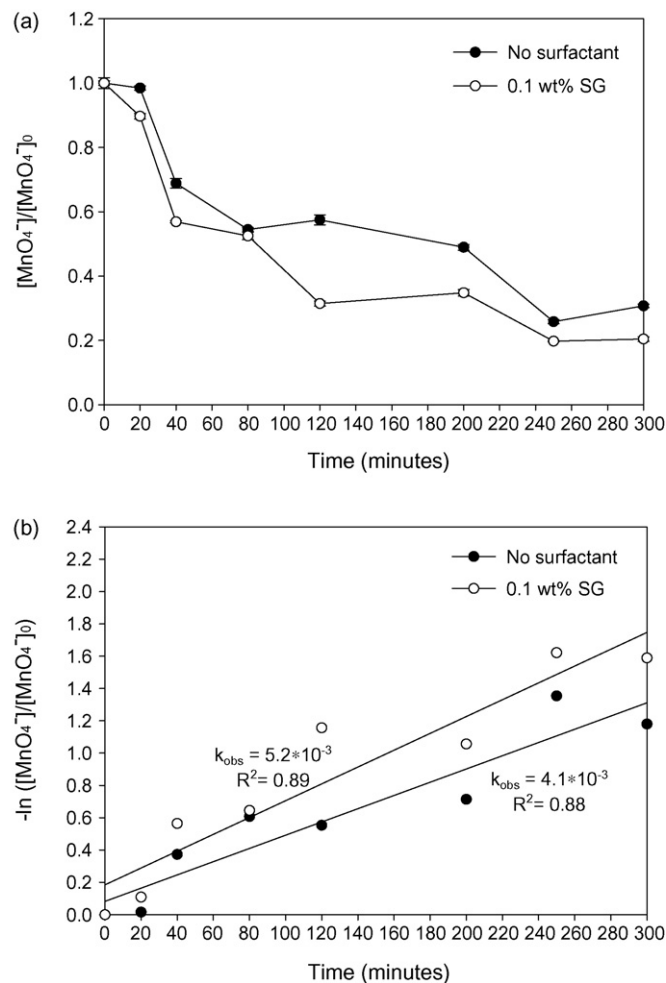


Fig. 4. The effect of surfactant SG addition on the KMnO_4 consumption rates as the initial KMnO_4 concentration was 96 mg L^{-1} and TCE concentration was $38.1 \mu\text{M}$: (a) KMnO_4 consumption concentration; (b) pseudo-first-order rate constants analyses (error bars show standard deviation in duplicate samples).

culated based on the stoichiometry for complete TCE degradation. The chloride generated was 6.7 and $2.9 \mu\text{M}$ for the condition as with 0.1 wt% SG addition and absence of surfactant, respectively, at 120 min of reaction time. The chloride generation concentrations were increased to 8.5 and $10.2 \mu\text{M}$ for two aforementioned surfactant SG addition conditions at 300 min. Chloride concentrations generated under these oxidation reactions were approximately one-tenth of the value ($114.1 \mu\text{M}$) based on stoichiometry calculation. These results indicated that intermittent by-products (e.g., *cis*-DCE and VC) might not be completely degraded under these oxidation reactions. The following column experiments might further confirm these results.

TCE degradation by KMnO_4 enhanced by surfactant SG was demonstrated in this study. The merits of surfactant addition during the remediation of TCE contaminated groundwater might include enhancing KMnO_4 mass transfer, augmenting oxidation efficiency, and preventing MnO_2 clogging problem. This study results showed that combination of KMnO_4 with a proper type of surfactant can improve contaminant removal. It is possible to combine surfactant-enhanced solubilization of chlorinated solvents with KMnO_4 oxidation in a synchronized "pump-while-treat" step [14]. The finding of this batch test was further verified by the following column studies.

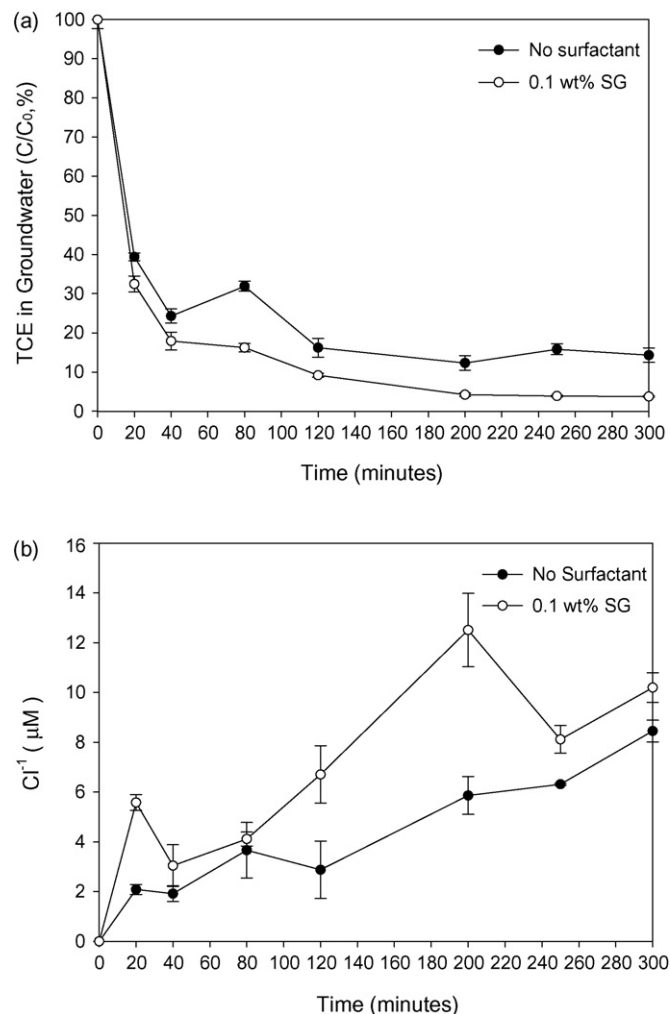


Fig. 5. The amounts of chloride generated and TCE degraded under the oxidation reaction with 96 mg L^{-1} KMnO_4 in the absence and presence of 0.1 wt% SG: (a) amounts of chloride generated; (b) concentration of TCE in groundwater (error bars show standard deviation in duplicate samples).

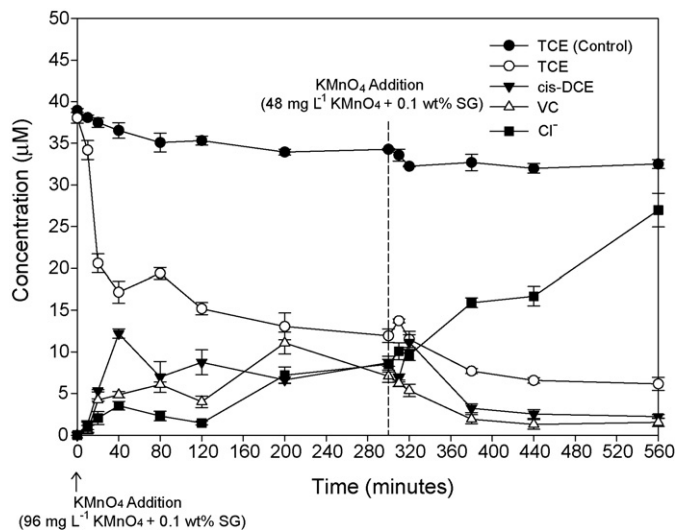


Fig. 6. The concentrations of chloride generation and by-products under the degradation of TCE in column experiment (error bars show standard deviation in duplicate samples).

3.2. Column experiment

Column experiment was conducted to evaluate the extent of oxidation of TCE by addition of oxidant KMnO_4 and surfactant SG. The concentrations of TCE degradation and chloride generation during the oxidation process are shown in Table 3 and Fig. 6. TCE concentration at the column outlet was approximately $38.1 \mu M$ initially. A pore volume of KMnO_4 (96 mg L^{-1}) solution containing 0.1 wt% of surfactant SG was injected into the soil column to oxidize the TCE within the first stage of the oxidation test. TCE was degraded from $38.1 \mu M$ to $17.2 \mu M$ in equivalent to 54.9% of TCE oxidized within first 40 min of the reaction. The dominant by-products of TCE degradation included *cis*-DCE and VC were also monitored. The concentration of *cis*-DCE was increased to the highest as $12.2 \mu M$ at 40 min while the concentration of VC reached the highest $11.1 \mu M$ at 200 min.

Table 3 and Fig. 6 also present that the production of chloride correlated with the occurrence of TCE degradation. The concentration of TCE was reduced from $38.1 \mu M$ to $11.9 \mu M$ while chloride concentration was increased from 0 mg L^{-1} to $8.5 \mu M$ for first 300 min oxidation reaction. With an additional 48 mg L^{-1} of KMnO_4 further injected, the concentration of TCE was reduced from $13.7 \mu M$ to $6.2 \mu M$ while chloride concentration was increased from $10.1 \mu M$ to $27.0 \mu M$ within the oxidation periods from 310 min to 560 min. The rate of chloride production and the rate of TCE degradation were greater in the presence of surfactant SG compared to the case without surfactant addition. The reaction constant k_{obs} was $3.3 \times 10^{-3} \text{ min}^{-1}$ while the half-life was 210 min for the condition with 96 mg L^{-1} of KMnO_4 initially injected. The reaction constant k_{obs} was reduced to $3.0 \times 10^{-3} \text{ min}^{-1}$ and half-life was 231 min for the second oxidation stage with 48 mg L^{-1} of KMnO_4 injection from 310 min to 560 min reaction (Fig. 7). The consumption rate of KMnO_4 was reduced that leads to less TCE degradation due to hindering of mass transfer efficiency. Following study results might further explain these phenomena.

The ratios of $[\text{TCE}]/[\text{MnO}_4^-]$ during two oxidation stages are shown in Fig. 8. Yan and Schwartz [19] reported that the complete dechlorination of TCE was achieved at the $[\text{TCE}]/[\text{MnO}_4^-]$ ratio of 0.06. Additional KMnO_4 need to be further employed to achieve complete TCE degradation if $[\text{TCE}]/[\text{MnO}_4^-]$ ratio is greater than 0.06. Potassium permanganate was continuously injected in this column test for the first ten min to increase the ratio of $[\text{TCE}]/[\text{MnO}_4^-]$ and to achieve the expected TCE degradation. The concentration of KMnO_4 in the outlet of the column was approaching 96 mg L^{-1} of oxidant initially added around 40 min of reaction. The ratio of $[\text{TCE}]/[\text{MnO}_4^-]$ at this reaction time equals to 0.03 indicating that complete dechlorination of TCE via *cis*-DCE and VC to chloride was achieved. The ratio of $[\text{TCE}]/[\text{MnO}_4^-]$ was increased from 0.08 to 0.12 for the reaction from 120 min to 300 min. This result demonstrated that further oxidant KMnO_4 needed to be added to achieve the complete TCE degradation. Therefore, an additional 48 mg L^{-1} of KMnO_4 was further injected at 300 min of the reaction. Though the ratios of $[\text{TCE}]/[\text{MnO}_4^-]$ were ranged from 0.03 to 0.04 indicating the feasible condition for complete dechlorination of TCE, the degradation rate of TCE was decreased for this second stage of oxidation from 300 min to 560 min reaction. The reduction of TCE degradation might be caused by emulsion of surfactant that clogged the pore volume of tested soil. The ratio of $[\text{TCE}]/[\text{MnO}_4^-]$ can be used as the indicator of the potential of oxidation reaction within the soil matrix.

3.3. Effect of surfactant on contaminant biodegradation

The biodegradation rates of TCE under two different concentrations of surfactant SG including 0.01 wt% and 0.1 wt% are shown

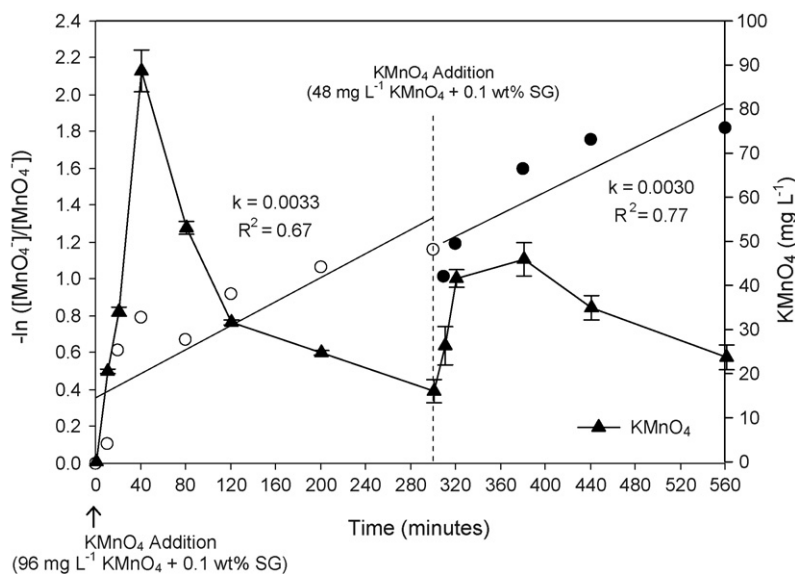


Fig. 7. Pseudo-first-order rate constant k_{obs} for $KMnO_4$ consumption rate under both oxidation stages.

Fig. 9. Results are demonstrated with an averaged concentration for duplicate samples. In microcosms with surfactant SG addition, 38.6–41.1% TCE degradation was observed after approximately 13 days of incubation where surfactant served as the primary substrate. The complete TCE degradation was further detected after 75 days of incubation with both 0.01 and 0.1 wt% of surfactant SG addition. Though the degradation of TCE was also detected in sludge microcosms without surfactant SG addition for the first 70 days of incubation, TCE degradation rate was slower than the microcosms with surfactant SG addition. The complete TCE degradation was not observed until 80 days of incubation for the microcosms without surfactant SG presence. Surfactants are useful for the biodegradation of contaminants because they are able to enhance desorption and solubility of hydrophobic compounds. Many studies have been conducted to enhance biodegradation of TCE employing surfactant in contaminated soil and groundwater [20–24]. Two predominant mechanisms including to enhance solubility of the substrate for the microbial cells and to interact with the cell surface might be respon-

sible for biodegradation enhancement. These mechanisms increase the surface of hydrocarbons allowing hydrocarbons substrates to contact more easily with microorganisms. Results from this study revealed that the addition of surfactant is a feasible method to enhance bioremediation efficiency for TCE contaminated groundwater.

TCE degradation rate in the order of 0.01 wt% SG (52.0%) > 0.1 wt% SG (48.4%) > sludge without SG (29.2%) > control (10.5%) at 18 days of incubation. Similarly, TCE degradation was in the order of 0.01 wt% SG (98.9%) > 0.1 wt% SG (97.8%) > sludge without SG (90.3%) > control (24.7%) at 70 days of experiments. TCE degradation rate was not enhanced as the increase dosing concentration at CMC (0.1 wt%) level of surfactant SG. In addition, the degradation rate was decreased ranging from 1.1% to 16.8% after 18 days and was level off toward the end of the experiments.

Similar researches [23,25–27] have pointed out that the biodegradation of hydrophobic hydrocarbons was not increased proportional to the dosage of surfactant. The reasons were

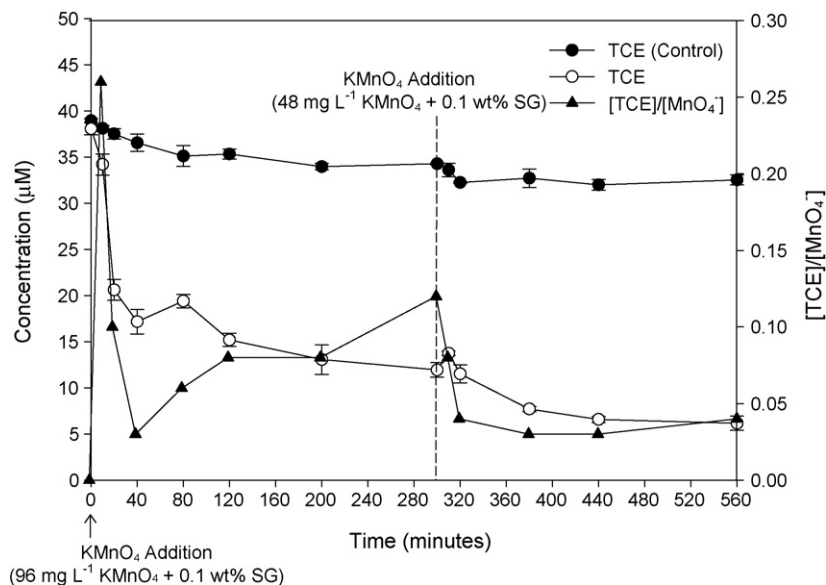


Fig. 8. The ratio of $[TCE]/[MnO_4^-]$ and TCE degradation during two oxidation testing stages (error bars show standard deviation in duplicate samples).

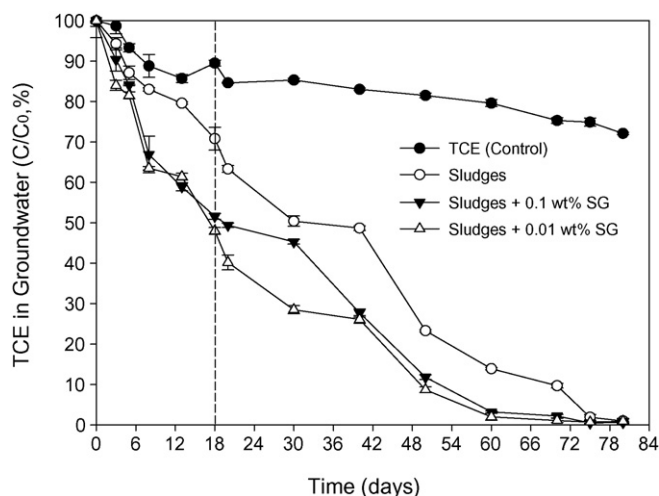


Fig. 9. TCE degradation under aerobic microcosm experiments with sludge and surfactant SG (0.01 wt% and 0.1 wt%) addition (error bars show standard deviation in duplicate samples).

attributed to that hydrocarbons entrapped within the micelle due to the increase surfactant addition might not be completely available for microorganism to utilize. With the addition of surfactant concentration at its CMC, the solubility of hydrocarbons was increased leading to the enhancement of biodegradation rate due to the mass transfer from non-aqueous liquid phase to aqueous phase. However, the concentration of hydrocarbons truly solubilized in aqueous phase was not increased though the mass transfer was occurred. Therefore, the bioavailability of hydrocarbons was not enhanced due to the effect of surfactant addition.

Both the sludge and the surfactant might act as the diffusion sources of substrates in this aerobic cometabolic microcosm study. The release of substrates enhanced the TCE removal via aerobic cometabolic processes. Because organic materials are released from sludge and surfactant continuously, sludge or surfactant can remain active for a long period of time in situ. Thus, an in situ chemical oxidation with sludge and surfactant might have the potential to become a cost effective remediation alternative to enhance the cometabolic process. Further studies need to be conducted for the scale-up application.

4. Conclusions

This study has demonstrated that the technique of surfactant-enhanced in situ chemical oxidation is a feasible remediation technology for the treatment of TCE contaminated groundwater. The following conclusions from the study can be drawn:

- (1) Results from CSBR and column experiments revealed that combination of KMnO_4 with surfactant SG can improve contaminant removal.
- (2) The amounts of TCE degraded by KMnO_4 were significantly enhanced, particularly when the surfactant SG concentration at its CMC so that the TCE solution concentration could be greatly increased due to solubilization by surfactant micelles.
- (3) Chloride concentrations generated under these oxidation reactions were approximately 23.7% (27 μM) of the value (114.1 μM) based on stoichiometry calculation. This result indicated that intermittent by-products (e.g., *cis*-DCE and VC) did not completely degrade under these oxidation reactions.
- (4) TCE can be biodegraded using surfactant as the primary substrates under aerobic cometabolism conditions. However, TCE

degradation rate was not enhanced as the increase dosing concentration at CMC (0.1 wt%) level of surfactant SG.

Due to the significant discrepancy in chloride production in the presence and absence of surfactant in this study, further studies to test different surfactants and contaminants need to be conducted. Nevertheless, this study has demonstrated that it is feasible to combine surfactant-enhanced solubilization of TCE with KMnO_4 oxidation in a synchronized “pump-while-treat” remediation approach. The experimental results are useful in designing a scale-up in situ chemical oxidation system to remediate TCE contaminated groundwater.

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