Application of potassium permanganate as an oxidant for in situ oxidation of trichloroethylene-contaminated groundwater: A laboratory and kinetics study

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Abstract

The objectives of this bench-scale study were to (1) determine the optimal operational parameters and kinetics when potassium permanganate ($KMnO_4$) was applied to in situ oxidize and remediate trichloroethylene (TCE)-contaminated groundwater and (2) evaluate the effects of manganese dioxide (MnO_2) on the efficiency of TCE oxidation. The major controlling factors in the TCE oxidation experiments included molar ratios of $KMnO_4$ to TCE (*P* value) and molar ratios of Na_2HPO_4 to Mn^{2+} (*D* value). Results show that the second-order decay model can be used to describe the oxidation when *P* value was less than 20, and the observed TCE decay rate was $0.8\,M^{-1}\,s^{-1}$. Results also reveal that (1) higher *P* value corresponded with higher TCE oxidation rate under the same initial TCE concentration condition and (2) higher TCE concentration corresponded with higher TCE oxidation rate under the same *P* value condition. Results reveal that significant MnO_2 production and inhibition of TCE oxidation were not observed under acidic (pH 2.1) or slightly acidic conditions (pH 6.3). However, significant reduction of $KMnO_4$ to MnO_2 would occur under alkaline condition (pH 12.5), and this caused the decrease in TCE oxidation rate. Results from the MnO_2 production experiments show that MnO_2 was produced from three major routes: (1) oxidation of TCE by $KMnO_4$, (2) further oxidation of Mn^{2+}, which was produced during the oxidation of TCE by $KMnO_4$, and (3) reduction of MnO_4^{-1} to MnO_2 under alkaline conditions. Up to 81.5% of MnO_2 production can be effectively inhibited with the addition of Na_2HPO_4. Moreover, the addition of Na_2HPO_4 would not decrease the TCE oxidation rate.
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1. Introduction

Groundwater at many existing and former industrial sites and disposal areas is contaminated by halogenated organic compounds that were released into the environment. The chlorinated solvent trichloroethylene (TCE) is one of the most ubiquitous of these compounds. The maximum contaminant level (MCL) (the concentration established under the Safe Drinking Water Act as being protective of human health and the environment) for TCE is $5\,\mu g/L$ [1,2]. Beyond the toxicity of TCE and its presence in the environment, many researchers have shown the compound to be very resistant to biodegradation. At many TCE spil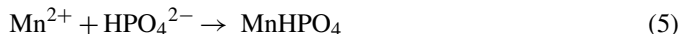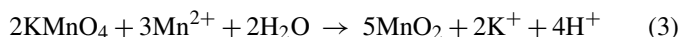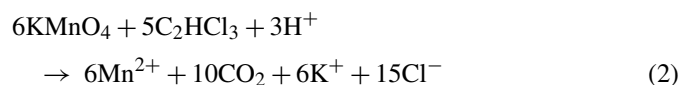l site, residual amounts of TCE persist in a pure liquid phase [commonly referred to as dense, non-aqueous-phase liquids (DNAPLs)] within pore spaces or fractures. The slow dissolution of residual TCE results in a contaminated plume of groundwater [3,4]. Therefore, more effective and aggressive approaches are desirable for TCE-contaminated groundwater remediation.

Oxidation converts hazardous contaminants to nonhazardous or less toxic compounds. The oxidizing agents most commonly used for the treatment of hazardous contaminants are potassium permanganate ($KMnO_4$), ultraviolet radiation, ozone, chlorine dioxide, hydrogen peroxide (H_2O_2), and Fenton's reagent [H_2O_2 oxidation in the presence of ferrous iron (Fe^{2+})] [5,6]. Among these oxidants, $KMnO_4$ has been receiving increased attention for the treatment of liquids, slurry soils, and sludges that contain oxidizable contaminants [7–9]. Laboratory and field studies have been conducted to determine the potential of using $KMnO_4$ for in situ remediation of organic contaminants. $KMnO_4$ is

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attractive as an in situ oxidant because of its relatively high oxidation potential ($E^0 = 1.7$ V), its ability to oxidize a variety of organic chemicals, its effectiveness over a wide range of pH, and its relatively low chemical cost [10–12]. Because oxidation reaction with MnO_4^{-1} proceed by electron transfer rather than more rapid free radical processes like Fenton's reagent, it appears amenable to application in low permeable subsurface.

Application of the in situ chemical oxidation (ISCO) to remediate chlorinated-hydrocarbon contaminated aquifer has been investigated in a variety of studies [13–15]. When $KMnO_4$ is used as the oxidant, TCE break down to CO_2, Cl^-, while MnO_4^- reduces to manganese dioxide (MnO_2) (a solid precipitate) or Mn^{2+} [16,17]. The reaction of TCE with $KMnO_4$ can be written as Eqs. (1) and (2) [18,19]. Based on Eq. (1), 1.81 g of MnO_4^- can react with 1 g of C_2HCl_3 (TCE) and produce 1.32 g of MnO_2, 0.67 g of CO_2, and 0.81 g of Cl^-. In Eq. (2), the produced Mn^{2+} would be further oxidized by MnO_4^- to form MnO_2 (Eq. (3)). Moreover, in the absence of reductants such as TCE, MnO_4^- can react with Mn^{2+} and produce MnO_2 particles. Eq. (4) shows that MnO_4^- reacts with water and produces MnO_2 in the system. Eq. (5) shows that when dibasic sodium phosphate (Na_2HPO_4) is supplied to the system, phosphate dibasic (HPO_4^{2-}) would be released [20]. The released HPO_4^{2-} reacts with Mn^{2+} and forms more soluble manganese phosphate dibasic ($MnHPO_4$). This would minimize the amount of produced MnO_2 particles and prevent the possible clogging problems.

$$2KMnO_4 + C_2HCl_3$$
$$\rightarrow 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^- \tag{1}$$

$$6KMnO_4 + 5C_2HCl_3 + 3H^+$$
$$\rightarrow 6Mn^{2+} + 10CO_2 + 6K^+ + 15Cl^- \tag{2}$$

$$2KMnO_4 + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+ \tag{3}$$

$$4MnO_4^- + 2H_2O \rightarrow 3O_2 + 4MnO_2 + 4OH^- \tag{4}$$

$$Mn^{2+} + HPO_4^{2-} \rightarrow MnHPO_4 \tag{5}$$

Based on Eq. (1), the following second-order reaction kinetics can be written:

$$\frac{d[TCE]}{dt} = -k[TCE][KMnO_4] \tag{6}$$

where [TCE] is the TCE concentration (mole/L), [$KMnO_4$] $KMnO_4$ concentration (mole/L), k is second-order rate constant ($M^{-1}s^{-1}$), and t is the reaction timeMoreover, another way to present the second-order reaction and obtain the k value follows [21–23]:

$$\frac{\ln M - X_A}{M(1 - X_A)} = (C_{B0} - C_{A0})kt \tag{7}$$

where C_{A0} is the initial TCE concentration (mole/L), C_{B0} is initial $KMnO_4$ concentration (mole/L), $M = C_{B0}/C_{A0}$, X_A is TCE

transformation rate $= (C_{A0} - C_A)/C_{A0} \times 100\%$, and C_A is the TCE concentration (mole/L)

The slope of the curve can be written as $(C_{B0} - C_{A0})k$. Previous researchers reported that the calculated k values varied from 0.64 to $0.92 M^{-1} s^{-1}$ (Juang et al., 2001; Junkeler et al., 2003). Recently, researchers have investigated oxidation of TCE by $KMnO_4$ and obtained satisfactory results. Some researchers have studied the kinetics and intermediates of the reactions between TCE and $KMnO_4$. However, little is focusing on the optimal dosage of $KMnO_4$ and effects of natural groundwater on oxidation efficiency. Thus, the principal objectives of this study were to (1) determine the optimal operational parameters [e.g., initial pH values, molar ratios of $KMnO_4$ to TCE (*P* value), TCE concentrations, natural of solutions, sediment permeability, and shaker speed (stability of the environment)] and kinetics of this ISCO system, (2) evaluate the effects of MnO_2 on the efficiency of TCE oxidation, and (3) determine the optimal operational parameter of *D* value (molar ratios of Na_2HPO_4 to Mn^{2+}) to inhibit the production of MnO_2. In this study, batch experiments were conducted to evaluate the insight into the ISCO system using $KMnO_4$ as the oxidant. Moreover, the extent of dechlorination, reaction orders, and degradation rates and kinetic behavior of TCE in reactions with permanganate were also demonstrated.

2. Study site description

Results from previous studies indicate that groundwater samples collected around a formal TCE spill site located in southern Taiwan were contaminated by TCE [24]. The detected TCE concentrations ranged from 500 µg/L to 32 mg/L in collected groundwater samples around the most contaminated area [24]. According to Taiwan's Soil and Groundwater Pollution Remediation Act [25], this TCE contaminated site needs to be remediated. Thus, efficient and effective remediation technologies are required.

The site soils are moderately acidic and well drained on low lands [26]. Results from our boring log data and grain-size distribution analysis indicate that the surficial aquifer sediments consist of yellowish-brown silty sand and light gray sandy loam with yellowish-brown mottles. Depth to the seasonal high water table is approximately 3.2 m. According to the results from hydrogeologic tests, the average hydraulic conductivity of the host geologic material is 3×10^{-5} m/s, and the groundwater slop is approximately 0.1%.

3. Materials and methods

In this study, 300-mL serum bottles (batch reactors) were used to perform the batch oxidation experiments. Each reactor capped with a Teflon-lined rubber stopper containing 150 mL of deionized (DI) water or groundwater collected from the studied aquifer. Each reactor contained: (1) a pH meter for continuous pH monitoring and (2) a three-way outlet attached on the top of the reactor for water sample collection and reagent injection.

Table 1
The objectives and operating conditions for five groups of experiments

Group	Objective	Control factor	Components	Initial conditions
1	Efficiency of TCE oxidation by $KMnO_4$	$P = 0, 2, 5, 10,$ and 20	150 mL of DI water + $KMnO_4$ + TCE	pH 6.3 TCE = 0.5, 5, 20, and 100 mg/L
2	Inhibition of MnO_2 production by Na_2HPO_4	$D = 0, 50, 100,$ and 200	150 mL of DI water or groundwater + Na_2HPO_4 + $KMnO_4$ + TCE	$P = 2$ and 20 pH 6.3 TCE = 5 mg/L
	Effect of Na_2HPO_4 addition on TCE oxidation	$D = 0$ and 300	150 mL of DI water or groundwater + Na_2HPO_4 + $KMnO_4$ + TCE	pH 6.3 $P = 2$ and 20 TCE = 5 mg/L
3	Effect of pH on MnO_2 production and TCE oxidation	pH 2.1, 6.3, and 12.5	150 mL of DI water + $KMnO_4$ + TCE	$P = 20$ TCE = 5 mg/L
4	Effects of shaker speed (stability of the environment) on TCE oxidation	Speed of shaker = 0, 50, and 200 rpm	150 mL of DI water + $KMnO_4$ + TCE	pH 6.3 $P = 20$ TCE = 5 mg/L
5	Effects of soil permeability on TCE oxidation	Sediment = silty sand, clayey silt, and silty clay	150 g of selected sediments + 150 mL of DI water + $KMnO_4$ + TCE	pH 6.3 $P = 20$ TCE = 5 mg/L

Five groups of batch experiments were performed to evaluate the variations in different controlling factors on the effectiveness of TCE oxidation. Table 1 shows the descriptions and major controlling factors of each oxidation group. The controlling factors for those five groups of batch experiments were varied (1) initial P values (0, 2, 5, 10, and 20), (2) initial D values (0, 50, 100, and 300), (3) initial pH values (pH 2.1, 6.3, and 12.5), (4) shaker speeds (0, 50, and 200 rpm), and (5) soil permeabilities (silty sand, clayey silt, and silty clay). Moreover, natural of solutions [deionized water (DI water) and groundwater] and effects of Na_2HPO_4 addition on TCE oxidation were also evaluated. Groundwater used in this study was collected from a background monitor well at the TCE contaminated site. Groundwater samples from the background monitor well were collected and analyzed quarterly during an 1 year investigation period. Collected groundwater samples were analyzed for organic compounds and geochemical indicators including TCE, inorganic nutrients, temperature, anions, pH, conductivity, redox potential (Eh), dissolved oxygen (DO), total dissolved solids (TDS), chemical oxygen demand (COD), and total organic carbon (TOC). Ion chromatography (Dionex) was used for inorganic nutrients and anions ($NH_3, Cl^-, NO_3^-, NO_2^-, CO_3^{-2}, HCO_3^-$, and SO_4^{-2}) analyses. TOC was analyzed by a Total Carbon Analyzer (Shimadzu). DO, Eh, pH, CO_2, and temperature were measured in the field. An Accumet 1003 pH/Eh meter (Fisher Scientific) was used for pH and Eh measurements, an Orion DO meter (Model 840) was used for DO measurements. Analyses were performed following the methods described in Standard Methods [27]. TCE analyses were performed in accordance with U.S. EPA Method 601, using a Tekmer Purge-and-Trap Model LSC 2000 with a Varian Model 3800 Gas Chromatograph (GC).

All experiments were operated in a shaker (Wisdom Orbital Shaker, OS-72, US) with a predetermined shaking speed. The ambient temperature was controlled at 25 °C. The main objective and operating conditions for each group of experiments were described in Table 1. In the soil permeability experiments, 150 g of selected sediments [one of those three sediment (silty sand, clayey silt, or silty clay)] were added into the serum bottles to evaluate the effects of sediments on oxidation efficiency. The initial pH in each reactor was adjusted by adding H_2SO_4 and NaOH in the solution. Three subsamples were collected at each time point and analyzed for TCE concentrations. At the end of the batch experiment, sodium thiosulfate ($Na_2S_2O_3$) was added into the reactor to terminate the oxidation experiments to obtain representative TCE concentrations. Selected samples were analyzed for the possible degradation by-products using GC/MS. The GC/MS was operated with the computer system MS ChemStation (HP) following the procedures described in Susarla et al. [28]. Chloride ion was analyzed by chloride ion meter (Inolab, pH/ION Level 2, US). Before the addition of sodium thiosulfate, collected samples were analyzed for the concentrations of MnO_4^- and MnO_2 in the dissolved phases. Because dissolved MnO_2 can be detected at both 526 and 418 nm, and MnO_4^- can be detected at 526 nm. Thus, concentrations of MnO_4^- and MnO_2 were analyzed by spectrophotometer (Hach, CR/4000U, US) at 526 and 418 nm, respectively [21,27,29].

4. Results and discussion

4.1. Effects of P value on TCE oxidation (Group 1)

From Eqs. (1)–(4), optimal amount of $KMnO_4$ is a necessity to reach the complete TCE oxidation and least MnO_2 production. Thus, optimal P value plays an important role in the improvement of the effectiveness of $KMnO_4$ oxidation. In this group of batch experiment, five different P values (molar ratios of $KMnO_4$ to TCE) (0, 2, 5, 10, and 20) and four different initial TCE concentrations (0.5, 5, 20, and 100 mg/L) were evaluated for the effects of P values on TCE removal efficiency when DI water was used and initial pH was 6.3. Fig. 1a–d show the percentage of TCE remaining (C/C_0 = remaining TCE concentration/initial TCE concentration) after oxidation under the conditions of varied P values with initial TCE concentrations of 0.5, 5, 20, and 100 mg/L, respectively. Although stoichiometry equations (Eqs. (1)–(3)) show that the P value must be greater than two to completely oxidize TCE to non-toxic end products, much higher P values are required to proceed the oxidation process. Results show that the percentage of TCE remaining (C/C_0) were 0.96, 0.92, 0.81, 0.63, and 0.42 when P values were 0, 2, 5, 10, and 20, respectively at the reaction time of 240 min and C_0 of 0.5 mg/L. Results indicate that the higher the P value, the higher the TCE removal efficiency. Thus, the highest TCE removal efficiency was observed at P value of 20. When C_0 equaled 5 mg/L and reaction time was 240 min, the percentage of TCE remaining was 0.95, 0.49, 0.15, 0.02, and 0.02 when P values were 0, 2, 5, 10, and 20, respectively. When C_0 equaled 20 mg/L and reaction

time was 240 min, the percentage of TCE remaining was 0.96, 0.3, 0.02, 0.002, and 0.002 when P values were 0, 2, 5, 10, and 20, respectively. When C_0 equaled 100 mg/L and reaction time was 240 min, the percentage of TCE remaining was 0.95, 0.24, 0.002, 0.002, and 0.001 when P values were 0, 2, 5, 10, and 20, respectively. Thus, the optimal P value was 10 when C_0 was approximately 5 and 20 mg/L, and the P value was close to 5 at C_0 equaled 100 mg/L. This indicates that the amount of $KMnO_4$ used to oxidize TCE would be close to the theoretical P value based on the stoichiometry equation at the source of the TCE spill location (DNAPL zone) or when extremely high TCE concentration (100 mg/L) was observed. However, higher P value is required when the treatment zone contains lower level of TCE concentration.

Fig. 2a and b present the efficiency of oxidation $[\ln(M - X_A/M(1 - X_A))]$ versus time under the conditions of varied P values with initial TCE concentration of 0.5 and 5 mg/L, respectively. Based on Eq. (7), the calculated second-order reaction rate was $0.8\,M^{-1}\,s^{-1}$, and the estimated efficiency curve $[\ln(M - X_A/M(1 - X_A))$ versus time] matched very well with the observed data. Moreover, the calculated second-order reaction rate ($0.8\,M^{-1}\,s^{-1}$) was close to the k values (0.64–$0.92\,M^{-1}\,s^{-1}$) reported by other researchers [17,21]. In Fig. 2b, the estimated efficiency curve with k value of $0.8\,M^{-1}\,s^{-1}$ also had a good match with the observed data. Fig. 2c and d present the efficiency of oxidation $[\ln(M - X_A/M(1 - X_A))$ versus time] under the conditions of varied P values with initial TCE concentration of 20 and 100 mg/L, respectively. Results indicate that the estimated efficiency curve with k value of $0.8\,M^{-1}\,s^{-1}$ did not
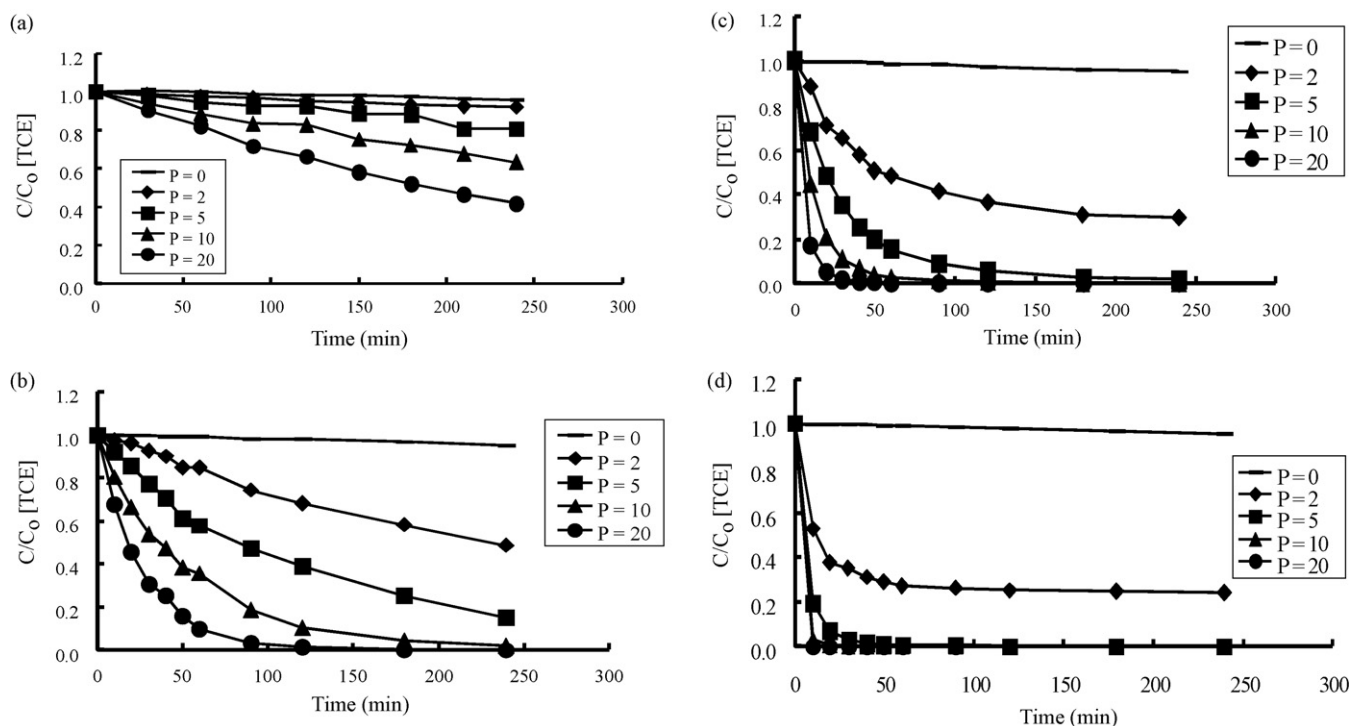

Fig. 1. (a) Percentage of TCE remaining vs. time under the conditions of varied P values with initial TCE concentration of 0.5 mg/L. (b) Percentage of TCE remaining vs. time under the conditions of varied P values with initial TCE concentration of 5 mg/L. (c) Percentage of TCE remaining vs. time under the conditions of varied P values with initial TCE concentration of 20 mg/L. (d) Percentage of TCE remaining vs. time under the conditions of varied P values with initial TCE concentration of 100 mg/L.
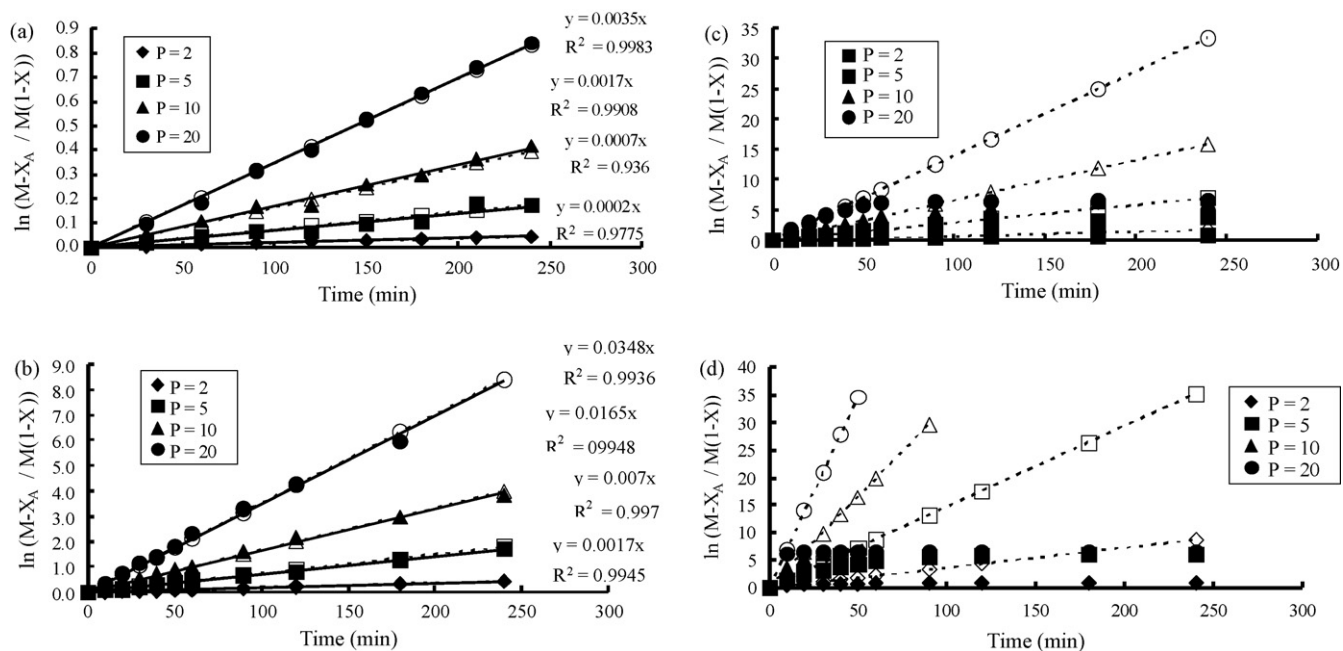
Fig. 2. (a) Efficiency of oxidation vs. time under the conditions of varied P values with initial TCE concentration of 0.5 mg/L. (b) Efficiency of oxidation vs. time under the conditions of varied P values with initial TCE concentration of 5 mg/L. (c) Efficiency of oxidation vs. time under the conditions of varied P values with initial TCE concentration of 20 mg/L. (d) Efficiency of oxidation vs. time under the conditions of varied P values with initial TCE concentration of 100 mg/L.

Table 2
Calculated second-order reaction rates with varied P values

TCE (mg/L)	$P = 2$	$P = 5$	$P = 10$	$P = 20$
0.5	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$
5	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$	$0.8\,M^{-1}\,s^{-1}$
20	$0.8\,M^{-1}\,s^{-1}$ (within 30 min of reaction time)	$0.8\,M^{-1}\,s^{-1}$ (within 30 min of reaction time)	$0.8\,M^{-1}\,s^{-1}$ (within 30 min of reaction time)	$0.8\,M^{-1}\,s^{-1}$ (within 30 min of reaction time)
100	NA[a]	NA	NA	NA

[a] The extra high initial TCE concentrations (20 and 100 mg/L) might cause the high reaction rate within a short period of time, and thus, the second-order mechanism could not fit the reaction.

match well with the observed data. The extra high initial TCE concentrations (20 and 100 mg/L) might cause the high reaction rate within a short period of time, and thus, second-order mechanism could not fit the reaction mechanisms. Table 2 presents the calculated second-order reaction rates with varied P values.

4.2. Effects of D value on TCE oxidation, MnO₂ production, and KMnO₄ depletion (Group 2)

From Eq. (5), the addition of HPO_4^{2-} would minimize the amount of produced MnO_2 particles and prevent the clogging of subsurface environment. Thus, Na_2HPO_4 was added and the effects of D value on the production of MnO_2 and effectiveness of TCE oxidation by $KMnO_4$ was evaluated in this group of experiment. Fig. 3 presents the produced MnO_2 (absorbance at 418 nm) with varied P (2 and 20) and D (0, 50, 100, and 200) values with the initial pH and TCE concentration of 6.3 and 5 mg/L, respectively in DI water solution. Results show that more MnO_2 was produced when D value was 0 with P values of 2 and 20. This indicates that the addition of Na_2HPO_4 is able to minimize the amount of produced MnO_2. Moreover, P value of

20 produced more MnO_2 than P value of 2 with D value of 0. This reveals that higher P value caused higher oxidation potential, released more Mn^{2+}, and thus, produced more MnO_2. Fig. 4 shows the percentage of inhibited MnO_2 production (compared
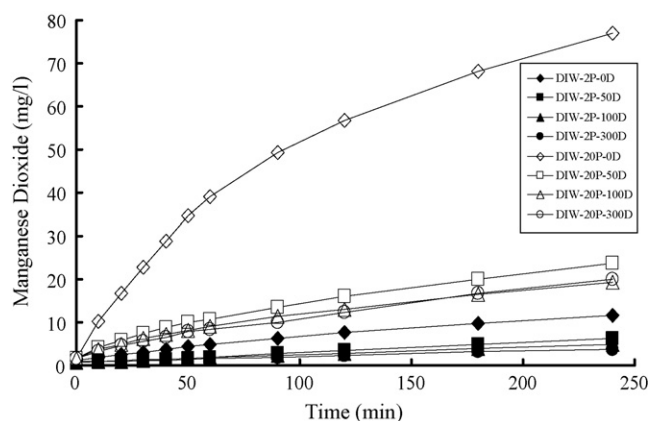

Fig. 3. Produced MnO_2 vs. time under the conditions of varied P and D values at the initial pH of 6.3 and TCE concentration of 5 mg/L in DI water solution.
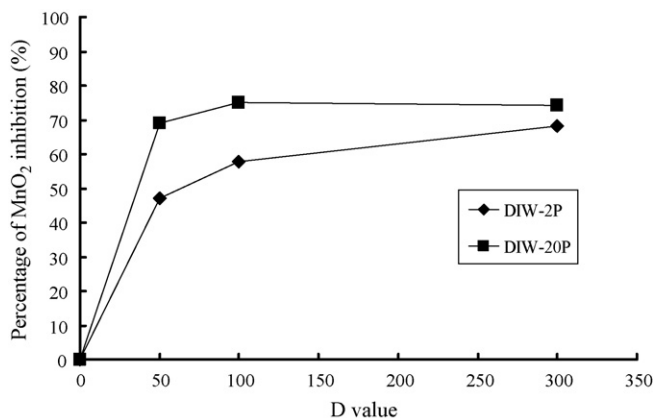
Fig. 4. Percentage of inhibited MnO_2 production under varied D values with P values of 2 and 20 at 240 min of reaction time.

with the MnO_2 produced at $D = 0$) under varied D values with P values of 2 and 20 at 240 min of reaction time. Results reveal that the percentage of inhibited MnO_2 production ranged from 69 to 75% and 47 to 68% when P values were 20 and 2, respectively. Results show that the percentage of MnO_2 reduction could reach 75% at D and P values of 100 and 20, respectively. Results indicate that significant amount of MnO_2 reduction could be obtained with the addition of Na_2HPO_4.

Fig. 5a and b show the percentage of TCE remaining after oxidation with (D value = 300) and without (D value = 0) the addition of Na_2HPO_4 with P values of 2 and 20, respectively when DI water or site groundwater was used as the solution.
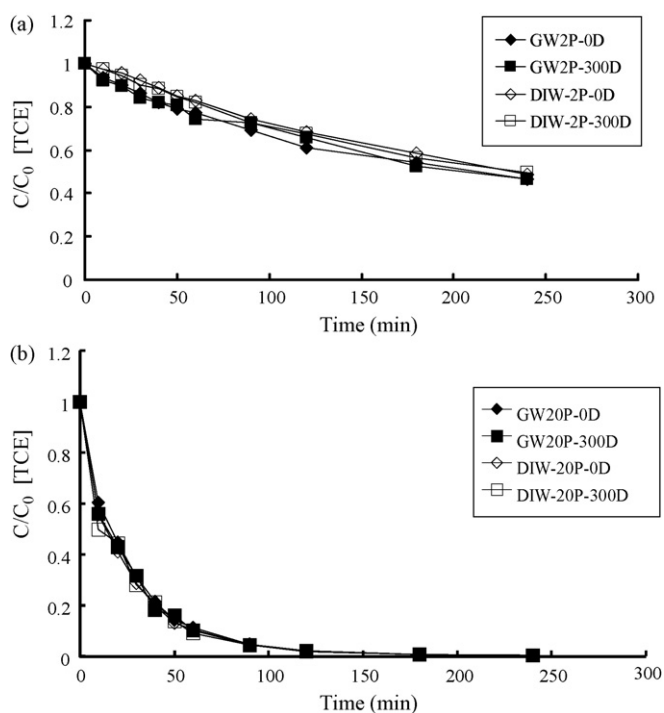

Fig. 5. (a) Efficiencies of TCE oxidation with (D value = 300) and without (D value = 0) the addition of Na_2HPO_4 at P value of 2 using DI water or groundwater as the solution. (b) Efficiencies of TCE oxidation with (D value = 300) and without (D value = 0) the addition of Na_2HPO_4 at P value of 20 using DI water or groundwater as the solution.

Table 3
Analytical results of the site groundwater

Item	Unit	Result
Temperature	°C	26.5
pH		6.3
Conductivity	μS/cm	164
DO	mg/L	3.80
Eh	mV	304
TDS	mg/L	62.0
TOC	mg/L	2.06
COD	mg/L	3.2
TCE	mg/L	ND
Chloride	mg/L	2.11
Nitrate	mg/L	6.218
Nitrite	mg/L	ND
Sulfate	mg/L	20.0
Carbonate	$mgCaCO_3$/L	0.004
Bicarbonate	$mgCaCO_3$/L	23.6
Ammonia	mg/L	2.5

ND: not detectable.

Results reveal that either the addition of Na_2HPO_4 or the characteristics of the solution (DI water or groundwater) had no significant effects on the efficiency of TCE removal. Table 3 presents the averaged analytical results of the site groundwater from four sampling events. Although groundwater used in this study contained some natural organic matter (TOC = 3 mg/L) (Table 3), the organics might be mainly humic substances, which were not easily oxidized using $KMnO_4$ as the oxidant compared with TCE. Thus, extra consumption of $KMnO_4$ might not occur at this TCE contaminated site.

Fig. 6 presents the produced MnO_2 (absorbance at 418 nm) with varied P (2 and 20) and D (0, 50, 100, and 200) values with the initial pH and TCE concentration of 6.3 and 5 mg/L, respectively using groundwater as the solution. Results show that the patterns of MnO_2 production with D value of 0 (P values of 2 and 20) leveled off after 50 min of reaction compared with the patterns in Fig. 3. However, oxidation results show that the efficiency of TCE removal were very close in experiments using DI water and groundwater as the solutions (Fig. 5a and b). This was due to the precipitation of black MnO_2 particles in experiments with groundwater as the solution without Na_2HPO_4 addition (D value = 0), which caused less absorbance value in this experiment. The following two hypotheses are
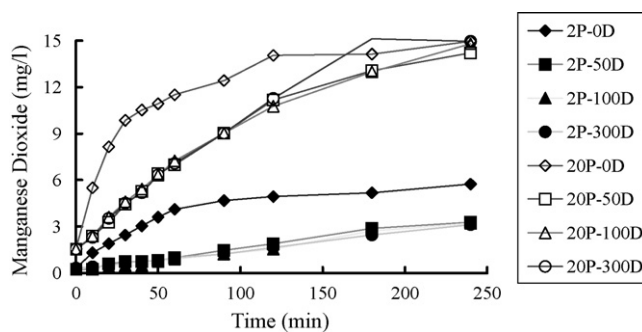

Fig. 6. Produced MnO_2 with varied P (2 and 20) and D (0, 50, 100, and 200) values with at initial pH of 6.3 and TCE concentration of 5 mg/L using groundwater as the solution.

Table 4
The observed and theoretical chloride ion concentrations in DI water solution for experiments with varied *P* and *D* values

| *P* value	Cl⁻ (mg/L)							
	0.5[a]		5[a]		20[a]		100[a]	
	Theoretical value	Observed value	Theoretical value	Observed value	Theoretical value	Observed value	Theoretical value	Observed value
0	0	0	0	0	0	0	0	0
2	0.03	0.03	2.06	2.00	11.2	9.45	62.7	57.8
5	0.09	0.08	3.40	3.06	15.7	14.1	79.8	71.7
10	0.14	0.12	3.92	3.55	16.0	14.7	79.8	72.3
20	0.24	0.21	3.99	3.68	16.0	14.8	79.8	72.3

[a] TCE (mg/L).

proposed for the formation of black MnO_2 particles: (1) the electrical repulsion force between the produced MnO_2 colloids would be destroyed due to the occurrence of the coagulation between the natural minerals (electrolytes) in groundwater (electric conductivity = 164 μS/cm) (Table 3) and MnO_2 and (2) occurrence of common ion effect, which was due to the existence of natural Mn^{2+} (0.08 mg/L) in groundwater.

Because the formation of black MnO_2 particles in the experiments using groundwater as the solution, the absorbance value of MnO_2 with *D* value of 0 in DI water experiment (Fig. 3) was used as the control to calculate the percentage of inhibited MnO_2 production. Results reveal that the percentage of inhibited MnO_2 production ranged from 81 to 82% and 72 to 73% when *P* values were 20 and 2, respectively. Compared to the results obtained in the DI water experiments, higher percentage of inhibited MnO_2 production was observed. The detected anions (Table 3) in natural groundwater might react with produced Mn^{2+}, and caused the decreased MnO_2 production.

Table 4 presents the observed and theoretical chloride ion concentrations in DI water for experiments with varied *P* and *D* values. Based on Eqs. (1) and (2), oxidation of 1 mM of TCE would produce 3 mM of chloride ion. Results reveal that the observed chloride concentrations were very close to the theoretical values. This indicates that all injected TCE in the reactors was oxidized completely, and this was confirmed by TCE results (data not shown).

4.3. Effects of pH value on TCE oxidation, MnO_2 production, and $KMnO_4$ depletion (Group 3)

Fig. 7a presents the effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the production of MnO_2 with the initial TCE concentration of 5 mg/L and *P* value of 20 in DI water. Results indicate that more MnO_2 was produced in experiments with pH of 12.5 than pH of 6.3 during the earlier reaction period (0–90 min). After 90 min of reaction, less MnO_2 was observed due to the precipitation of MnO_2 particles. Results from other study also indicate that MnO_4^- would be reduced to MnO_2 under higher pH conditions [13]. This can be expressed as the following equation:

$$MnO_4^- + 3e^- + 2H_2O = MnO_2 + 4OH^- \quad pH3.5–12 \quad (8)$$
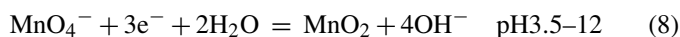
The reaction direction of the above equation is affected by several factors including pH, oxidation–reduction potential, and
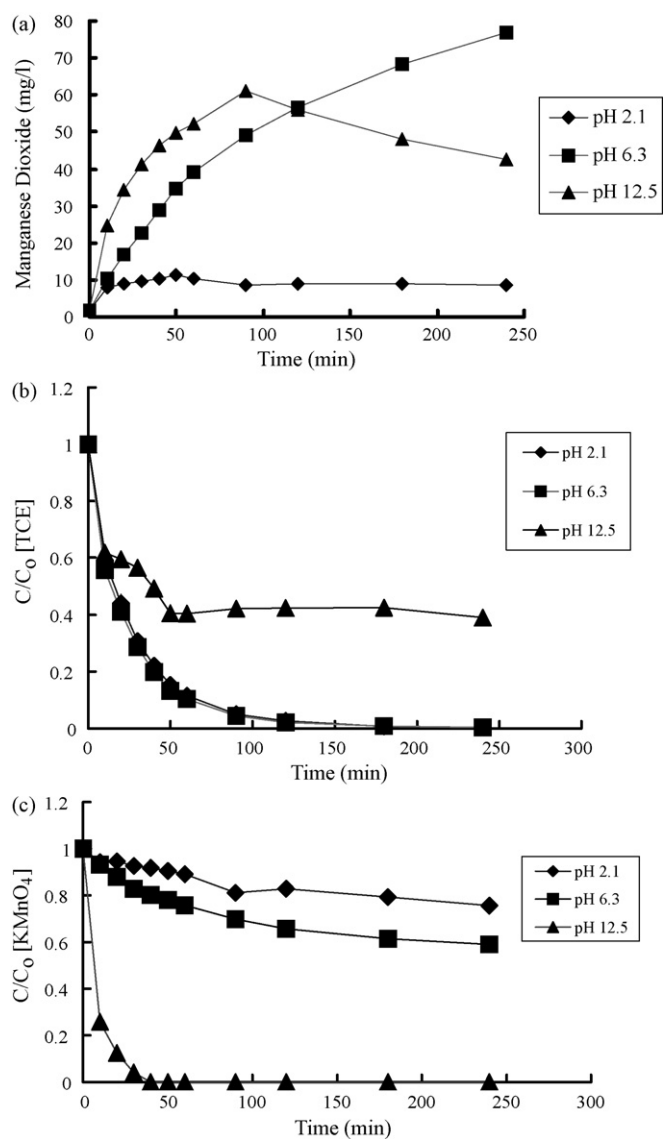

Fig. 7. (a) Effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the production of MnO_2 with the initial TCE concentration of 5 mg/L and *P* value of 20 in DI water solution. (b) Effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the efficiency of TCE removal with the initial TCE concentration of 5 mg/L and *P* value of 20 in DI water solution. (c) Effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the consumption of $KMnO_4$ with the initial TCE concentration of 5 mg/L and *P* value of 20 in DI water solution.

concentrations of MnO_4^- and MnO_2. Because redox potential value in normal environmental conditions is usually in the range between 0.5 and $-0.5\,V$, MnO_4^- would be reduced to MnO_2 under higher pH conditions [13,30]. Results from Fig. 7a also show that less MnO_2 was produced in experiments with lower initial pH value (pH 2.1). This might be due to the effect that MnO_4^- was reduced to soluble Mn^{2+} under lower pH conditions [13]. This can be expressed as the following equation:

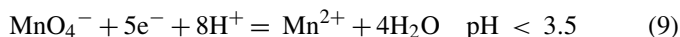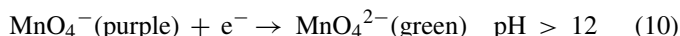$$MnO_4^- + 5e^- + 8H^+ = Mn^{2+} + 4H_2O \quad pH < 3.5 \quad (9)$$

Fig. 7b presents the effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the percentage of TCE remaining with the initial TCE concentration of 5 mg/L and P value of 20. Results indicate that lower TCE removal efficiency was observed in experiments with high pH value (pH 12.5). Furthermore, complete TCE removal was observed in experiments with pH values of 2.1 and 6.3, and the TCE degradation trends were very similar in both pH conditions (Fig. 7b). Researchers [22] described that MnO_4^- would be reduced to MnO_4^{2-} under high pH conditions, and this can be expressed as the following equation:

$$MnO_4^-(purple) + e^- \rightarrow MnO_4^{2-}(green) \quad pH > 12 \quad (10)$$

The formation of MnO_4^{2-} can be confirmed by the occurrence of green color in the solution at the beginning of the experiment. Reduction of MnO_4^- to MnO_4^{2-} would cause the reduced oxidation power and decreased TCE removal efficiency.

Fig. 7c presents the effects of varied initial pH values (pH 2.1, 6.3, and 12.5) on the consumption of $KMnO_4$ (percentage of remaining $KMnO_4$) with the initial TCE concentration of 5 mg/L and P value of 20. Results indicate that complete consumption of MnO_4^- was observed at high pH condition (pH 12.5) within 45 min of reaction. This was due to the reduction of MnO_4^- to MnO_4^{2-} at high pH condition (Eq. (10)). This can also be confirmed by the decreased TCE removal efficiency (Fig. 6). Compared to low pH condition (pH 2.1), more $KMnO_4$ consumption was observed in experiments with pH 6.3. Because the produced Mn^{2+} from the reduction of $KMnO_4$ would be further oxidized by MnO_4^- to form MnO_2 (Eqs. (2) and (3)), more $KMnO_4$ would be consumed in experiments with pH 6.3. However, only Mn^{2+} could exist in low pH conditions (pH 2.1) [30], and thus, Mn^{2+} could not be further oxidized to MnO_2 in experiments with pH 2.1. This caused the higher remaining of $KMnO_4$ in the low pH (pH 2.1) experiments.

4.4. Effects of shaker speed and soil permeability on TCE oxidation (Groups 4 and 5)

Fig. 8 presents the effects of varied shaker speeds (0, 50, and 200 rpm) on the efficiency of TCE oxidation with the initial TCE concentration of 5 mg/L and P value of 20 in DI water solution. Results show that shaker speed had no significant effect on the efficiency of TCE removal. This indicates that $KMnO_4$ had a very effective dispersion and diffusion ability in the reactor without the provision of mixing power. Results also reveal that groundwater recirculation system (e.g., pump-and-treat) might not be a necessity to enhance
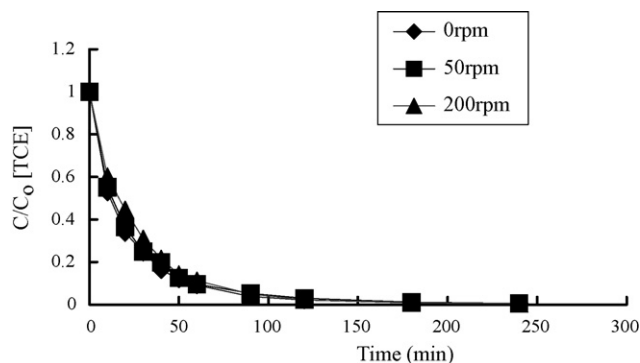

Fig. 8. Effects of varied shaker speeds (0, 50, and 200 rpm) on the efficiency of TCE oxidation with the initial TCE concentration of 5 mg/L and P value of 20 in DI water solution.
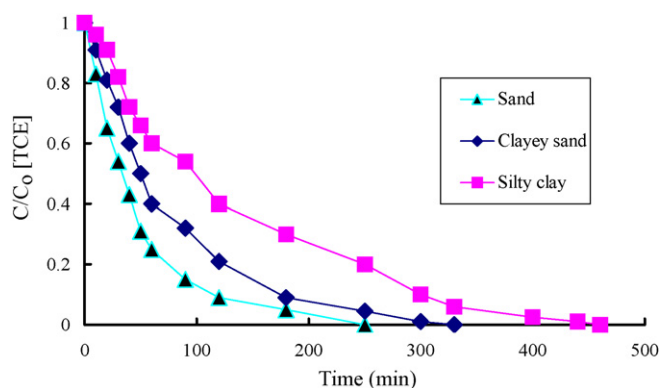

Fig. 9. Effects of soil permeability on the efficiency of TCE oxidation with the initial TCE concentration of 5 mg/L and P value of 20 in DI water solution.

the oxidation efficiency of TCE on site using $KMnO_4$ as the oxidant.

To evaluate the effects of soil permeability on TCE oxidation, three different sediments (silty sand, clayey sand, and silty clay) were used in this test (Table 1). Fig. 9 presents the effects of soil permeability on the efficiency of TCE oxidation with the initial TCE concentration of 5 mg/L and P value of 20. Results show that the reaction time of complete TCE removal for tests containing silty sand, clayey sand, and silty clay were 250, 330, and 460 min, respectively (Fig. 9). Although more reaction time is required for tests containing less permeable sediment materials, complete TCE oxidation can still be obtained. Results reveal that $KMnO_4$ is a more stable and dispersive oxidant, which is able to disperse into the sediment materials and react with organic contaminants effectively.

5. Conclusions

Conclusions regarding the TCE oxidation efficiency include the following: (1) The second-order kinetics can be applied to estimate the efficiency of oxidation when the initial TCE concentration is less than 20 mg/L. The calculated overall reaction rate is 0.8 $M^{-1}s^{-1}$. (2) Higher P values would cause higher TCE oxidation rates under the same initial TCE concentration conditions. Conclusions of the MnO_2 production and inhibition (P value effect) include the following: (1) MnO_4^- would be

reduced to MnO_2 or Mn^{2+} depending on the pH conditions. More MnO_2 would be produced under alkaline conditions. (2) Higher P values would cause more MnO_2 production under the same reaction time conditions. (3) Addition of Na_2HPO_4 would minimize the amount of $KMnO_4$ usage and minimize the amount of MnO_2 production without the decrease in TCE oxidation rate. (4) Higher D values would cause more significant inhibition of MnO_2 production under the same initial TCE concentration conditions. Conclusions of pH on TCE oxidation and MnO_2 production include the following: (1) less MnO_2 was produced under the low initial pH conditions (pH 2.1). (2) Under high initial pH condition (pH 12.5), $KMnO_4$ would be reduced to MnO_2, and thus, TCE oxidation efficiency would decrease due to the consumption of $KMnO_4$.

This performance study provides us insight into the characteristics and kinetics of TCE oxidation by $KMnO_4$ under different controlled conditions. These findings would be helpful in designing a practical in situ groundwater remediation system to remediate TCE-contaminated groundwater using $KMnO_4$ as the oxidant.

Acknowledgements

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