



Evaluation of the kinetic oxidation of aqueous volatile organic compounds by permanganate



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HIGHLIGHTS

- Oxidation of chlorinated and non-chlorinated VOCs in aqueous phase by permanganate was investigated.
- A second-order kinetic model simulated the oxidation process of TCE, toluene, and ethanol.
- Errors in k due to the inappropriate use of the pseudo first-order model were discussed.

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ABSTRACT

The use of permanganate solutions for in-situ chemical oxidation (ISCO) is a well-established groundwater remediation technology, particularly for targeting chlorinated ethenes. The kinetics of oxidation reactions is an important ISCO remediation design aspect that affects the efficiency and oxidant persistence. The overall rate of the ISCO reaction between oxidant and contaminant is typically described using a second-order kinetic model while the second-order rate constant is determined experimentally by means of a pseudo first order approach. However, earlier studies of chlorinated hydrocarbons have yielded a wide range of values for the second-order rate constants. Also, there is limited insight in the kinetics of permanganate reactions with fuel-derived groundwater contaminants such as toluene and ethanol. In this study, batch experiments were carried out to investigate and compare the oxidation kinetics of aqueous trichloroethylene (TCE), ethanol, and toluene in an aqueous potassium permanganate solution. The overall second-order rate constants were determined directly by fitting a second-order model to the data, instead of typically using the pseudo-first-order approach. The second-order reaction rate constants ($M^{-1} s^{-1}$) for TCE, toluene, and ethanol were 8.0×10^{-1} , 2.5×10^{-4} , and 6.5×10^{-4} , respectively. Results showed that the inappropriate use of the pseudo-first-order approach in several previous studies produced biased estimates of the second-order rate constants. In our study, this error was expressed as a function of the extent (P/N) in which the reactant concentrations deviated from the stoichiometric ratio of each oxidation reaction. The error associated with the inappropriate use of the pseudo-first-order approach is negatively correlated with the P/N ratio and reached up to 25% of the estimated second-order rate constant in some previous studies of TCE oxidation. Based on our results, a similar relation is valid for the other volatile organic compounds studied.

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1. Introduction

Groundwater contamination with volatile organic compounds (VOCs) is a major environmental problem at sites (formerly) occupied by large-scale chemical industries or small scale users such as dry-cleaners or fuel stations (Rivett et al., 2011; Schubert et al., 2011). These compounds are also present in some household products and automobile liquids (Berscheid et al., 2010). VOCs are groundwater contaminants of widespread concern because of (1) very large volumes

that are sometimes released into the environment, (2) their toxicity, and (3) the fact that some VOCs, once they have reached groundwater, tend to persist and migrate to drinking water wells or upward by diffusion through the unsaturated zone to indoor spaces. Exposure to some VOCs may cause damage to the central nervous system and internal organs and may lead to symptoms such as headache, respiratory tract irritation, dizziness and nausea, known as the Sick Building Syndrome (Yu and Lee, 2007).

Of the different VOCs present, we selected for our study TCE, toluene, and ethanol as the model VOCs (target compounds) for chlorinated solvents, mineral oil, and biofuel, respectively. TCE has been widely used as a dry cleaning solvent, degreasing product and chemical extraction

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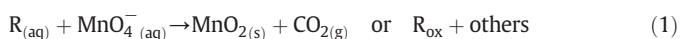
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agent. Inappropriate TCE disposal has produced widespread groundwater contamination. Since TCE is carcinogenic, its movement from contaminated groundwater and soil into the indoor air of overlying buildings is a serious concern (EPA, 2011). Similarly, toluene, an additive to improve the octane number of gasoline, is one of the main organic compounds found frequently in indoor environments. Toluene is listed as one of the six major classes of indoor VOCs (aromatic, aldehyde, alkane, ketone, alcohol, and chlorocarbon) (Yu and Lee, 2007). Exposure to toluene may cause irritation of the eye, nasal and mucous membranes, and the respiratory tract (Yu and Lee, 2007).

More recently, ethanol is being used increasingly in (renewable) fuel alternatives and as a replacement for methyl tertiary-butyl ether (MTBE), which, despite helping to accomplish Clean Air Act goals, has caused widespread water contamination (Capiro et al., 2007; Johnson et al., 2000). Also, the presence of ethanol in groundwater can reduce the biodegradation rates of benzene, toluene, ethylbenzene, and xylene isomers (BTEX) in groundwater and soil (Freitas et al., 2010; Mackay et al., 2007). Extended exposure to ethanol can damage liver, kidneys, and the central nervous system (Yu and Lee, 2007). A need hence exists to improve our understanding of the oxidation and fate of ethanol in contaminated groundwater.

In-situ chemical oxidation (ISCO) is one of the technologies available for in-situ remediation of VOC-contaminated groundwater. Chemical oxidation technology is a potent soil remedial option that can effectively eliminate an extensive range of VOCs (Yen et al., 2011). The oxidizing agents most commonly used for the treatment of hazardous contaminants are permanganate, ozone, hydrogen peroxide, and Fenton's reagent. Of these oxidants, potassium permanganate has received much attention for the treatment of liquid, slurry soils, and sludges polluted with VOCs. Potassium permanganate is often used as an ISCO agent for the following five reasons: (1) its oxidation potential ($E_0 = 0.5\text{--}1.7\text{ V}$), (2) its ability to oxidize a variety of organic chemicals (Powers et al., 2001; Siegrist et al., 2001; Struse et al., 2002; Mumford et al., 2004; Hønning et al., 2005; Mumford et al., 2005; Urynowicz, 2008), (3) its effectiveness over a wide range of pH values, (4) its relatively low cost, and (5) its significantly higher stability in the subsurface as compared to other chemical oxidants (Bryant et al., 2001; Huang et al., 1999).

Depending upon the soil matrix and groundwater composition, permanganate in an aquifer may be stable for as long as several weeks (Cave et al., 2007; Siegrist et al., 2001). The injection of dissolved potassium permanganate into plumes to remediate contaminated groundwater has been used for the in-situ treatment of chlorinated hydrocarbons (Damma et al., 2002). Moreover, since oxidation reactions with permanganate proceed by electron transfer rather than more rapid free radical processes, as with Fenton's reagent, potassium permanganate appears amenable to application in low permeability soils (Kao et al., 2008). Permanganate reacts with organic compounds to produce manganese dioxide (MnO_2) as well as carbon dioxide (CO_2) or intermediate organic compounds (Yin and Herbert, 1999) of the form:

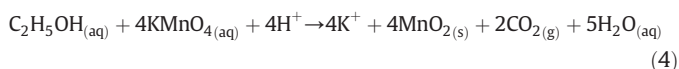
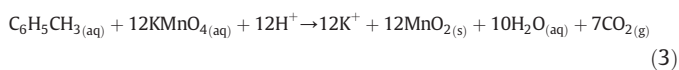


where R denotes an organic contaminant and R_{ox} is an oxidized intermediate organic compound.

A number of processes such as cleaving, hydroxylation, and hydrolysis lead to the production of intermediates and eventually to carbon dioxide and water. The permanganate ion is especially useful in oxidizing organics that have carbon-carbon single and double bonds (for example, chlorinated ethylenes, aldehyde groups, or hydroxyl groups) (Lee et al., 2003).

The full oxidation of TCE, toluene, and ethanol by permanganate follows Eqs. (2) to (4), respectively. Permanganate breaks down TCE to CO_2 and Cl^- , while ethanol and toluene are transformed into CO_2 and H_2O . In all reactions, MnO_4^- reduces to manganese dioxide which is a solid precipitate at circumneutral pH values. Moreover, in the absence

of reductants, permanganate can react with water and produce manganese dioxide particles (Kao et al., 2008) as given by Eq. (5). However, this reaction typically takes place at very low rates.



For the design and monitoring of an ISCO remediation approach, the kinetics of oxidation reactions is an important aspect that may affect the efficiency and oxidant persistence. ISCO using potassium permanganate solution is a well-established remediation technology, particularly for targeting chlorinated ethenes (Huang et al., 2001; Urynowicz, 2008; Waldemer and Tratnyek, 2006). However, the earlier studies of chlorinated ethenes have yielded a wide range for the estimated second-order rate constants. In large part these estimates were derived using the pseudo-first order experimental approach that requires one of the reactants to be present in significant excess (Huang et al., 2001; Siegrist et al., 2001; Urynowicz, 2008; Waldemer and Tratnyek, 2006). Also, there is still limited insight in the kinetics of permanganate reactions with fuel-derived VOC groundwater contaminants such as toluene (Rudakov and Lobachev, 2000; Waldemer and Tratnyek, 2006) and ethanol (Barter and Littler, 1967). In this study we therefore determined kinetic parameters for the oxidation of three dissolved VOCs (TCE, toluene and ethanol) by permanganate. For this purpose we performed a series of batch experiments with three objectives: (1) to determine the oxidation kinetic parameters of TCE, toluene, and ethanol by aqueous permanganate, (2) to establish a suitable kinetic reaction rate model, and (3) to estimate errors caused by the inappropriate use of the pseudo first-order model.

2. Materials and methods

2.1. Materials

Chemicals used in this study included TCE, ethanol, and toluene (99% purity, Sigma-Aldrich, Merck and ACROS, respectively), potassium permanganate (99% purity, Sigma-Aldrich), sodium bicarbonate (99.7% purity, Merck), ammonium chloride (99.8% purity, Merck) and oxalic acid (99% purity, Merck). Stock solutions of aqueous-phase TCE, ethanol, and toluene were individually prepared in 2-liter glass vessels by dissolving the chemicals in deionized (DI) water. The vessels were vigorously shaken and allowed to equilibrate overnight. Then, they were preserved at 8 °C for further use. Potassium permanganate solutions of desired concentrations were prepared by dissolving solid potassium permanganate in DI water. To prevent the photodecomposition of permanganate, the stock solutions were covered by aluminum foil.

Two separate buffer solutions of pH 9.0 and 6.0 were prepared. This was performed by adding the required amounts of either sodium bicarbonate (for the pH of 9.0) or ammonium chloride (for the pH of 6.0) to DI water. A solution of oxalic acid was prepared by dissolving an appropriate amount of oxalic acid in DI water.

2.2. Sampling and analyses

During the batch experiments, aqueous samples of 1.5 ml were periodically taken from the kinetic (including both reactant) and control batches using a 2.5 ml gas tight syringe (SGE Analytical Science, Australia). The aqueous sample was injected to a 10-ml transparent

glass vial. 100 μ l of oxalic acid (0.5 M) was immediately added to each sample to prevent any further oxidation of the VOC compounds. Then, the sample was capped with a magnetic cap and hard septum (Magnetic Bitemall; Red lacquered, 8 mm center hole; Pharma-Fix-Septa, Silicone blue/PTFE gray; Grace Alltech). Batches were sampled until no detectable VOC concentration was found in the kinetic batches.

Concentrations of the target compounds were measured with a gas chromatograph (GC). The GC (Agilent 6850) was equipped with flame ionization detector (FID) and separation was done on an Agilent HP-1 capillary column (stationary phase: 100% dimethylpolysiloxane, length: 30 m, ID: 0.32 mm, film thickness: 0.25 μ m). A temperature programmed run was used to analyze the samples. The concentration of VOC compounds was determined using a headspace method as used in previous studies (e.g. Almeida and Boas, 2004; Przyjazny and Kokosa, 2002; Sieg et al., 2008; Snow, 2002). The limits of quantification (LOQ) were calculated by using a signal-to-noise ratio of 10:1 (Kubinec et al., 2005).

To measure the concentration of permanganate, the samples were diluted immediately after collection and centrifuged (Heraeus/Kendro Biofuge) for 4 min at 13,000 rpm to settle suspended manganese dioxide particles. The aqueous concentration of permanganate was measured subsequently using a UV-Spectrophotometer (UV-1800, Shimadzu) at a wavelength of 525 nm. TCE oxidation was also monitored by measuring the production of chloride. Chloride concentrations were determined by ion chromatography (e.g. He and Zhao, 2005; Huang et al., 1999; Morales et al., 2000; Tyrrell et al., 2009). The ion chromatograph (Dionex DX-120) was equipped with a 4-mm Dionex IonPac™ AS22 capillary column. During the experiments, acidity was measured using a pH meter (HANNA, HI 8314).

2.3. Experimental and simulation procedure

The oxidation of target compounds with potassium permanganate was investigated in 120-ml glass vial reactors at room temperature (21 ± 1 °C). All experiments were carried out using a basic orbital laboratory shaker (IKA KS 260 B). The experiments were conducted using different combinations of the initial concentrations of the target compounds and potassium permanganate (Table 1). For two experiments, the initial concentration of the potassium permanganate was identical, while the initial concentration of the target compounds was different. For two other experiments, the initial concentration of permanganate was different, but with identical initial concentration of the target compounds.

We also prepared a series of control batches containing stock solutions of either the VOC or potassium permanganate. Control experiments were performed for each compound under identical conditions to ensure that the loss of target compound or permanganate due to

reaction with water, photodecomposition or adsorption to the rubber stopper was negligible over the course of the experiments.

Additional experiments for each compound were performed with the pH buffer to determine the effect of pH on the kinetics of oxidation of target compounds by permanganate. All the experiments were performed in duplicate.

The second-order rate constants were derived by fitting a second-order rate model to the batch data. The obtained kinetic parameters for TCE, toluene and ethanol were compared with literature values derived mostly using pseudo-first-order approaches (Table 2). The second-order rate constants were also estimated using the pseudo-first order experimental approach. Then, the error due to the inappropriate use of pseudo-first-order reaction rate was estimated by comparing k of the pseudo-first-order reaction rate model with the value of second-order reaction rate model. Estimated errors were plotted versus the P/N value for data from the present study and TCE data from the literature (Huang et al., 1999; Huang et al., 2001; Kao et al., 2008; Urynowicz, 2008). All data points in figures are shown with 5% error bar.

2.4. Kinetics of VOC oxidation

The stoichiometric reaction for a target compound can be written in the following form:



where A and B denote the target compound and potassium permanganate, respectively, and N is the number of moles of potassium permanganate in the stoichiometric reaction.

As shown by the stoichiometric reaction, full oxidation of one mole of a target compound requires N moles of potassium permanganate. Thus, the consumption of permanganate and target compounds is related by:

$$\Delta C_B = N\Delta C_A \quad (7)$$

where C_A denotes the concentration of the compound (M), C_B is the concentration of potassium permanganate (M), and ΔC denotes the consumed concentration of reactants (M).

Typically, second-order reaction rate constants for the oxidation of VOC compounds by permanganate have been obtained using a pseudo-first-order approach by assuming that either the contaminant or permanganate concentration is constant (Urynowicz, 2008; Waldemer and Tratnyek, 2006). However, the general form of a second-order reaction rate equation, as a function of the target compound and potassium permanganate concentrations in the aqueous phase, can be written as follows:

$$\frac{dC_A}{dt} = -kC_A C_B \quad (8)$$

where k denotes the reaction rate constant and t represents the time (s).

We now reformulate Eq. (8) in terms of consumed fraction of reactants, $X_A (= (C_{A0} - C_A) / C_{A0})$ and $X_B (= (C_{B0} - C_B) / C_{B0})$. Here, C_{A0} is the initial concentration of target compound (M). From Eq. (7) and the definition of $P (= C_{B0} / C_{A0})$, we have: $X_B = NX_A / P$. Substitution of these definitions into Eq. (8) and rearranging yields the following equation:

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(P - NX_A) \quad (9)$$

Integration of Eq. (9) gives the following general formula for the variation of X_A with time:

$$\frac{1}{C_{A0}(P - N)} \ln \left[\frac{(P - NX_A)}{P(1 - X_A)} \right] = kt \quad \text{where } P \geq N. \quad (10)$$

Table 1

Experimental conditions for the three target compounds.

Compound	Experiment	[VOC] ^o (mM)	[KMnO ₄] ^o (mM)	~P/N
TCE	1	42.0×10^{-3}	17.0×10^{-2}	2.0
	2	42.0×10^{-3}	3.4×10^{-1}	4.0
	3	85.0×10^{-3}	17.0×10^{-1}	10.0
	4	42.0×10^{-3}	17.0×10^{-1}	20.0
	5	21.0×10^{-3}	17.0×10^{-1}	40.5
Toluene	1	15.0×10^{-1}	100.0	5.5
	2	65.0×10^{-2}	100.0	12.8
	3	32.5×10^{-2}	100.0	25.6
	4	32.5×10^{-2}	200.0	51.3
	5	16.2×10^{-2}	100.0	51.3
Ethanol	1	40.0	200.0	1.25
	2	40.0	400.0	2.5
	3	30.0	400.0	3.33
	4	10.0	400.0	10.0
	5	2.5	200.0	20.0

Table 2
Second-order rate constants and the corresponding experimental conditions for the oxidation of target compounds with potassium permanganate.

VOC	[VOC] (mM)	[KMnO ₄] (mM)	pH	T (°C)	-P/N	Method	K (M ⁻¹ s ⁻¹)	Reference
TCE	8.0 × 10 ⁻²	3.2 × 10 ⁻¹	6.0–8.0	RT	1.0	NA	7.9 × 10 ⁻¹ (DI water), 8.5 × 10 ⁻¹ (in tap water)	Vella and Veronda (1993)
	8.0 × 10 ⁻³	7.0 × 10 ⁻¹	8.0	RT	21.85	NA	4.2 × 10 ⁻¹	Tratnyek et al. (1998)
	3.1 × 10 ⁻² –8.3 × 10 ⁻²	3.7 × 10 ⁻¹ –1.2	4.0–8.0	21.0	3.0–3.6	First-order model	6.7 × 10 ⁻¹ ± 3.0 × 10 ⁻²	Yan and Schwartz (1999)
	1.0 × 10 ⁻¹	6.3	4.0–8.0	21.0	15.75	First-order model	6.5 × 10 ⁻¹ –6.8 × 10 ⁻¹	Yan and Schwartz (2000)
	1.4 × 10 ⁻¹ ± 7.0 × 10 ⁻²	1.9 ± 7.0 × 10 ⁻²	7.0	20.0	3.4	First-order model	8.0 × 10 ⁻¹ ± 1.2 × 10 ⁻¹	Huang et al. (2001)
	NA	NA	6.9	20.0	NA	First-order model	8.9 × 10 ⁻¹	Siegrist et al. (2001)
Toluene	1.0–4.0	1.0 × 10 ⁻¹	7.0	25.0	6.25 × 10 ⁻³ –2.5 × 10 ^{-2a}	First-order model	7.6 × 10 ⁻¹ ± 3.0 × 10 ⁻²	Waldemer and Tratnyek (2006)
	3.8 × 10 ⁻² –1.5 × 10 ⁻¹	7.6 × 10 ⁻² –7.6 × 10 ⁻¹	6.3	25.0	0.5–12.5	Second-order model	8.0 × 10 ⁻¹	Kao et al. (2008)
	9 × 10 ⁻¹	6.3	NA	20.0	10.85	First-order model	9.5 × 10 ⁻¹	Urynowicz (2008)
	2.1 × 10 ⁻² –8.5 × 10 ⁻²	3.4 × 10 ⁻¹ –1.7	4.3–7.0	20.0	2.0–4.0	First-order model	6.7 × 10 ⁻¹ (r ² = 0.99)	This study
	4.0	1.0 × 10 ⁻¹	7.0	25.0	1.67 × 10 ^{-4a}	Second-order model	8.0 × 10 ⁻¹ (r ² = 0.99)	This study
	NA	NA	5.0–7.0	20.0	NA	First-order model	83.2 × 10 ⁻⁵	Waldemer and Tratnyek (2006)
Ethanol	NA	NA	5.0–7.0	30.0	NA	First-order model	23.0 × 10 ⁻⁵	Rudakov and Lobachev (2000)
	NA	NA	7.0–8.5	20.0	25.7–51.2	First order model	61.0 × 10 ⁻⁵	Rudakov and Lobachev (2000)
	16.2 × 10 ⁻² –1.5	100–200	4.6	20.0	3.35 × 10 ^{-3a}	Second-order model	18.8 × 10 ⁻⁵ (r ² = 0.96)	This study
	171.5	9.2	4.6	30.0	3.35 × 10 ^{-3a}	First-order model	25.0 × 10 ⁻⁵ (r ² = 0.99)	Barter and Littler (1967)
	171.5	9.2	4.6	30.0	1.25–2.0	First-order model	16.7 × 10 ⁻⁴	Barter and Littler (1967)
	2.5–80.0	200–400	7.0–7.8	20.0	1.25–2.0	Second-order model	40.3 × 10 ⁻⁴	This study

NA: not available, RT: room temperature, r²: the square of linear correlation coefficient.

^a Concentration of the target compound was kept constant.

According to Eq. (10), a plot of $1/C_{A0}(P - N)\ln[(P - NX_A) / (P - X_A)]$ vs. time should yield a straight line, with its slope being the second-order reaction rate constant k .

The solution for X_B follows from Eq. (10) by substituting $X_A = PX_B / N$ to obtain:

$$\frac{P}{C_{B0}(P-N)} \ln \left[\frac{N(1-X_B)}{(N-PX_B)} \right] = kt \quad \text{where} \quad N > PX_B. \quad (11)$$

The assumption for the commonly used pseudo-first-order approach of constant concentration of one of the reactants is only valid if the amount of the target compound or permanganate is sufficiently high to neglect any change in the concentration during the course of an experiment (Huang et al., 2001; Siegrist et al., 2001; Urynowicz, 2008; Waldemer and Tratnyek, 2006). If permanganate is in excess, this means that P/N is much larger than unity. Therefore, Eq. (10) for such conditions may be simplified to yield:

$$\frac{1}{C_{B0}} \ln \frac{C_A}{C_0} = -kt \quad \text{where} \quad P \gg N. \quad (12)$$

To estimate k using the pseudo-first-order approach, Eq. (12) can be used with a constant concentration of permanganate, equal to its initial value.

3. Results and discussion

3.1. Oxidation of VOC compounds

The oxidation of VOC compounds by permanganate was monitored until VOC concentrations were below detection. Fig. 1 depicts the normalized concentration (C/C_0) of the VOC compounds as a function of time. The experiments lasted from less than an hour for TCE to up to a week for toluene, with experimental durations for ethanol oxidation being intermediate. Concentration of the target compounds in the controls did not decrease during the experiments. Since no additional peaks were observed in the chromatogram of the samples, we concluded that the VOCs were fully mineralized according to Eqs. (2) to (4).

The experiments were conducted with excess potassium permanganate using varying initial reactant concentration ratios that deviated from the stoichiometry of the reactions (Table 1). The extent of the deviations was expressed as the ratio of the initial molar concentration of potassium permanganate over the required stoichiometric concentration (i.e., P/N). As illustrated in Fig. 1, oxidation rates increased for larger values of P/N .

Both the VOC and permanganate concentrations were found to decrease as expected based on the stoichiometry of full oxidation according to reactions 2–4. Also, for TCE, approximately 97.5% of the chloride ions for the TCE experiments with an initial concentration of 0.042 (mM) were recovered during the TCE oxidation stage (Fig. a, Supplementary material). This also indicated that TCE was completely oxidized to produce CO_2 , H^+ , and Cl^- . The measured Cl^- concentration in all TCE experiments closely followed the calculated value based on the stoichiometric reaction (Eq. (2)).

Results revealed that the measured consumed fractions of permanganate agreed with values calculated based on stoichiometric reactions (Fig. b, Supplementary material). This means that the consumption of permanganate was only due to the oxidation of target compounds, and that decomposition reactions with water were negligible during the experiments.

3.2. Kinetics analysis of data

We used Eq. (10) and all data from experiments 1–5 (Table 1), to estimate k for each compound. Fig. 2 shows that the plots of $1/C_{A0}(P - N)\ln[(P - NX_A) / (P - X_A)]$ vs. time for all compounds. The square of

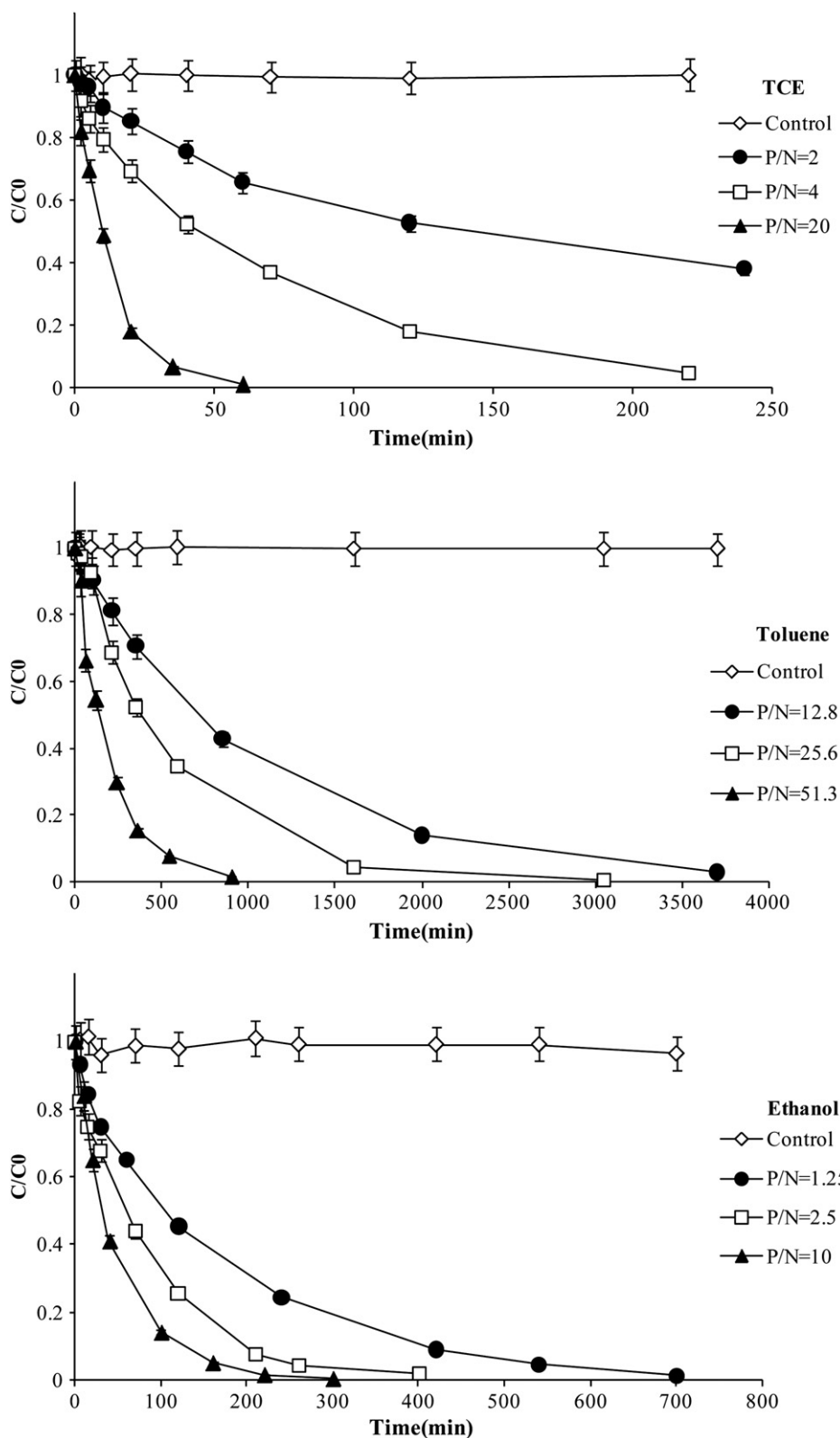


Fig. 1. Oxidation of TCE, toluene, and ethanol vs. time for three different P/N ratios.

linear correlation coefficients (r^2) values of the regressions obtained for TCE, toluene, and ethanol were 0.990, 0.987 and, 0.971, respectively. The corresponding reaction rate constants are given in Table 2. The results showed that the reaction rate constant for TCE was higher than for ethanol and toluene, consistent with previous studies on the oxidation of these compounds by permanganate in both aqueous (Waldemer and Tratnyek, 2006) and vapour phase (Mahmoodlu et al., 2013).

We also used Eq. (11) to estimate k again; this time based on the consumed fraction of permanganate (X_B). Fig. c (Supplementary material) depicts plots of $P/C_{B0} (P - N) \ln[N(1 - X_B) / (N - PX_B)]$ vs. time for all target compounds. The results show that Eq. (11) can simulate very effectively the consumption of permanganate during oxidation of the target compounds. Reaction rate constants ($M^{-1} s^{-1}$) based on Eq. (11) were found to be 7.83×10^{-1} , 2.60×10^{-4} , and 6.67×10^{-4}

for TCE, toluene, and ethanol, respectively. For the calculations we used all available data for the degradation of potassium permanganate.

We applied Eq. (12) to all data from experiments 1–5 for each compound. Fig. 3 shows plots of $1/C_{A0} \ln[(P-N)X_A/P(1-X_A)]$ versus time for all compounds. Values of k were calculated from the slope of the line for each

compound. The r^2 values for the pseudo-first order approach were smaller than those for the second-order model, having values of 0.977, 0.969, and 0.956 for TCE, toluene, and ethanol, respectively.

Comparison of simulation results obtained with the two models revealed that the oxidation reaction of the target compounds was better

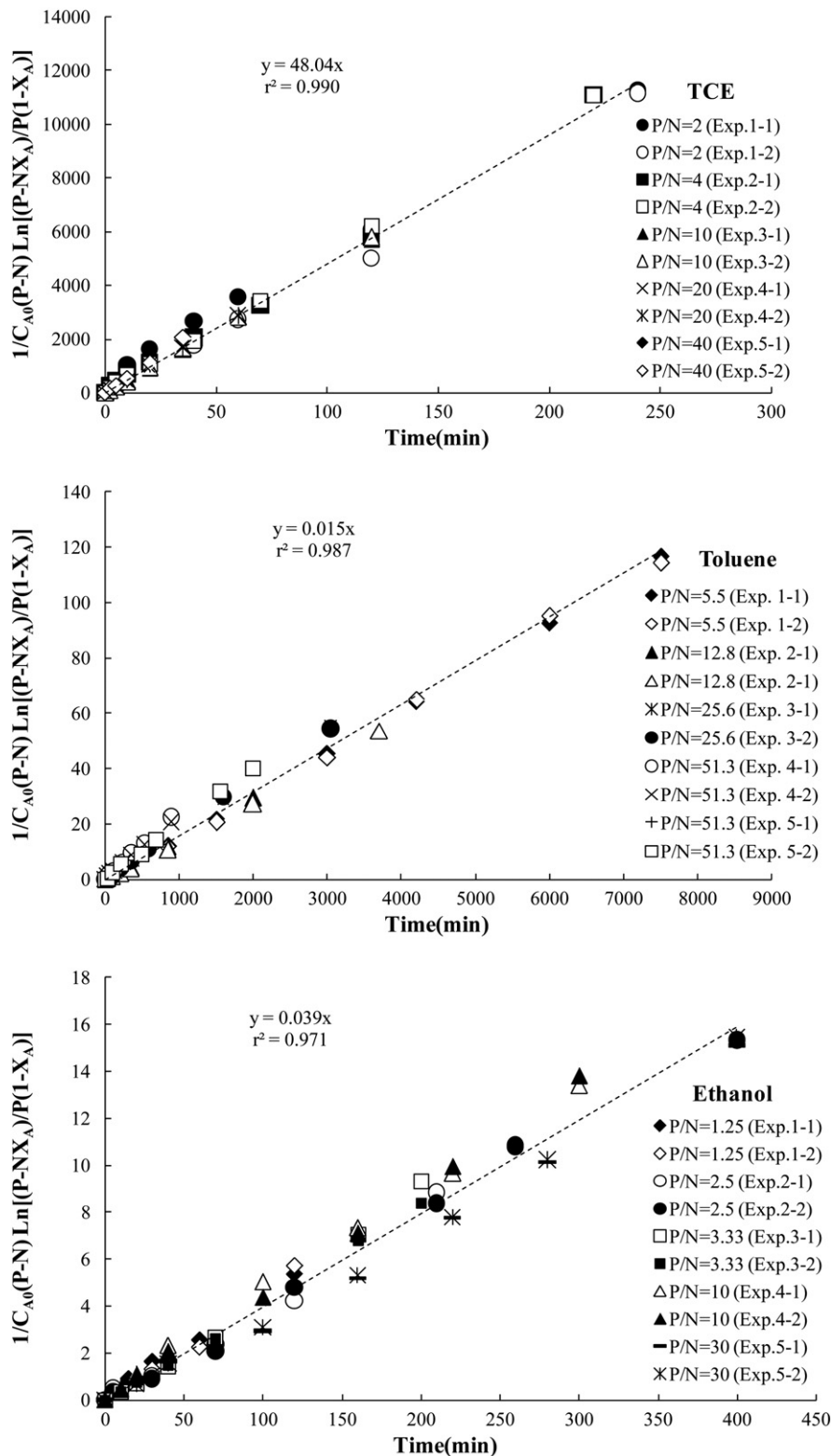


Fig. 2. Plots of $1/C_{A0}(P-N) \ln[(P-N)X_A/P(1-X_A)]$ vs. time for the target compounds, corresponding to Eq. (10) (Exp. x – y: x denotes number of experiments and y is the experiment repetition).

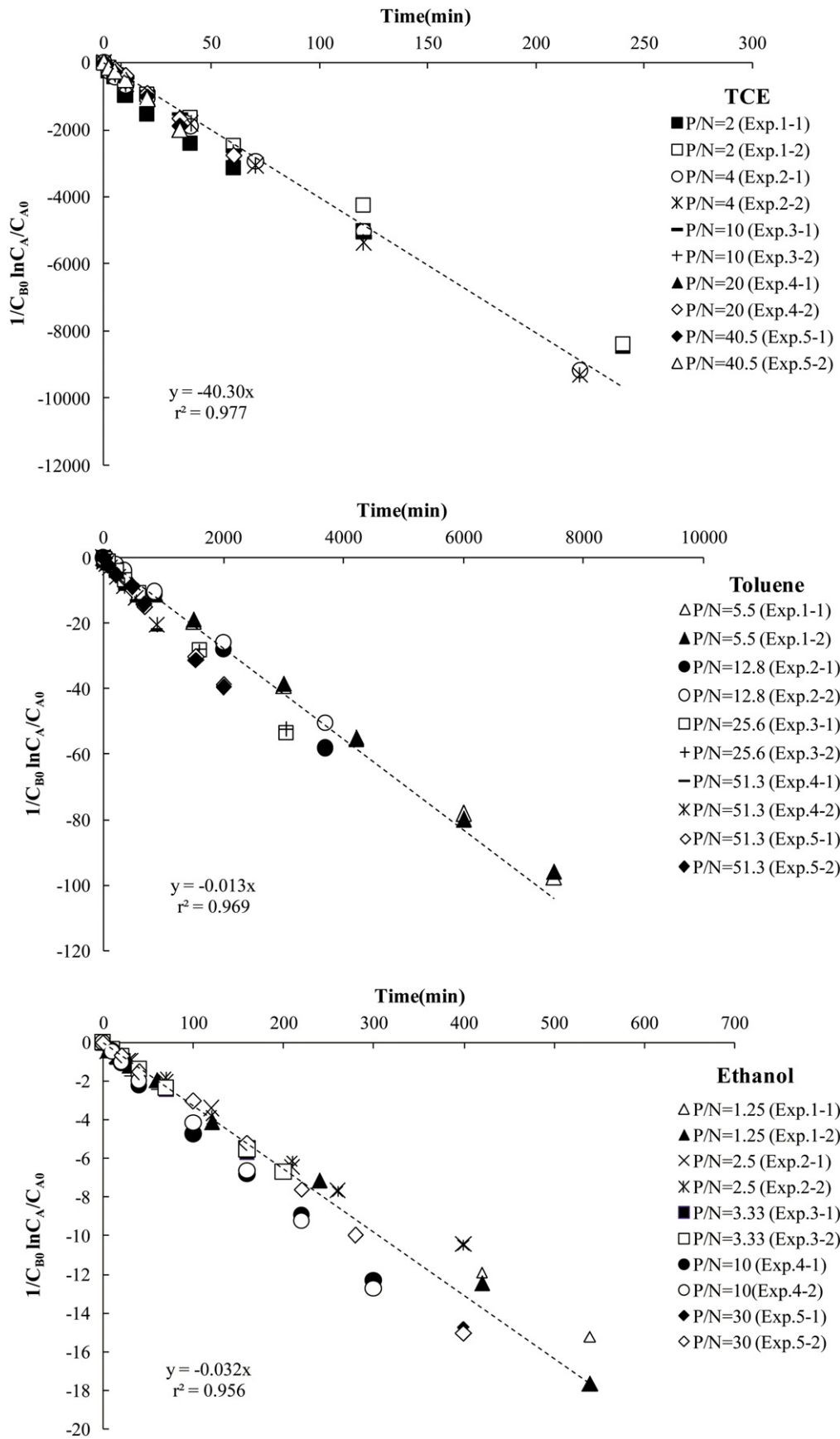


Fig. 3. Plots of $1/C_{B0} \ln C_A / C_0$ vs. time for the target compounds, corresponding to Eq. (12).

represented by the second-order model, rather than the pseudo-first order model. This indicates that the permanganate abundances (P/N up to 50) were insufficient to ignore changes in the initial permanganate concentrations. Rate constants derived using the second-order model hence should be considered more appropriate.

With increasing stoichiometric abundance of one of the reactants, the error associated with assuming a constant initial concentration in the pseudo-first-order approach is expected to decrease. To assess the influence of reactant abundance on the error in estimating second-order rate constants with a pseudo-first order approach, Eqs. (10) and (12) were used to determine k for each experiment (experiments 1 to 5) individually. We subsequently estimated the error by comparing k of a pseudo-first-order reaction rate model with the value of second-order reaction rate model. The results show that the errors were negatively correlated with the P/N, with the largest error corresponding to the lowest ratio of P/N ratio (Fig. 4). Moreover, for the largest values of P/N, the errors became smaller, but never zero since the consumption of excess reactant is never really zero. However, with a stoichiometric excess of P/N > 40, the error (using the pseudo-first-order model to estimate the second-order rate constant) fell below 5%.

Literature has shown a range of estimated second-order rate constants, mainly using the pseudo-first order approach (Table 2). As these studies used varying degrees of reactant excess, we investigated to what extent this range was influenced by errors due to the inappropriate use of the pseudo-first order approach. For this purpose we fitted the second-order and pseudo first-order models to literature data for TCE oxidation (Huang et al., 1999; Huang et al., 2001; Kao et al., 2008; Urynowicz, 2008) and calculated the difference between the k values of the two models for different P/N values (Fig. 4). The results confirmed that the magnitude of errors was negatively correlated with P/N ratio, similar to the analysis of our own data (Fig. 4).

In Table 2, the reported estimates for the second-order reaction rate constants for the oxidation of target compounds by permanganate and their corresponding experimental conditions are presented. Evidently, a wide range of the second-order reaction rate constant values are reported for TCE oxidation. Those values varied between 4.2×10^{-1} and $11.9 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for different conditions (Huang et al., 2001; Kao et al., 2008; Siegrist et al., 2001; Waldemer and Tratnyek, 2006). Our value for the TCE reaction rate constant, $8.0 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$, was identical to the value obtained by Kao et al. (2008), who also used the second-order modeling approach. Hence, despite different experimental conditions, the calculated value of the TCE reaction rate constant in our study was consistent with this literature value for the second order rate constant.

Several studies provided data on the oxidation of toluene by permanganate (Rudakov and Lobachev, 2000; Waldemer and Tratnyek, 2006). A comparison of all available reaction rate constants for toluene and their corresponding experimental conditions showed that our value of $2.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ is at the low end of the reported range. The estimation method used to determine the second-order reaction

rate constant (either the pseudo-first-order or second order modeling approach) can be a reason for this difference.

For the second-order reaction rate constant of ethanol oxidation by permanganate, only two values could be found in the literature (Table 2). Those values are higher than the value obtained in our study ($6.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at $\sim 20^\circ \text{C}$). In the study by Barter and Littler (1967), the ethanol concentration was kept in excess (P/N $\ll 1$), which should yield a very low error using the pseudo-first-order approach, equivalent to a P/N of 298. However, their study was conducted at much lower pH values of about 3–4, while our experiments were performed at groundwater relevant pHs in the range of 7 to 7.8. Higher oxidation rates at lower pHs may be explained by the overall reaction equation (Eq. (4)), which shows a net 1:1 proton demand for each mol of permanganate consumed. A similar pH dependency may be expected for the oxidation of toluene (Eq. (3)). Changes in pH during our toluene and ethanol oxidation experiments were however limited, and did not affect the reaction rates. The results of our experiments showed, the pH decreased from 7 down to 4.3 during TCE oxidation, but increased to 7.8 and 8.6 for ethanol and toluene oxidation, respectively. As shown by Eqs. (2)–(4), the oxidation of TCE produced H^+ , which caused a decrease in pH, while ethanol and toluene oxidation produced OH^- , which caused an increase in pH.

Since groundwater pH values are commonly around 7, an experiment was performed at this pH value for each compound (Fig. d, Supplementary material). The results produced the same reaction rate constants, thus showing that the pH does not have a significant effect on the reaction rate constant within the range of pH values from 4.3 to 7.0, 7 to 8.5, and 7.0 to 7.8 for TCE, toluene, and ethanol, respectively. These results are consistent with those by Waldemer and Tratnyek (2006) and Kao et al. (2008) who found that the pH did not significantly affect the TCE reaction rate within this pH range.

4. Conclusions

In this study, the kinetics of the oxidation of dissolved chlorinated hydrocarbon (TCE) and non-chlorinated hydrocarbons (toluene and ethanol) by permanganate were investigated at room temperature ($\sim 20^\circ \text{C}$). The results showed that the oxidation rate of ethanol and toluene by permanganate were lower compared to TCE. Rather than employing the common pseudo-first-order kinetic analysis, we used a more realistic and accurate second-order formulation for the oxidation of target compounds by permanganate. The reaction rate constants based on the second-order model for TCE, toluene, and ethanol were found to be $8.0 \times 10^{-1} \text{ (M}^{-1} \text{ s}^{-1})$, $2.5 \times 10^{-4} \text{ (M}^{-1} \text{ s}^{-1})$, and $6.5 \times 10^{-4} \text{ (M}^{-1} \text{ s}^{-1})$, respectively.

Our results further revealed that the reaction rate constants of TCE, toluene, and ethanol are independent of pH within the range of 4.3–7.0, 7–8.5, and 7.0–7.8, respectively. For TCE, this dependency had been reported previously in the literature (Kao et al., 2008; Waldemer and Tratnyek, 2006). The oxidation of toluene and ethanol is however expected to increase with increasing acidity.

The degree of reactant excess (P/N value) was found to strongly influence the accuracy of the pseudo-first-order approach. In general, the reaction rate constant obtained from the pseudo-first-order model is smaller than the second-order rate constant. The difference is larger for P/N ratios closer to unity. The inappropriate use of the pseudo-first-order model resulted in a deviation of 5% to 25% from the actual second-order reaction rate constant. Neglecting these errors may have a significant effect on design, modeling, and performance of an ISCO remediation approach. Therefore, errors in k can also affect the desired injection rate and concentration of potassium permanganate solution at a contaminated site.

Despite the slower oxidation kinetics of ethanol and toluene in comparison to TCE, their reaction rates, correspond to half-lives of one to several hours, are still fast enough for the field application of permanganate to remediate these compounds.

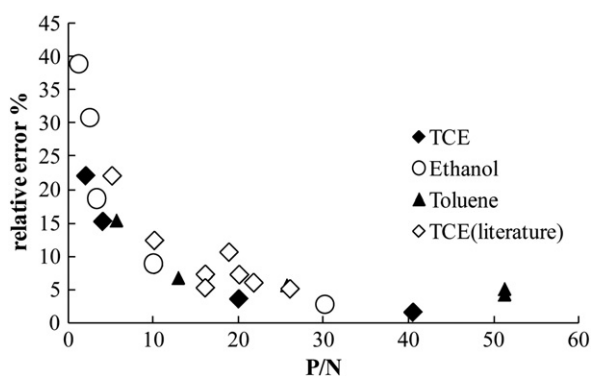


Fig. 4. Relative errors in k using the pseudo first-order reaction rate model versus the P/N value.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.11.066>.

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