



## 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  $8.0 \times 10^{-1}$ ,  $2.5 \times 10^{-4}$ , and  $6.5 \times 10^{-4}$ , 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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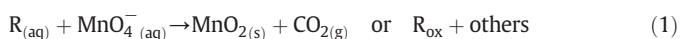
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agent. Inappropriate TCE disposal has produced widespread groundwater contamination. Since TCE is carcinogenic, its movement from contaminated groundwater and soil into the indoor air of overlying buildings is a serious concern (EPA, 2011). Similarly, 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 ( $\text{MnO}_2$ ) as well as carbon dioxide ( $\text{CO}_2$ ) or intermediate organic compounds (Yin and Herbert, 1999) of the form:

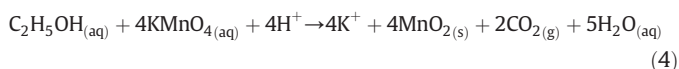
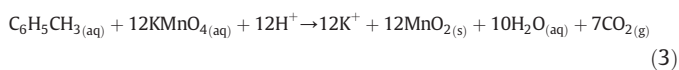


where R denotes an organic contaminant and  $\text{R}_{\text{ox}}$  is an oxidized intermediate organic compound.

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  $\text{CO}_2$  and  $\text{Cl}^-$ , while ethanol and toluene are transformed into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In all reactions,  $\text{MnO}_4^-$  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

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