



## Oxidation of volatile organic vapours in air by solid potassium permanganate



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### HIGHLIGHTS

- ▶ Oxidation of chlorinated and non-chlorinated hydrocarbon vapours by solid potassium permanganate was investigated.
- ▶ A linear kinetic oxidation model effectively predicted the degradation rate of TCE, ethanol, and toluene.
- ▶ The reaction rate constants for TCE, ethanol, and toluene in gas phase by solid potassium permanganate were calculated.

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### ABSTRACT

Volatile organic compounds (VOCs) may frequently contaminate groundwater and pose threat to human health when migrating into the unsaturated soil zone and upward to the indoor air. The kinetic of chemical oxidation has been investigated widely for dissolved VOCs in the saturated zone. But, so far there have been few studies on the use of in situ chemical oxidation (ISCO) of vapour phase contaminants. In this study, batch experiments were carried out to evaluate the oxidation of trichloroethylene (TCE), ethanol, and toluene vapours by solid potassium permanganate. Results revealed that solid potassium permanganate is able to transform the vapour of these compounds into harmless oxidation products. The degradation rates for TCE and ethanol were higher than for toluene. The degradation process was modelled using a kinetic model, linear in the gas concentration of VOC [ $\text{ML}^{-3}$ ] and relative surface area of potassium permanganate grains (surface area of potassium permanganate divided by gas volume) [ $\text{L}^{-1}$ ]. The second-order reaction rate constants for TCE, ethanol, and toluene were found to be equal to  $2.0 \times 10^{-6} \text{ cm s}^{-1}$ ,  $1.7 \times 10^{-7} \text{ cm s}^{-1}$ , and  $7.0 \times 10^{-8} \text{ cm s}^{-1}$ , respectively.

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### 1. Introduction

Volatile organic compounds (VOCs) are defined as organic compounds with boiling points (at 1 atm) below  $260^\circ\text{C}$  (De Nevers, 2000). VOCs have high vapour pressures under normal conditions, so they can easily vaporize into the atmosphere or form vapour plumes in the soil (Kim et al., 2007). VOCs are present in some household products and automobile liquids (Berscheid et al., 2010). Releases of VOCs to the environment have occurred through surface spills, leaking underground storage tanks, and inadequate disposal practices (Berscheid et al., 2010).

Small quantities of VOCs may contaminate large volumes of water. When released as free product, VOCs may migrate downward to significant depths through the soil. In addition, VOC vapours can migrate upwards to the surface through diffusion and

produce elevated concentrations within indoor air spaces (Berscheid et al., 2010). Exposure to some VOCs might affect central nervous system and internal organs, and might cause symptoms such as headache, respiratory tract irritation, dizziness and nausea, known as the Sick Building Syndrome (SBS) (Yu and Lee, 2007).

We have chosen TCE, ethanol, and toluene, as model VOCs (target compounds) for chlorinated solvents, biofuel, and mineral oil, respectively, for the reasons explained below.

TCE is one of the most common man-made chemicals found in soil (Albergaria et al., 2012). It has been widely used as a dry cleaning solvent, degreasing agent, and chemical extraction agent. Since TCE is carcinogenic, its movement from contaminated groundwater and soil into the indoor air of overlying buildings is of serious concern (EPA, 2011).

Ethanol is being increasingly used in (renewable) fuel alternatives and as replacement for methyl tertiary-butyl ether (MTBE), which, despite helping to accomplish Clean Air Act goals, has caused widespread water contamination problems (Johnson et al., 2000; Capiro et al., 2007). Ethanol can reduce the biodegra-

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duction rate of light non-aqueous phase liquid (LNAPL) such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) in groundwater and soil (Mackay et al., 2007; Freitas et al., 2010).

Toluene is found frequently in indoor environments. Toluene is mainly used as an additive to improve the octane number of gasoline (Yu and Lee, 2007).

One of most common treatment techniques for unsaturated zone polluted with VOCs is soil vapour extraction (SVE). This is a long-term operation and does not convert a contaminant to less toxic compounds. A promising alternative is in situ oxidation of VOC that can lead to favourable results in less time. Oxidation of VOCs may convert hazardous contaminants to harmless compounds. The oxidizing agents most commonly used for the treatment of hazardous contaminants are potassium permanganate, ultraviolet radiation, ozone, chlorine dioxide, hydrogen peroxide, sodium persulfate, and Fenton's reagent ( $\text{H}_2\text{O}_2$  oxidation in the presence of ferrous iron,  $\text{Fe}^{2+}$ ).

Among these oxidants, potassium permanganate has been receiving increased attention for the treatment of liquids, slurry soils, and sludges polluted with VOCs (Kao et al., 2008). Early laboratory studies have indicated that dissolved potassium permanganate can remediate a variety of organic compounds, chlorinated alkanes (Waldemer and Tratnyek, 2006), chlorinated ethylenes (Huang et al., 1999; Hood et al., 2000; Yan and Schwartz, 2000; Waldemer and Tratnyek, 2006; Kao et al., 2008; Urynowicz, 2008), oxygenates (Jaky et al., 2000; Damm et al., 2002; Waldemer and Tratnyek, 2006), BTEX (Gardner, 1996; Rudakov and Lobachev, 2000; Waldemer and Tratnyek, 2006), substituted phenols (Jin et al., 2003; Waldemer and Tratnyek, 2006) and PAHs (Forsey, 2004), in aqueous phase. However, the potential of solid potassium permanganate to oxidize VOC vapours in unsaturated zone is currently unknown.

In this study, we demonstrate the ability of solid potassium permanganate to oxidize VOC vapours.

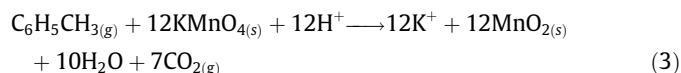
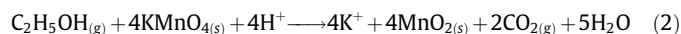
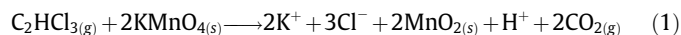
Currently, the literature lacks data on the reaction between solid oxidants such as permanganate and vapour phase of contaminants. Therefore, we planned a series of batch experiments with two objectives: (1) to evaluate the ability of solid potassium permanganate to fully oxidize vapour phase contaminants, (2) to determine kinetic parameters for TCE, ethanol, and toluene oxidation by solid potassium permanganate.

## 2. Materials and methods

### 2.1. Materials

We used  $4.8 \times 10^{-6}$ ,  $3.5 \times 10^{-6}$ ,  $2.3 \times 10^{-6}$  mole of TCE, ethanol, and toluene vapours, respectively. These values were calculated based on 1.5 mL of gas samples (under normal conditions) which were obtained from the headspace of their highly pure li-

quid phases. Solid potassium permanganate of 99% purity was obtained from Sigma–Aldrich. The required potassium permanganate for complete oxidation of VOCs was calculated based on the following reactions for TCE, ethanol, and toluene, respectively:



The required amount of potassium permanganate for oxidizing  $4.8 \times 10^{-6}$  mole of TCE,  $3.5 \times 10^{-6}$  mole of ethanol, and  $2.3 \times 10^{-6}$  mole of toluene were estimated to be 1.25, 2.22, and 4.44 mg, respectively. These were calculated based on reactions in aqueous environment, assuming a full dissolution of crystals. In dissolved form, potassium permanganate may be fully available for oxidation. But, in the solid form only the surface of potassium permanganate grains is in contact with the gas phase. Accordingly, more potassium permanganate is needed to avoid limitation in the degradation rate. Hence, excess amount of potassium permanganate (2.703 g) was used for each batch.

Potassium permanganate grains were put inside 12-mL transparent glass vials, which were capped with a hard septum to prevent any leakage. VOC vapour was injected using a gas tight syringe (2.5 mL Hamilton, SGE) and 16 mm disposable needles ( $\varnothing 0.5$  mm, Terumo).

In order to get kinetic parameters, three batch experiments at three different initial amounts of vapour and potassium permanganate were performed for all compounds (Table 1). All experiments were carried out in duplicate. For each experiment, we prepared several identical batches and each batch was allocated to a given sampling time.

A control experiment was also performed in duplicate for each compound to ensure that the loss of target compound due to leakage was negligible over the course of the experiments. To prepare a control batch, a 12-mL transparent glass vial was capped with a hard septum. Then VOC vapour was injected into the vial.

All experiments were carried out in a vertical rotary shaker, at room temperature,  $20 \pm 2$  °C, and air humidity of  $37 \pm 2\%$ , which is also the initial humidity inside the vials.

### 2.2. Sampling and measurements

Reaction and control batches were periodically sampled using a gas tight syringe until no detectable concentration was found in the reaction vial. To eliminate the effect of pressure drop due to sampling, each vial was used only once.

The concentrations of target compounds, TCE, ethanol, and toluene were measured by a gas chromatograph (GC). Gas samples of

**Table 1**  
Initial experimental conditions for each compound.

Compound	Experiment	$n$ (mol)	$M_{\text{KMnO}_4}$ (g)	$A$ ( $\text{cm}^2$ )	$V$ ( $\text{cm}^3$ )	$S_0$ ( $\text{cm}^{-1}$ )
TCE	1	$4.8 \times 10^{-6}$	2.703	2703	10.5	257.43
	2	$2.4 \times 10^{-6}$	2.703	2703	10.5	257.43
	3	$4.8 \times 10^{-6}$	1.351	1351.5	11.25	120.13
Ethanol	1	$3.5 \times 10^{-6}$	2.703	2703	10.5	257.43
	2	$1.75 \times 10^{-6}$	2.703	2703	10.5	257.43
	3	$3.5 \times 10^{-6}$	1.351	1351.5	11.25	120.13
Toluene	1	$2.3 \times 10^{-6}$	2.703	2703	10.5	257.43
	2	$1.15 \times 10^{-6}$	2.703	2703	10.5	257.43
	3	$2.3 \times 10^{-6}$	1.351	1351.5	11.25	120.13

$n$  = Initial number of VOC moles.  $M_{\text{KMnO}_4}$  = mass of solid potassium permanganate.  $A$  = surface area of potassium permanganate,  $V$  = volume of the gas phase.  $S_0$  = initial relative surface area.

2 mL were taken using the headspace syringe of the GC from each vial. Then, samples were injected into the GC. The GC (Agilent Technologies 6850) equipped with a capillary column (0.25 mm × 60 m), a flame ionization detector, and a purge and trap.

Specific surface area of potassium permanganate was measured using 10-point Brunauer–Emmett–Teller (BET) method by a Nova 3000 from Quantachrome. Performance of this machine was controlled using reference 173 from Community Bureau of Reference. Samples were degassed at 120 °C overnight before measurements. The relative surface area was calculated as the surface area per volume of gas (Table 1).

To calculate the amount of the potassium permanganate consumption, at end of experiment potassium permanganate grains were dissolved in deionized (DI) water and its concentration was measured using a UV-spectrophotometer (UV-1800, Shimadzu) at a wavelength of 525 nm.

### 3. Results and discussion

#### 3.1. Oxidation study

Fig. 1 depicts the normalized concentration ( $C/C_0$ ) of the target compounds as a function of time, where  $C$  denotes the observed concentration of the target compound for a given time and  $C_0$  is the initial concentration of the target compound. Degradation of target compounds shows an exponential trend, as indicated by the fitted formula in the graph (Fig. 1). These results also show that solid potassium permanganate was able to rapidly oxidize the vapour phase of TCE and ethanol. Toluene was also degraded but less rapidly.

No VOC intermediates or by-products were found in vapour samples. During the experiment, potassium permanganate crystals turned into dark colour, which is the colour of a coating layer of produced manganese dioxide ( $MnO_2$ ).

#### 3.2. Kinetics analysis of data

Since the degradation of three reactants showed an exponential trend, we assumed that the kinetics followed a first-order reaction rate. We also assumed that only surface of solid potassium permanganate reacts with compounds. So, to a proper calculation of the reaction rate coefficient, we should have an equation that involves the physical properties of potassium permanganate, such as the surface area and mass of potassium permanganate. Such an equation may be written as:

$$\frac{dC}{dt} = -kCS \quad (4)$$

where  $k$  denotes the reaction rate constant,  $C$  is the vapour concentration of compound [ $ML^{-3}$ ],  $t$  is time [T], and  $S$  is the relative surface area of solid potassium permanganate [ $L^{-1}$ ], which is defined as:

$$S = \frac{A}{V} \quad (5)$$

where  $A$  is the surface area of the potassium permanganate [ $L^2$ ] and  $V$  is the volume of the gas phase [ $L^3$ ].

First, we assumed the relative surface area not to alter significantly during the course of the reaction. To validate this assumption, we determined the amount of potassium permanganate that was consumed, at the end of the experiment. This was done by dissolving potassium permanganate grains which were used in the experiments in DI water and then using a spectrophotometer to determine its mass. We compared this to the initial mass and the

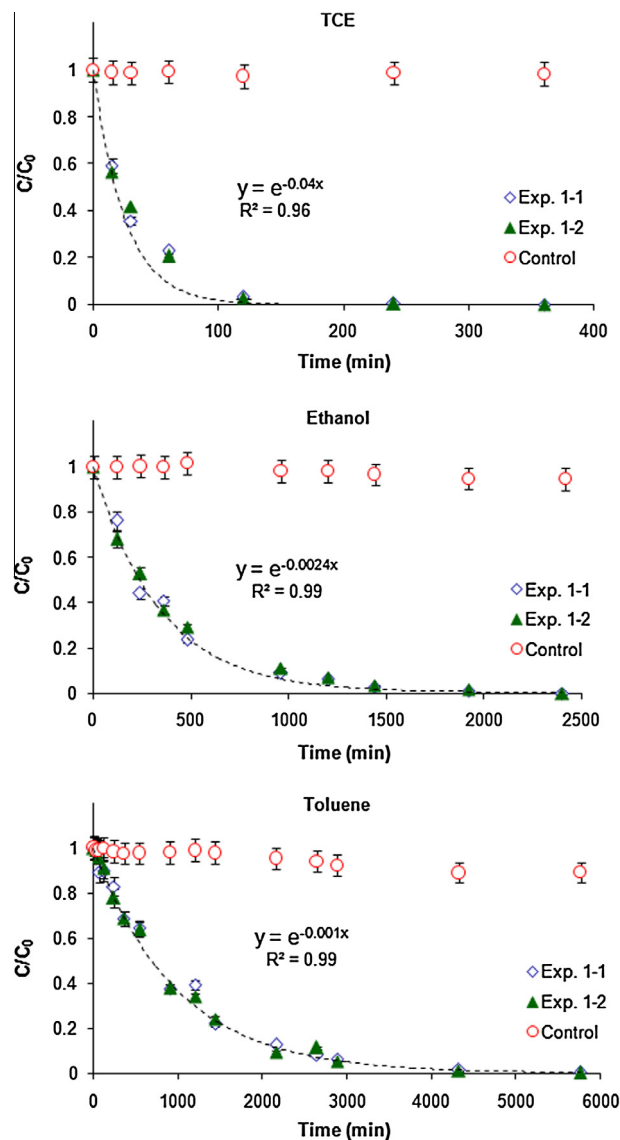


Fig. 1. Degradation of TCE, ethanol, and toluene vs. time using experiment 1 (exp.  $x$ – $y$ :  $x$  denotes number of experiment and  $y$  is the experiment repetition).

result showed that there was no significant consumption of solid potassium permanganate during our experiments.

With  $S$  set equal to  $S_0$  Eq. (4) can be solved to obtain:

$$\frac{1}{S_0} \ln \frac{C}{C_0} = -kt \quad (6)$$

where  $S_0$  denotes the initial relative surface area of potassium permanganate [ $L^{-1}$ ].

According to Eq. (6), plot of  $1/S_0 \ln C/C_0$  vs. time should yields a straight line. Then, the reaction rate constant  $k$  can be obtained from the slope of this line.

We used all data from Experiments 1, 2, and 3 to estimate  $k$  for each compound. Fig. 2 shows that the plots of  $1/S_0 \ln C/C_0$  vs. time for all compounds. The square of linear correlation coefficients ( $R^2$ ) obtained for TCE, ethanol, and toluene were  $9.6 \times 10^{-1}$ ,  $9.9 \times 10^{-1}$ , and  $9.9 \times 10^{-1}$ , respectively. Results suggest that the degradation of the target compounds can be modelled by Eq. (6) as long as sufficient relative surface area of potassium permanganate is available. These results also show the accuracy of reaction rate constants which are given in Table 2.

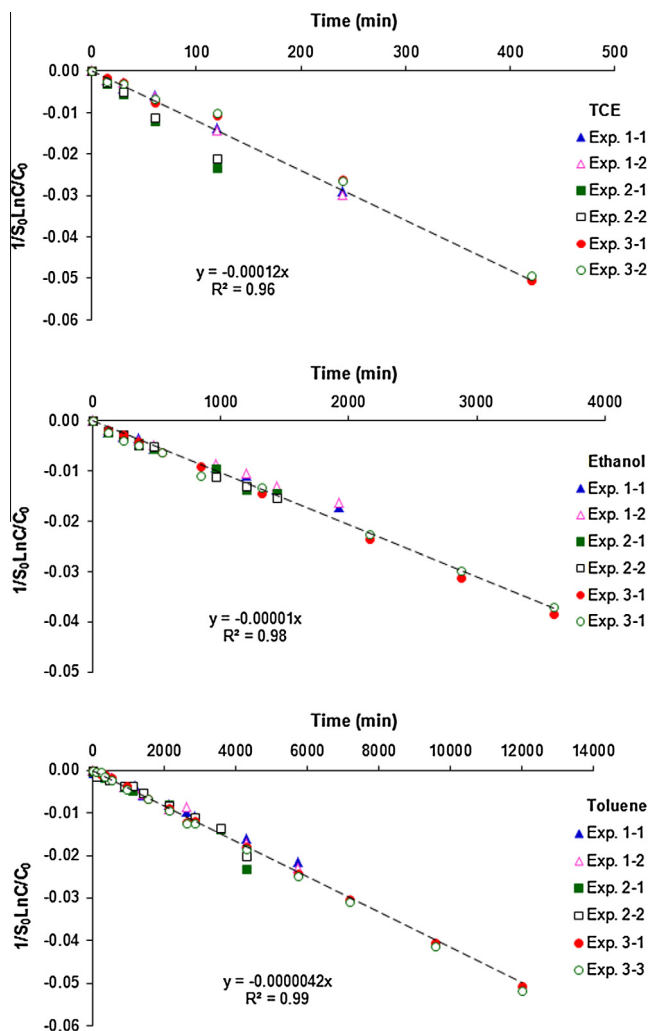


Fig. 2. Plot of  $1/S_0 \ln C/C_0$  (denoted by  $y$ ) vs. time (denoted by  $x$ ) for evaluating  $k$  following Eq. (6).

We compared results of our experiments with the oxidation of VOCs in aqueous phase reported in the literature (Waldemer and Tratnyek, 2006). We found that the oxidation process in both phases follows a first-order model. This comparison also revealed that the oxidation rates for VOCs in vapour phase are much smaller than for aqueous phase. However, in both phases, the reaction rate for TCE is higher than for ethanol and toluene.

As mentioned above, as a result of oxidation,  $MnO_2$  is produced and coats the grains. This may affect the efficiency of oxidation process. To analyze the effect of surface coating, we accounted for the reduction of the relative surface area during the experiment. This was done by supplementing Eq. (4) with an equation relating the relative surface area to the  $MnO_2$  concentration. This resulted in the following equation:

Table 2

Reaction rate constants for oxidation of TCE, ethanol, and toluene in vapour phase at 20 °C.

Compound	$K$ ( $cm\ s^{-1}$ )	$R^2$
TCE	$2.0 \times 10^{-6}$	$9.6 \times 10^{-1}$
Ethanol	$1.7 \times 10^{-7}$	$9.8 \times 10^{-1}$
Toluene	$7.0 \times 10^{-8}$	$9.9 \times 10^{-1}$

$R^2$  = the square of the correlation coefficient.

$$\frac{dC}{dt} = -kC \left[ S_0 - \frac{\omega}{\gamma} (C_0 - C) \right] \quad (7)$$

where  $\omega$  is the number of moles of  $MnO_2$  produced per mole of target compound (based on stoichiometry reaction) and  $\gamma$  is the coating factor (number of moles of produced  $MnO_2$  per area of potassium permanganate grains) [ $ML^{-2}$ ].

The numerical solution of Eq. (7) was fitted to the TCE experimental data. Results showed a maximum reduction of around 4% in the relative surface area. This confirms the validity of our assumption that there is a negligible change in the relative surface area of potassium permanganate during our TCE experiments.

Although the largest amount of  $MnO_2$  was produced during degradation of ethanol and toluene (based on stoichiometry reaction), there was still a large excess of the relative surface area during the ethanol and toluene experiment (based on the amount of potassium permanganate we used). Moreover, we calculated the amount of used potassium permanganate for all three compounds. On all cases, this was found to be small fraction of initial amount (around 4%).

#### 4. Conclusions

In this study, we investigated the kinetic parameters of both chlorinated and non-chlorinated hydrocarbon vapours by solid potassium permanganate under room temperature and humidity conditions. Results showed that potassium permanganate is able to oxidize the vapour of TCE and ethanol, and toluene. We also found that TCE and ethanol in vapour phase can be rapidly oxidized by solid potassium permanganate. However, toluene was degraded slower. A linear kinetic oxidation model, based on the concentration of VOC in gas and a constant relative surface area, effectively predicted the rate of TCE, ethanol, and toluene degradation. Results revealed that the reaction rate constants for TCE, ethanol, and toluene are  $2.0 \times 10^{-6} cm\ s^{-1}$ ,  $1.7 \times 10^{-7} cm\ s^{-1}$ , and  $7.0 \times 10^{-8} cm\ s^{-1}$ , respectively. Results also showed that the amount of used potassium permanganate for all three compounds was small fraction of initial amount (around 4%).

These findings will be helpful in designing a horizontal permeable reactive barrier with solid potassium permanganate in unsaturated zone for vapour intrusion. The performance of such methodology may be affected by moisture content, pH, and temperature of the soil matrix. Also, one has to consider the health effects of by-product gases such as ethane (Pant and Pant, 2010) and methane (Freitas et al., 2010) that can be produced under anaerobic biodegradation of TCE and ethanol, respectively.

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