Oxidation of dissolved trichloroethylene, ethanol, and toluene by potassium permanganate: A kinetic study

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1. Introduction:

Volatile organic compounds (VOCs) are present in some household products and automobile liquids (Berscheid et al., 2010). When released as free product, VOCs may migrate downward to significant depths through the soil. In addition, VOC vapours can migrate upwards from groundwater to the surface through diffusion and produce elevated concentrations within indoor air spaces (Berscheid et al., 2010). Exposure to some VOCs is hazardous may lead to the so-called Sick Building Syndrome.

Information on the kinetics of oxidizing agents reacting with VOCs is required for the optimization of remediation systems and the modeling of treatment progress. In this study, we determined the kinetic parameters of the oxidation model of dissolved VOCs by potassium permanganate.

We have chosen TCE, ethanol, and toluene, as model VOCs (target compounds) for chlorinated solvents, biofuel, and mineral oil, respectively. Early laboratory studies have indicated that dissolved $KMnO_4$ can remediate a variety of organic compounds. However, the potential of solid $KMnO_4$ to oxidize VOC vapours in unsaturated zone is currently unknown. We demonstrate the ability of solid $KMnO_4$ to oxidize TCE, ethanol, and toluene in both gas and aqueous phases. Since $KMnO_4$ and VOC vapour can dissolve into (stagnant and capillary) water in unsaturated zone (Fig. 1), we have performed a series of batch and column experiments with three objectives: (1) to determine kinetic parameters values for the oxidation of TCE, ethanol, and toluene by aqueous $KMnO_4$, (2) to estimate the impact of variation in $KMnO_4$ concentration on the reaction rate constants, and (3) to establish a suitable kinetic reaction rate model.
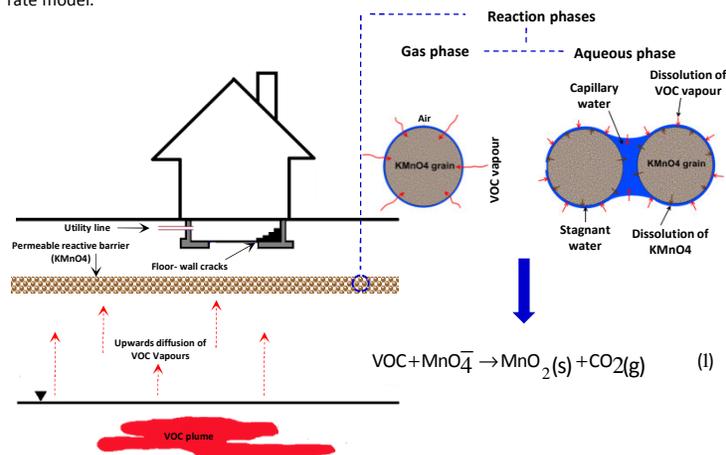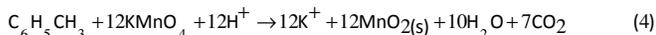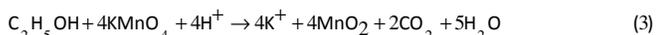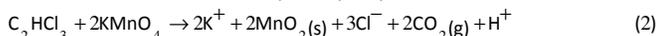

$$VOC + MnO_4^- \rightarrow MnO_2(s) + CO_2(g) \qquad (1)$$

Fig.1: A schematic view of a horizontal reactive permeable barrier.

2. Chemical reactions

Reactions for TCE, ethanol, and toluene, respectively, may be written as:

$$C_2HCl_3 + 2KMnO_4 \rightarrow 2K^+ + 2MnO_2(s) + 3Cl^- + 2CO_2(g) + H^+ \qquad (2)$$

$$C_2H_5OH + 4KMnO_4 + 4H^+ \rightarrow 4K^+ + 4MnO_2 + 2CO_2 + 5H_2O \qquad (3)$$

$$C_6H_5CH_3 + 12KMnO_4 + 12H^+ \rightarrow 12K^+ + 12MnO_2(s) + 10H_2O + 7CO_2 \qquad (4)$$

3. Gas phase batch experiments and results

Reaction rate law:

$$\frac{1}{S_0}Ln\frac{C}{C_0} = -kt, \qquad S_0 = \frac{A_0}{V_{gas}} \qquad (5)$$

k: the reaction rate constant, C: the vapour concentration of compound, C_0: Initial vapour concentration of compound t: time, S_0: the relative surface area of solid $KMnO_4$, A_0: Initial surface area of $KMnO_4$ and V_{gas}: the volume of the gas phase.

Table 1: Reaction rate constants in vapour phase at 20 °C.

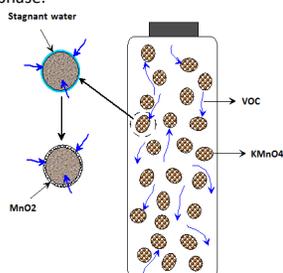| VOC	k(cm min⁻¹)
TCE	1.2×10^{-4}
Ethanol	1.0×10^{-5}
Toluene	4.2×10^{-6}

Fig.2: a schematic view of batch experiment.

4. Aqueous phase experiments and results

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

$$A + NB \rightarrow Products \qquad (6)$$

We formulated our equations in terms of consumed fractions of reactants, X_A (= $C_{A0}-C_A/C_{A0}$) and X_B (=$C_{B0}-C_B/C_{B0}$). Here, C_A denotes the concentration of compound, C_B is the concentration of $KMnO_4$, C_{A0} and C_{B0} are their initial concentrations, respectively. First order reaction rate law formula can be written as follows:

$$\frac{dX_A}{dt} = -kC_{A0}(1-X_A)(P-NX_A) \qquad (7)$$

Where k is the reaction rate constant, $P=C_{B0}/C_{A0}$. Integration of Equation 7 gives the following general formula for the variation of X_A with time:

$$\frac{1}{C_{A0}(P-N)}Ln\left[\frac{(P-NX_A)}{P(1-X_A)}\right] = -kt \qquad (8)$$

For cases that P/N>>1, Equation 8 reduces to a first order model:

$$\frac{1}{C_{B0}}Ln\frac{C_A}{C_0} = -kt \qquad (9)$$

Comparison of results of two models revealed that the oxidation reaction of target compounds closely behaved as a second-order process (Fig.3). Hence, results suggested k from second order model is the true value of reaction rate constant. Then, we estimated the error due to use of a pseudo first-order reaction rate model (Fig.4).
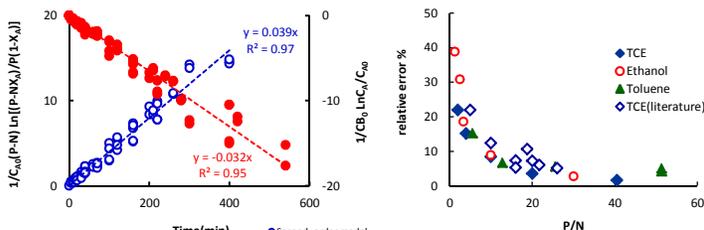

Fig. 3: Oxidation of ethanol vs. time for different P/N ratios including all experiments.

Fig.4: Relative errors, versus P/N values for data from the present study and TCE data from the literature (Huang et al., 2001; Kao et al., 2008; Urynowicz, 2008).

5. Conclusion

Results showed that the oxidation rate of ethanol and toluene by permanganate is significantly lower compared to TCE. We found that applying a first-order kinetic model may cause errors, which magnitudes are negatively correlated with the P/N ratio. In other words, the first-order model is only valid for large values of P/N; i.e. for sufficiently large excess amount of $KMnO_4$. We also fitted second-order and pseudo first-order models to data from the literature for TCE oxidation experiment and obtained same correlation between the P/N ratio and the error.

Table 2: Reaction rate constants (mol s⁻¹) in aqueous phase based on first and second order reaction rate models at 20 °C.

VOC	TCE	Ethanol	Toluene
k (1st model)	6.7×10^{-1}	5.3×10^{-4}	1.9×10^{-4}
k (2nd model)	8.0×10^{-1}	8.5×10^{-4}	2.5×10^{-4}
R² (1st model)	9.8×10^{-1}	9.5×10^{-1}	9.7×10^{-1}
R² (2nd model)	9.9×10^{-1}	9.7×10^{-1}	9.9×10^{-1}

References

Berscheid, M., et al., 2010. Proven Technologies and Remedies Guidance: Remediation of Chlorinated Volatile Organic Compounds in Vadose Zone Soil. California Department of Toxic Substances Control.

Huang, K.C., et al., 2001. Oxidation of chlorinated ethenes by potassium permanganate: a kinetics study. J. Hazard. Mater.

Kao, C.M., et al., 2008. Application of potassium permanganate as an oxidant for in-situ oxidation of trichloroethylene-contaminated groundwater: A laboratory and kinetics study. Hazard. Mater.

Mahmoodlu, M.G., et al., 2013. Oxidation of volatile organic vapours in air by solid potassium permanganate. Chemosphere.

Urynowicz, M.A., 2008. In-situ chemical oxidation with permanganate: assessing the competitive interactions between target and nontarget compounds. Soil & Sediment Contam.
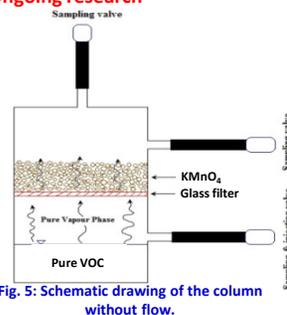
➤ Ongoing research

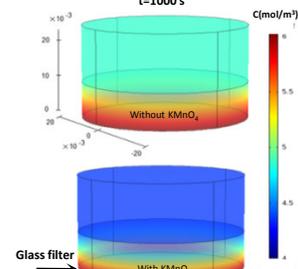Fig. 5: Schematic drawing of the column without flow.

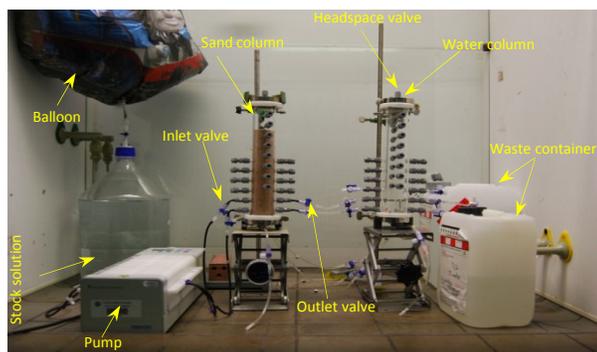Fig. 6: Comparison between simulation results for TCE in column with and without dry $KMnO_4$.

Fig. 7: Experimental set-up for the column with flow (Current work).