1. Introduction:
Volatile organic compounds (VOCs) are present in some household products and automobile
information on the kinetics of oxidizing agents reacting with VOCs is required for the
oxidation 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 K(MnO)4 can remediate a variety of organic compounds. However, the potential of
potassium permanganate: A kinetic study

2. Chemical reactions
Reactions for TCE, ethanol, and toluene, respectively, may be written as:

\[ C_2HCl_3 + 2K MnO_4 \rightarrow 2K^+ + 2MnO_4^{2-} + 3Cl^-, 2CO_2(g) + H^+ \] (2)

\[ C_2H_5OH + 4K MnO_4 + 4H^+ \rightarrow 4K^+ + 4MnO_2 + 2CO_2(g) + SH_2O \] (3)

\[ C_6H_5CH_2 + 12K MnO_4 + 12H^+ \rightarrow 12K^+ + 12MnO_2(s) + 10H_2O + 7CO_2 \] (4)

3. Gas phase batch experiments and results
Reaction rate law:
\[ \frac{1}{S_0} \frac{dC}{dt} = -k_t \] (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 K(MnO)4, \( V_{gas} \): the volume of the gas phase.

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

<table>
<thead>
<tr>
<th>VOC</th>
<th>k(cm min⁻¹)</th>
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<tbody>
<tr>
<td>TCE</td>
<td>1.2 × 10⁴</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.0 × 10⁵</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.2 × 10⁵</td>
</tr>
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4. Aqueous phase experiments and results
Stoichiometry reaction for a target compound can be written in the following form:

A + NB → Products

We formulated our equations in terms of consumed fractions of reactants, \( X_a = C_0 - C_a/C_{tot} \) and \( X_b = C_0 - C_b/C_{tot} \). Here, \( C_a \) denotes the concentration of compound, \( C_0 \) is the concentration of K(MnO)4, \( C_{tot} \) and \( C_a \) are their initial concentrations, respectively. First reaction rate law formula can be written as follows:

\[ \frac{dX_a}{dt} = -k_{r1} \] (6)

Where \( X_a \) is the reaction rate constant, \( P = C_0/C_{tot} \), integration of Equation 7 gives the following general formula for the variation of \( X_a \) with time:

\[ \frac{1}{C_{tot}(1-P)} \ln \left( \frac{P - NX_a}{P(1-X_a)} \right) = -kt \] (8)

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

\[ \frac{1}{C_{tot}P} \ln \left( \frac{C_{tot}P - NX_a}{C_{tot}P(1-X_a)} \right) = -kt \] (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).

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 K(MnO)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.

References