# Phase-transfer-catalysis On The Oxidation Of Chlorinated Solvents By Potassium Permanganate

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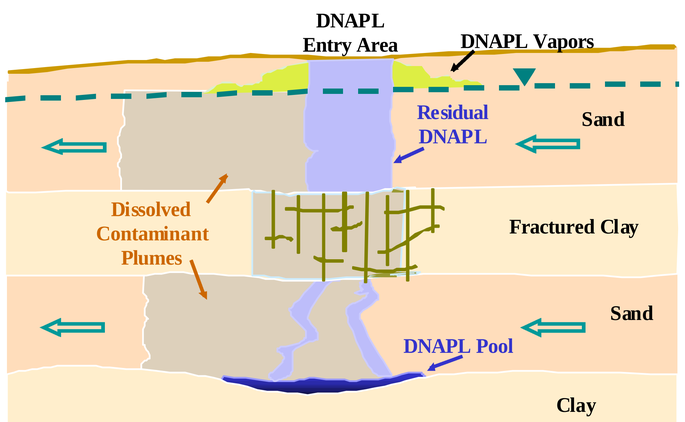
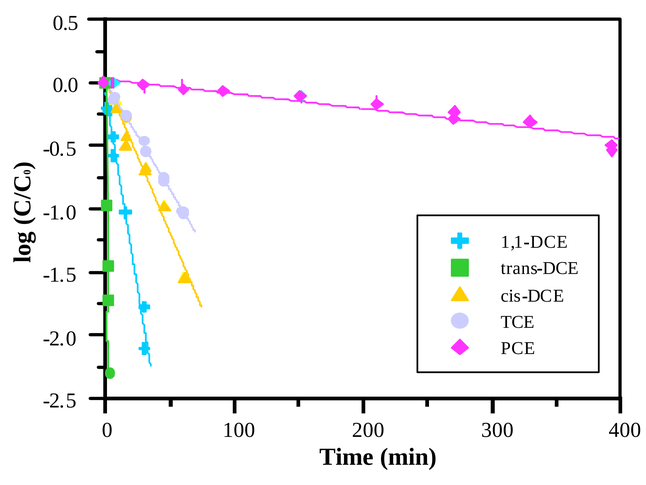
## Background

A conceptualization of a DNAPL source illustrates the modes of occurrence that need to be addressed in source zone flooding schemes.




Both laboratory and field experiments have demonstrated the ability of potassium permanganate to oxidize common chlorinated ethylenes like trichloroethylene (TCE) and tetrachloroethylene (PCE).

Chlorinated ethylenes can be rapidly degraded by permanganate in aqueous solution. The half lives of TCE, cis-1, 2-DCE, trans-1,2-DCE and 1,1-DCE with 1 mM $MnO_4^-$ range from 0.4-18 minutes. The half-life of PCE, however, is much longer, about four hours (Yan and Schwartz, 1998).



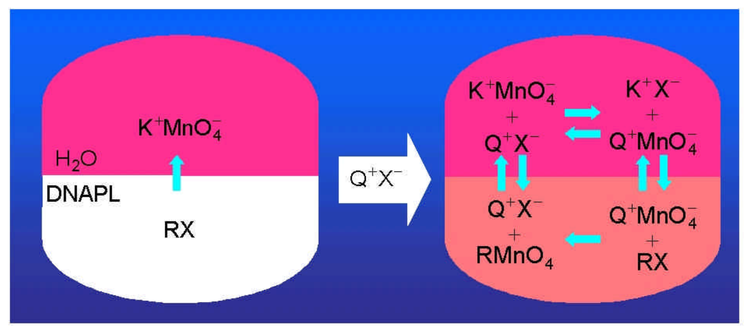

Oxidation schemes have some limitations because of the low solubility of chlorinated ethylenes (e.g., TCE) in the aqueous phase (Yan ans Schwartz, 1998 and Zhang and Schwartz, 2000). An ongoing thrust of our work is to find methods that increase the efficiency of permanganate oxidation. Following here is an update of recent work on the use of catalysts to speed up the reaction.

## Objective

- to introduce the concept of phase transfer catalysis for the oxidation of chlorinated solvents,
- to evaluate whether the catalyzed oxidation scheme can enhance the oxidation of TCE with $MnO_4^-$,
- to test whether or not adding a PTC could enhance the oxidation rates of the most common chlorinated solvents occurring as binary mixtures.

## Catalytic Permanganate Oxidation

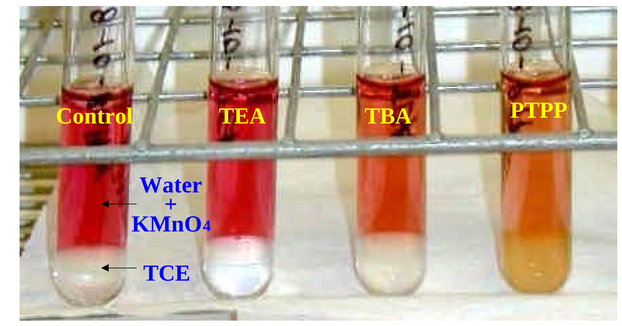
Phase transfer catalysis is a technique for converting similar chemical species situated in two or more phases. Due to their amphiphilic nature, the catalysts distribute themselves between aqueous and organic phases, form an association with the reactive anion (e.g. $MnO_4^-$), and bring them into the organic phase in a form suitable for reactions.




Extraction Constants;

$$K_E = \frac{[Q^+MnO_4^-]_{org}}{[Q^+]_{aq}\cdot[MnO_4^-]_{aq}} = \frac{[Q^+MnO_4^-]_{org}}{[MnO_4^-]^2_{aq}}$$

$$K_E = \frac{\text{solubility of } QMnO_4 \text{ in organic solvent (M)}}{(\text{solubility of } QMnO_4 \text{ in water})^2\ (M^2)}$$




## Kinetic Batch Experiment with TCE

We conducted kinetic batch experiments to study the rate of permanganate oxidation of TCE in the presence of the selected catalysts (Table 1). We evaluated samples for TCE degradation by measuring the chloride concentration and UV absorbance for $MnO_4^-$.

PTPP led to a marked increase in the $Cl^-$ concentration in the aqueous phase during the first 20 to 25 minutes of the experiment. The pattern of reaction speedup, PTPP > TBA > TEA >Blank, is consistent with the extraction constants ($K_E$) calculated based on the solubilities in the organic phase of methylene chloride.

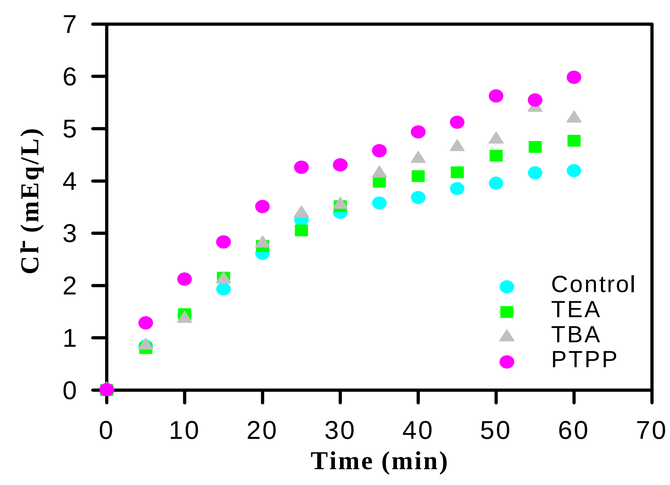



Table 1. Chemical properties of selected PTC- $MnO_4^-$ ion pairs.

| Name/PTCs | Abbr. | FW[a] | $S_w$[b] | $S_o$[b] | $\log K_E$[c] |
|---|---|---|---|---|---|
| tetraethylammonium | TEA | 165.71 | $7.30 \times 10^{-4}$ | 0.235 | 1.64 |
| tetrabutylammonium | TBA | 277.92 | $2.10 \times 10^{-4}$ | 0.417 | 4.98 |
| pentyltriphenylphosphonium | PTPP | 413.35 | $2.40 \times 10^{-4}$ | 1.460 | 7.40 |

FW; formula weight (g/mole), $S_w$; solubility (M) in water, $S_o$; solubility (M) in methylene chloride, a; formula weight of bromide salts only, b; Karaman, *et al.*, (1984), c; calculated

Figures show the spectra of UV-Vis scans. The larger spacing between spectra indicate the accelerated disappearance of permanganate (526 nm) in catalytic TCE oxidation. Pseudo-first-order rate constants ($k$) were determined from the slopes of the log ($c_t/c_o$) versus time data in Table 3.

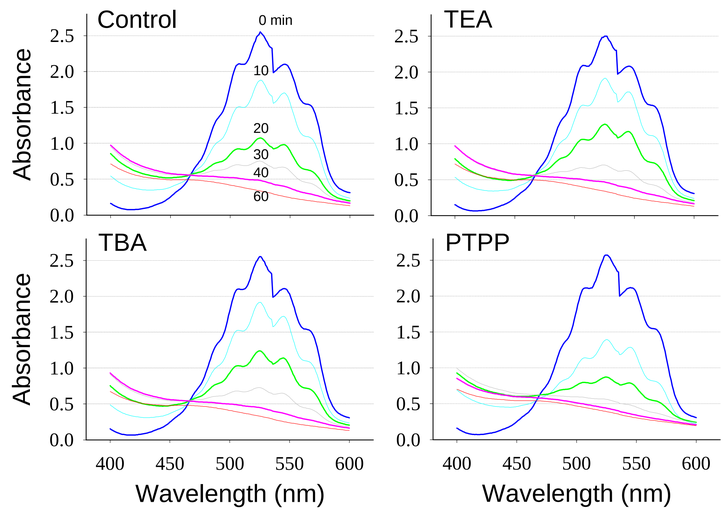
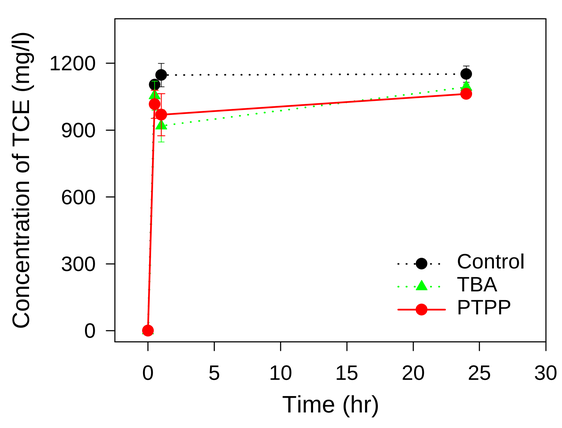



Table 2. Pseudo-first order rate constants for permanganate consumption

| catalyst | Control | TEA | TBA | PTPP |
|---|---|---|---|---|
| $k$ (min$^{-1}$) | 0.0475 | 0.0424 | 0.0408 | 0.0791 |
| $r^2$ | 0.9857 | 0.9926 | 0.9962 | 0.9927 |

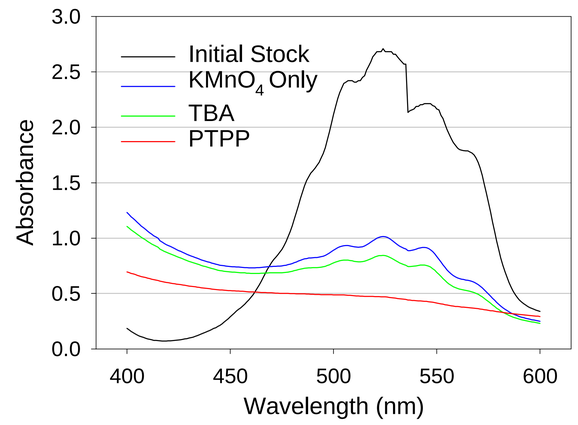
## Solubility Enhancement of TCE with PTC

Kinetic batch experiments, looking at TCE increase in solution with time as a function of the additives, showed no significant difference in TCE concentration for the first 30 minutes, as compared to trials without PTCs (control) .



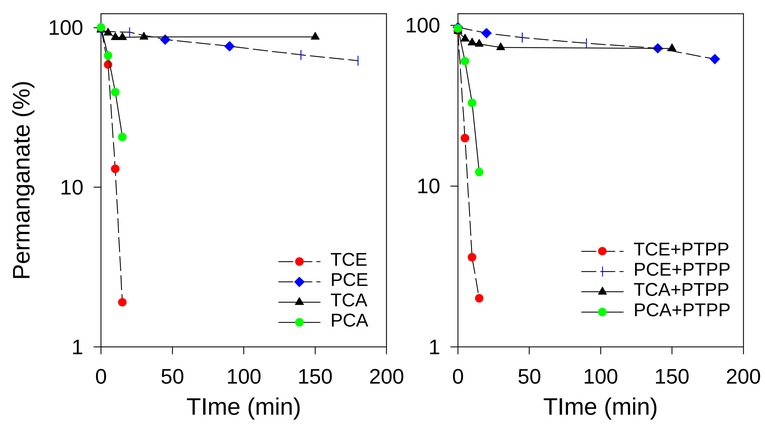

## Column Experiments

Effluent from the column residually saturated with TCE was monitored with UV-Vis spectrometer to quantify $MnO_4^-$ consumption. The large interfacial area speeds up not only the dissolution of TCE into aqueous phase but also the transfer of $MnO_4^-$-catalyst pair into TCE.




## Enhanced Oxidation in Pure / Binary DNAPL

Kinetic batch experiments with selected DNAPL (Table 3) and their mixtures (1:1, v/v) were performed in test tubes to assess reaction rates with the PTPP. The disappearance of $MnO_4^-$, which was evidence of the oxidative decomposition of DNAPLs, was quantified by capturing digital images of the tubes. This rapid photographic monitoring approach was validated by comparison with an UV-Vis spectrophotometer method.

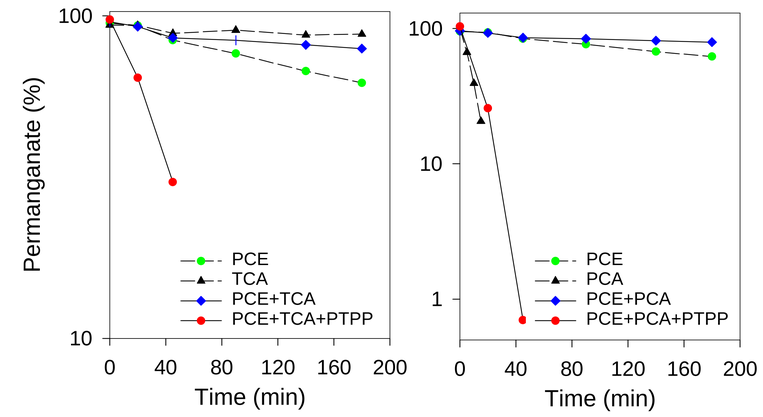



Due to their high extraction capabilities for catalyst-$MnO_4^-$ ion pairs, TCA and PCA appeared to increase the $MnO_4^-$ consumption significantly when they were mixed with TCE or PCE. The increase in consumption rates with PTPP was most remarkable with a mixture of PCE and TCA.

Table 3. Characteristics of selected chlorinated DNAPLs.

| DNAPL | Formula | Mol.wt. | $S_W$[a] | Density[a] | $e$[a] | $K_{E\text{-NBu4Br}}$[b] |
|---|---|---|---|---|---|---|
| TCE | $ClCH{=}CCl_2$ | 131.39 | 1101 | 1.48 | 3.39 | 0.2 |
| PCE | $Cl_2C{=}CCl_2$ | 165.83 | 260 | 1.50 | 2.27 | n.a. |
| TCA | $ClCH_2\text{-}CHCl_2$ | 149.32 | 4439 | 1.44 | 7.19 | 8.6 |
| PCA | $Cl_2CH\text{-}CHCl_2$ | 167.85 | 3009 | 1.49 | 8.50 | 145 |

Mol. wt. (molecular weight, g/mole), a; $S_W$ (solubility in water, mg/L), specific density and $e$ (dielectric constant) from CRC (1999), b; $K_{E\text{-NBu4Br}}$ (extraction constant of ion pair with tetrabutylammoniumbromide) from Bränström (1976).



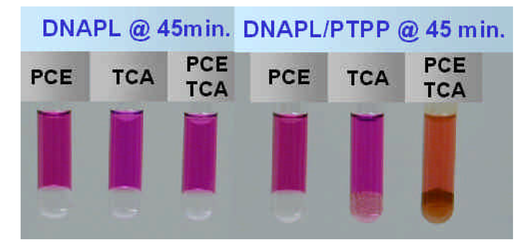




Table 4. Pseudo-first order rate constants for $MnO_4^-$ consumption (min$^{-1}$)

| DNAPL | | 2nd DNAPL | | PTC (PTPP) | 2nd DNAPL | |
|---|---|---|---|---|---|---|
| | | TCA | PCA | | TCA | PCA |
| TCE | 0.102 | 0.0459 | 0.0749 | 0.124 | 0.145 | 0.155 |
| PCE | 0.0012 | 0.0007 | 0.0066 | 0.0012 | 0.0112 | 0.0407 |
| TCA | 0.0004 | - | | 0.0009 | | |
| PCA | 0.0435 | - | | 0.0561 | | |

## Conclusion

- PTCs increased the rate of TCE decomposition by catalyzing permanganate oxidation in the organic phase.
- PTCs might be useful in field situations where contaminants occur as a mixture of DNAPLs when one component is effectively oxidized by $MnO_4^-$ and the other is capable of extracting the PTC from the aqueous phase.
- There is significant potential for testing this scheme under field conditions.

## Selected Reference

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