Chapter 4

OXIDATION OF DNAPL MIXTURES USING POTASSIUM PERMANGANATE WITH A PHASE-TRANSFER-CATALYST: KINETIC RESULTS FROM A DIGITAL PHOTOGRAPHIC MONITORING METHOD

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Introduction

There has been considerable interest in the use of potassium permanganate for the in-situ destruction of chlorinated solvents. Proof-of-concept studies in the field have demonstrated the potential for mineralizing chlorinated ethenes (e.g., TCE, PCE) occurring as a dissolved phase in aqueous solution or as a pure phase (Schnarr *et al.*, 1998). Laboratory studies have documented the reaction mechanisms, pathways, and kinetics (Yan, 1998; Yan and Schwartz, 1999).

At the present stage of development, significant opportunities remain in increasing the overall efficiency of flooding schemes and in speeding up the oxidation reaction. In some cases, the oxidation reactions are relatively slow in part because the reactions occur only in aqueous phases and typical chlorinated compounds, like TCE or DCE, are not particularly soluble in water. In other cases, the oxidation reactions themselves are slow for specific chlorinated ethenes (e.g., PCE) and chlorinated ethanes (e.g. TCA and PCA).

Our recent work has shown that phase-transfer-catalysts (PTCs) can speed up the overall rates of DNAPL oxidations. PTCs work by having the oxidation reaction take place in both the aqueous and DNAPL phases. A preliminary study on the effect of PTCs on TCE oxidations (Seol and Schwartz, 2000) showed that the rates of the oxidative decomposition increased considerably with the addition of PTCs. The goal of this present study is to extend understanding on the behavior of PTCs in mixtures of chlorinated solvents. Theory suggests that the rate of oxidation of DNAPLs can be even more enhanced in mixtures of solvents (e.g., TCE+PCA). This study was designed to test whether or not adding a PTC could enhance the oxidation rates of the most common chlorinated solvents, occurring either as pure phases or binary mixtures. The main hypotheses of this study are (1) that the overall oxidation rates of DNAPLs or DNAPL mixtures in solutions carrying a PTC would be noticeably higher than would otherwise be the case with MnO_4^- only in aqueous phases; and (2) that some organic solvents may be reactive with MnO_4^- in binary organic solvents even though they are recalcitrant in the aqueous phase. In other words, (2) examines whether the combination of a PTC with mixtures of DNAPLs could yield the meaningful oxidation of a compound like PCE that is slow to be oxidized in the aqueous phase.

The relative complexity of the experimental design pushed us to develop a rapid method for collecting data from a large number of kinetic experiments. Thus, another objective in this paper is to describe a digital image-based monitoring method for measuring MnO_4^- consumption. The approach is sufficiently general that it could be applied to a variety of kinetic experiments routinely conducted for the design of remedial systems.

Background

Permanganate Oxidation and Phase Transfer Catalysis

Generally, permanganate-oxidation reactions occur in the aqueous phase because the potassium permanganate is soluble and ends up dissolved only in the aqueous phase. Because of its polarity, MnO_4^- is not soluble in DNAPL phases. To transfer MnO_4^- into the DNAPL phase, a phase-transfer agent, like quaternary ammonium or phosphonium salt or crown ether can be employed (Starks, 1971). Phase transfer catalysis is a technique for facilitating reactions between two or more agents in two or more phases, when the reaction otherwise might be inhibited. The reaction works by complexing MnO_4^- with a PTC. The DNAPL phase can extract the association of ion and PTC, called an ion pair (Bränström, 1976) out of the aqueous phase. PTCs distribute themselves between aqueous and organic phases, form ion pairs with reactive anions (e.g. MnO_4^-), and bring them into a common (organic) phase in a form suitable for reactions.

The reaction of an organic compound with MnO_4^- in the presence of a PTC (Figure 4.1) involves two reaction steps. The extraction step partitions the ionic pairs into the nonaqueous phase (Eq. 4.1). The intrinsic displacement reaction (Eq. 4.2) attaches the MnO_4^- to the organic reactant;

$$[Q^+X^-]_{org} + K^+_{aq} + MnO^-_{4\,aq} \longleftrightarrow [Q^+MnO^-_4]_{org} + K^+_{aq} + X^-_{aq} \quad (4.1)$$

$$RX_{org} + [Q^+MnO^-_4]_{org} \longleftrightarrow RMnO_{4\,org} + [Q^+X^-]_{org} \quad (4.2)$$

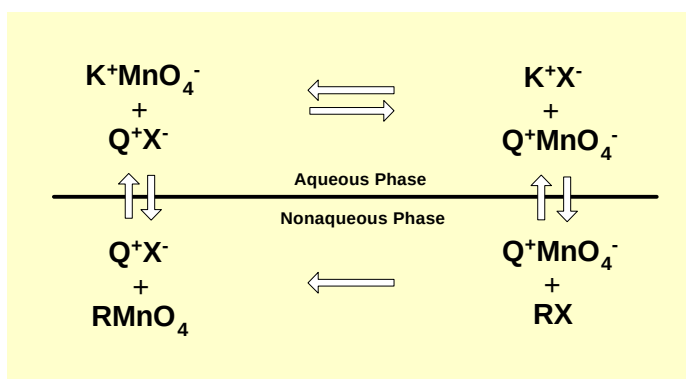

Figure 4.1. Schematic representation of phase-transfer-catalyzed MnO_4^- displacement on chlorinated organic solvents

where R is the organic reactant (e.g. TCE) with a leaving group, X (e.g. Cl^-) and Q^+ is the quaternary cation as a PTC.

The ability of a nonpolar solvent to extract ion pairs from an aqueous phase is traditionally represented by an extraction constant, K_E, (Karaman *et al.*, 1984), which can be experimentally determined using solubility data with Eq. 4.3;

$$K_E = \frac{\text{solubility of } QMnO_4 \text{ in organic solvent (M)}}{(\text{solubility of } QMnO_4 \text{ in water})^2 \ (M^2)} \qquad (4.3)$$

A rough estimate of extraction constants provides a useful guide for predicting the relative magnitude of the MnO_4^- transfer into different organic phases. The extraction constant appears to depend on the chemical structure (Bränström, 1976) and the dielectric constant of the organic solvent (Table 4.1).

Yan and Schwartz (1999) documented the rates of MnO_4^- oxidation for common chlorinated ethenes in an aqueous phase. In general, TCE is degraded much more rapidly than PCE; alkenes are oxidized much more rapidly than alkanes, which hardly react at all. Experiments involving MnO_4^- and PTCs have been performed so far only for a single component DNAPL system, where the organic phase is the target compound as well as the solvent (Seol and Schwartz, 2000). Although the rates of DNAPL oxidation have yet to be evaluated in detail, it is reasonable to assume that the kinetics of reactions involving MnO_4^- oxidation in the DNAPL phase would be different than in aqueous phases.

In our earlier work, we did not examine whether PTCs would be effective in speeding up the oxidation of pure-phase PCE. Indications were that PTCs would be of little help because the extraction capability for MnO_4^- ion pairs in PCE was small. In other words, the oxidation reaction in the PCE phase was negligible because only an infinitesimal amount of MnO_4^- was being transferred as the ion pair. Extractions, however, would be higher for a mixture of PCE and a chlorinated ethane, such as TCA or PCA, which is an excellent solvent for permanganate ion pairs. It is likely that a catalytic reaction system will work better in a mixture than a single component DNAPL, when one of the compounds is efficient in extracting MnO_4^- ion pairs into the mixture. Our experiments here will examine this issue in detail with tests of DNAPL mixtures.

Digital Image-based Monitoring Method

The conventional approach for measuring MnO_4^- concentrations in aqueous solutions relies on UV-Vis spectrophotometry. The analytical procedure requires several experimental steps, including solution transfer from some reaction vessel to a cuvette and scanning a certain range of wavelengths. During the transfer step and one or two minutes of scanning, reactions are still underway. There are obvious difficulties then in simultaneously handling a number of samples with rapid reaction rates.

To overcome this problem, we have developed a quick quantification scheme for measuring the concentration of MnO_4^- in aqueous phases. This digital image-processing method provides the relative concentration of residual MnO_4^- indirectly as a function of the transmittance (T) of visible light. The transmittance is the ratio of the emerging light intensity (I) to the incident light intensity (I_o). It is logarithmically related to the absorbance (A) of light passing through the solution (Eq. 4.4).

$$A = \log\left(\frac{I_0}{I}\right) = -\log T \qquad (4.4)$$

The absorbance of light in a permanganate solution is directly proportional to the concentration of an absorbing species (e.g. MnO_4^-). This effect is known as the Beer-Lambert Law;

$$A = a \cdot [C] \cdot l \qquad (4.5)$$

where $[C]$ is the concentration of the absorbing species in the solution, a is molar absorptivity, and l is the length of a light path. Therefore, the concentration can be obtained from the negative logarithmic relationship with the transmittance as;

$$[C] = -s \cdot \log T + b \qquad (4.6)$$

where s is a slope of relationship between the transmittance and the concentration and b is an intercept. Both parameters, s and b are estimated from the calibration of standards.

MnO_4^- exhibits a maximum absorbance at the wavelength of 525nm (Stewart, 1965), which falls in the range (500-578 nm) for green in the visible spectrum. Thus, the transmittance of green light through the potassium permanganate solution will be influenced mostly by the absorbance by MnO_4^-. The brightness level, in other word, the luminance in the green channel for a selected area in an image can then be interpreted

Table 4.1. Characteristics of selected chlorinated DNAPLs.

DNAPL	Formula	Mol.wt.	S_W[a]	Density[a]	ε[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 ε (dielectric constant) from CRC (1999), b; $K_{E\text{-NBu4Br}}$ (extraction constant of ion pair with tetrabutylammoniumbromide) from Bränström (1976).

Table 4.2. Chemical properties of selected catalyst- MnO_4^- ion pairs.

Name/PTC	Abbr.	Mol. wt.	S_w [a]	S_o [a]	$\log K_E$ [b]
pentyltriphenylphosphonium ,$CH_3(CH_2)_4P(C_6H_5)_3$	PTPP	333.45	2.4×10^{-4}	1.46	7.40

Mol. wt.; g/mole, S_w; solubility (M) in water, S_o; solubility (M) in methylene chloride, a; Karaman, *et al.*, (1984), b; calculated with Eq. (8) in Seol and Schwartz (1999).

as the transmittance of light in the green spectral range. The luminance level in the green channel provided by image processing software can be compared with those of standards and converted to some concentration of MnO_4^- using equation (Eq. 4.6). However, the concentration of standards would be represented on a relative scale as would the unknowns.

Materials and Methods

Four chlorinated organic solvents, trichloroethylene (TCE, 99.5%, Aldrich), 1,1,2-trichloroethane (TCA, 98%, Acros), tetrachloroethylene (PCE, 99%, Aldrich), 1,1,2,2-tetrachloroethane (PCA, 99.5%, Acros) were selected. The solvents vary in their molecular structures, extraction constants (K_E) and dielectric constants (ε) (Table 4.1), which indicate the variability in their reactivity with MnO_4^- and the solubility of the catalyst- MnO_4^- ion pair in the organic phase.

The study used pentyltriphenylphosphonium bromide (PTPP, 99.8%, Aldrich) as the PTC for the oxidation of pure or two-component DNAPLs (Table 4.2). The selection of PTPP was based on results from Seol and Schwartz (2000), which showed it to be the most efficient catalyst for the oxidation of pure-phase TCE. The concentration of the PTC in all experiments was kept below its aqueous phase solubility in order to avoid any potential problems of aggregation or precipitation of catalyst-permanganate salts.

Kinetic batch experiments were performed in duplicate in test tubes with selected chlorinated solvents and their mixtures (1:1, v/v). The $KMnO_4$ solution (1.25 mM) was prepared by dissolving $KMnO_4$ crystals in a phosphate-buffered solution (0.1 M, KH_2PO_4 : K_2HPO_4, pH=8). A catalyst stock solution (3.78mM) was also prepared with the same buffer solution. 3.0 mL of $KMnO_4$ solution was added over the DNAPL phase (1.0 mL) in each tube. 0.1 mL of concentrated catalyst solution was then added to bring the final catalyst concentration to about 10 mole % of the $KMnO_4$. All test tubes in this experiment were separated into two groups, one for the TCE group and the other for the PCE group. Each group was further divided into two

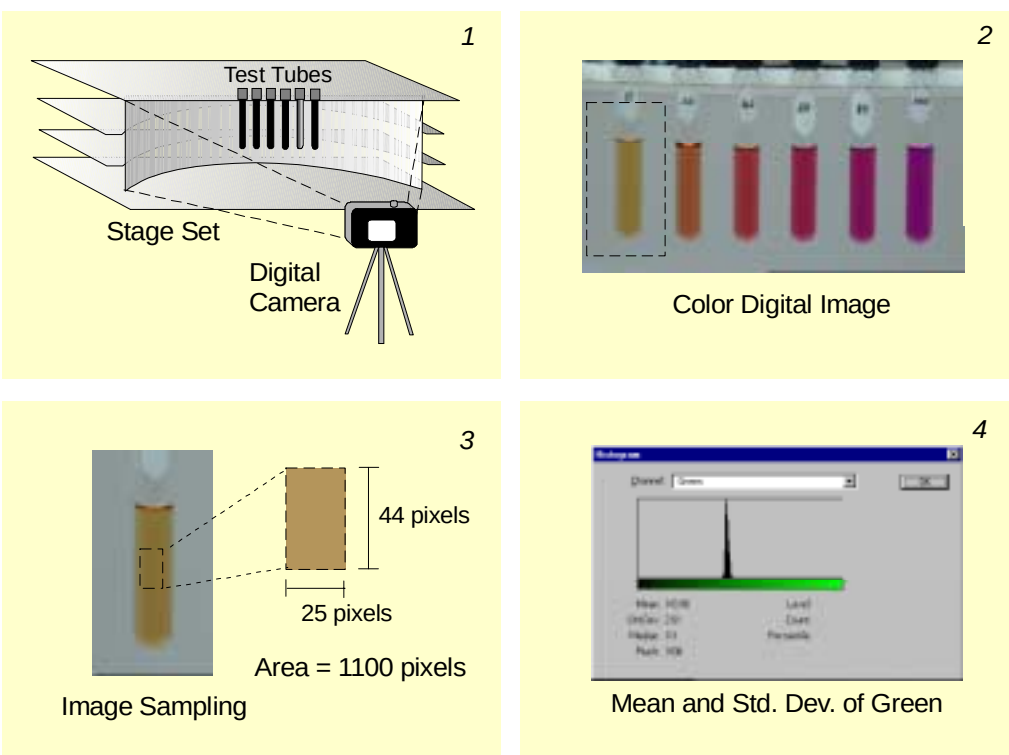

Figure 4.2. Schematic procedure of digital photographic approach for rapid measurements of MnO_4^- concentration.

sets of tubes, one of which contained PTPP as a PTC and the other which did not. Each set consisted of five tubes containing three single phases; (TCE or PCE), TCA and PCA, and two mixtures; (TCE or PCE)+TCA and (TCE or PCE)+PCA, respectively. All the tubes were mechanically agitated on a reciprocating platform shaker at 200 rpm. As the MnO_4^- disappeared, solutions changed in color from purple to clear. This pattern of change was recorded by taking digital photographs of each set of test tubes at several pre-selected times. Digital images were taken using a Nikon Coolpix® 950 Digital Camera under ambient light. In order to minimize any interference, test tubes were placed in the center of a rounded screen set, which was made of non-reflective white panels (Figure 4.2). The positions of tubes, exposure and shutter speed for camera were optimized from a series of test shots. The same conditions were applied to the entire set of digital photographs. The digital photographs were taken at 0, 5, 10, 30, and 150 min for TCE group and at 0, 20, 45, 90, 140, and 180 min for PCE group.

Adobe Photoshop® was used to obtain the brightness level in the green channel, in other word, transmittance in green, for an 1100-pixel square in the center of each tube image (Figure 4.2). Due to a slight variation in the brightness over the course of the experiments, a small correction was applied to the data to maintain consistency in the brightness. Standards for the residual permanganate concentration (%) were prepared by mixing the initial permanganate solution (100 %) with a solution (0 %) in which MnO_4^- was used up through the oxidation reaction. Calibration of the standards showed a linear relationship between log [transmittance in green] and the residual permanganate concentration (%) (Figure 4.3). For some cases where there were significant reactions in the DNAPL phase, diffusive transfer of reaction products from the organic phase caused the aqueous phase to become dark brown and cloudy with suspended particles. Because this effect resulted in an abnormally low transmittance in green, the image-based monitoring scheme couldn't be used once these products started to accumulate and affected the brightness. Fortunately, this problem tended to develop midway through an experiment so that the rate of MnO_4^- loss could be estimated using early-time data that were unaffected by the formation of particles.

The image-based monitoring approach was validated using a kinetic batch experiment with TCE and MnO_4^-, where the MnO_4^- concentration was monitored using the conventional analytical approach (UV-Vis spectrophotometer) as well as the photographic monitoring. Two sets of four test tubes were prepared in the same way as described above. All the tubes were shaken for only 2.5 minutes in every five minutes. One tube from each set was removed from the shaker every five minutes for measurements via digital image capture and UV-Vis spectrometer. Spectrophotometric measurements for MnO_4^- concentration were performed as described in Seol and Schwartz (2000).

Results and Discussion

Validation of Digital Image-based Monitoring Method

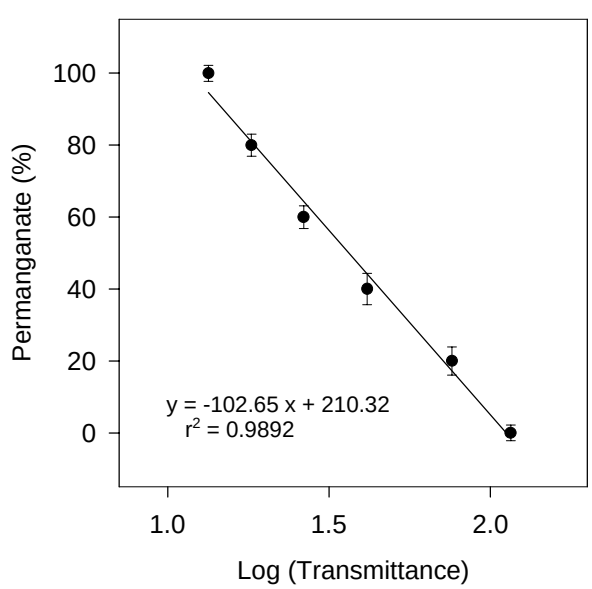

Figure 4.3. Calibration of MnO_4^-concentration with the transmittance of visible light at the wavelength of green, determined using Adobe Photoshop®

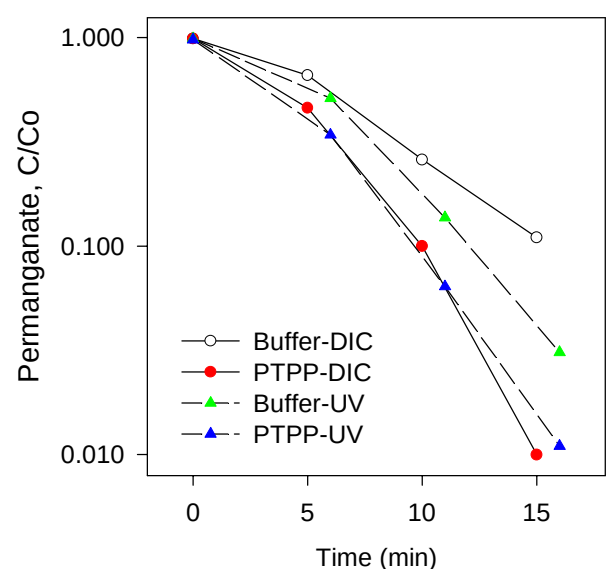

Figure 4.4. Comparison of results from the digital image capture technique (DIC) for the rapid detection of MnO_4^- consumption with absorbance measurements from a UV-Vis spectrophotometer (UV)

One way to quantify reaction rates in a $KMnO_4$-DNAPL system is to monitor the change in concentration of MnO_4^- in the aqueous phase. As mentioned, the concentration of MnO_4^- can be determined simply by observing how the purple color disappears. We tested this photographic approach by comparing results from the digital image method with conventional spectrophotometric measurement. It is worth recognizing that the spectrometric method may underestimate the concentration because the scanning starts from the upper wavelength for a certain range of wavelengths. Absorbance at the lower wavelength (418 nm) for the reaction product (MnO_2) could be higher than what it should be at the time when absorbance at the higher wavelength (526nm) for the reactant (MnO_4^-) is measured because the reaction has been progressing during the scanning time.

Generally, the photographic estimates of MnO_4^- consumption agreed reasonably well with the results obtained from the UV-Vis spectrometer (Figure 4.4), even though the former were slightly higher than the latter. Pseudo-first order rate constants (*k*) were calculated with the relative concentrations (C/C_o) during the first 5 or 10 minutes of the reaction time (Table 4.3). The digital-photographic monitoring approach appears to provide a fast and inexpensive alternative to the conventional spectrophotometric analysis.

Table 4.3. Comparison of pseudo-first order rate constants (min^{-1}) for MnO_4^- consumption obtained with digital image capture (DIC) and UV-Vis spectrophotometer (UV).

	DIC	UV
Control	0.0365 - 0.0539	0.0484 - 0.0716
PTPP	0.0671 - 0.0932	0.0777 - 0.102

Values obtained with the data from the reaction time of 5 and 10 minutes

Rates of Oxidation of Unmixed DNAPLs

The first series of experiments looked at the rates of oxidation of TCE, PCA, PCE, and TCA by themselves. The experiments were monitored photographically, as described above, to obtain rates of the permanganate consumption. The most rapid utilization of MnO_4^- was evident with TCE and PCA (Figure 4.5). The slow to negligible decline of MnO_4^- in test tubes containing PCE and TCA provided indications of near-zero oxidation rates (Figure 4.5). We fitted pseudo-first order rate constants to obtain the estimates of MnO_4^- consumption. The rates of MnO_4^- consumption were TCE > PCA > PCE > TCA (Table 4.4).

Some of these kinetic results are in agreement with data from Yan and Schwartz (1998). PCE degradation is slower than TCE because the deficiency of electrons in the carbon double bond of PCE is too high for electrophile addition (Burdon and Tatlow, 1958). However, this model does not explain why PCA should be oxidized more rapidly than TCA. Reportedly, the permanganate oxidation of alkanes proceeds via rate-determining carbon-hydrogen bond scission to activate carbon (Stewart and Spitzer, 1978; Wiberg and Fox, 1963). It has been conjectured that the activation of carbon was easier for PCA than TCA even though speculation on the reaction mechanism is beyond the scope of this study.

When the reactions with the set of unmixed DNAPLs were catalyzed with PTPP, there was visual evidence that MnO_4^- was being transferred and reacting in the DNAPL phases. The normally clear and colorless organic phase became purple colored. Quantitatively, this change was more evident with TCA and PCA, and to a lesser extent with TCE. The color of the PCE did not appear to change. As the oxidation reaction progressed, the purple solvents gradually changed in color to light brown, pointing to the oxidation of pure-phase DNAPLs. This second color change was most evident in TCE and PCA, while TCA remained a purple color.

As before, the digital monitoring looked specifically at color changes in the aqueous phase for direct comparison with noncatalyzed systems. The same relative order in MnO_4^- consumption was observed with small increases (Table 4.4). The increases were most obvious in test tubes containing TCE and PCA, which already exhibited large reaction rates without the PTC. Also, the increases were proportionally large for the alkanes as compared with the alkenes. These results show that MnO_4^- promoted oxidative reactions with the alkanes because these compounds were able to extract significant quantities of the MnO_4^--catalyst ion pairs. The rates of MnO_4^- consumption were barely increased for PCE and TCA with the addition of the PTC due to the extremely low extraction capability or the lack of reactivity with MnO_4^- in the aqueous phase.

Rates of Oxidation in Binary DNAPL Mixtures

The rates of MnO_4^- consumption in DNAPL mixtures without the PTC were about the same as the weighted average

Table 4.4. Pseudo-first order rate constants for MnO_4^- consumption (min^{-1}) calculated from the linear portion of the MnO_4^- concentration (%)–time curves.

DNAPL		2nd DNAPL	
		TCA	PCA
TCE	0.102	0.0459	0.0749
PCE	0.0012	0.0007	0.0066
TCA	0.0004	-	-
PCA	0.0435	-	-

Phase Transfer Catalyst; PTPP

DNAPL		2nd DNAPL	
		TCA	PCA
TCE	0.124	0.145	0.155
PCE	0.0012	0.0112	0.0407
TCA	0.0009	-	-
PCA	0.0561	-	-

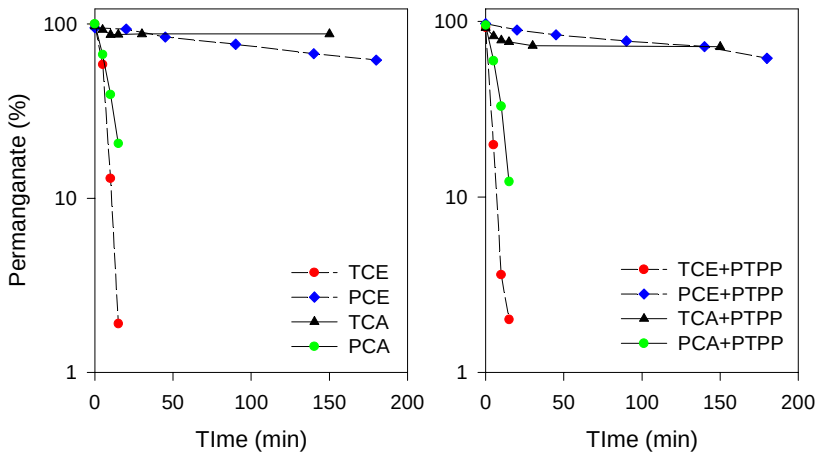

Figure 4.5. Degradation of selected chlorinated DNAPLs with and without PTPP, as represented by MnO_4^- consumption with time

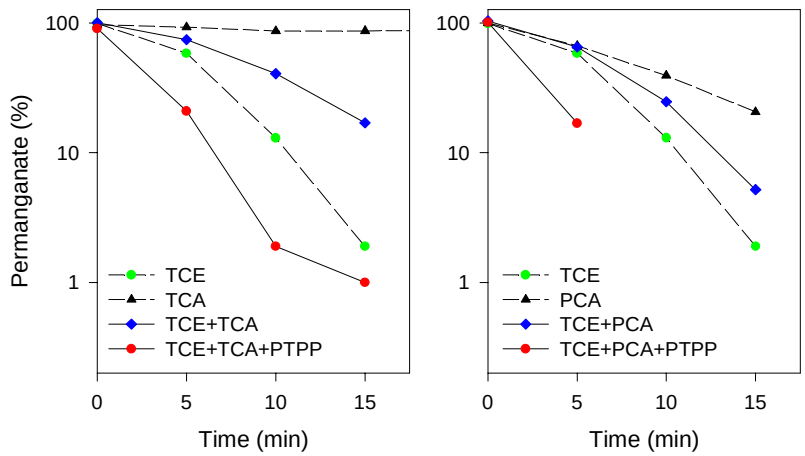

Figure 4.6. Degradation of TCE, TCA, PCA and their mixtures with and without PTPP, as represented by MnO_4^- consumption with time

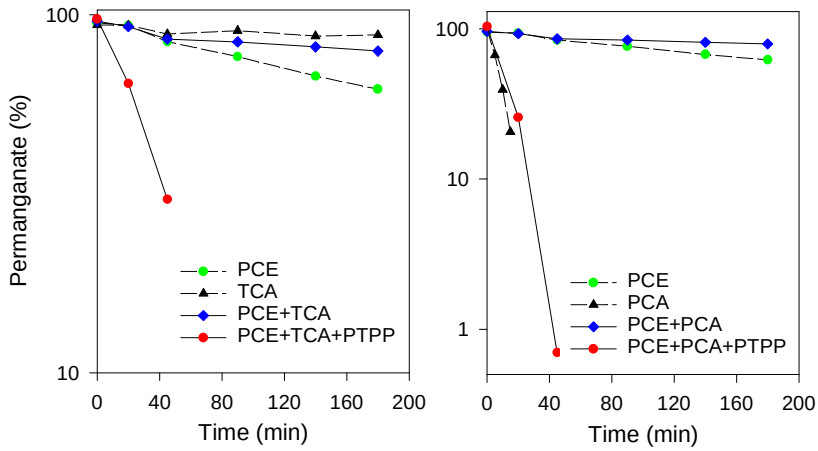

Figure 4.7. Degradation of PCE, TCA, PCA and their mixtures with and without PTPP, as represented by MnO_4^- consumption with time

of consumption for the single components. For example, the MnO_4^- consumption rates for TCE and PCA were 0.102 and 0.0435 min^{-1} (Table 4.4). The consumption rate for the 1:1 mixture of TCE and PCA was 0.0749 min^{-1} (Table 4.4). It might be caused by reduced dissolution of reactive components (e.g. TCE) into the aqueous phase only where the permanganate reaction could take place.

When the PTC was added to the system to oxidize the DNAPL, the consumption rates of MnO_4^- increased (Figure 4.6). The rates with the various TCE mixtures were increased two or three times as compared to those without PTPP (Table 4.4). The observed rate for TCE+TCA (0.145 min^{-1}) was greater than that of pure TCE (0.124 min^{-1}). The presence of TCA enhances the ability of the mixture to extract MnO_4^--PTPP ion pairs for the reaction of TCE in the DNAPL phase, even though TCA itself does not have a fast oxidation rate. PCA not only was effective in extracting the ion pair but also tended to be oxidized at a relatively rapid rate. Thus, the MnO_4^- consumption rate was highest (0.155 min^{-1}) when one component (e.g., PCA) of the mixture especially promoted the extraction of the PTC and both components had relatively large oxidation rates.

The increase in the consumption rates of MnO_4^- with PTPP was most remarkable with the mixture of PCE and TCA (Figure 4.7), considering that neither compound by itself reacts with MnO_4^-, even with the catalyst added. Based on the results from pure phase experiments, it was believed that TCA barely reacts with MnO_4^- in either the aqueous or the TCA phase. Therefore, the large increase in the consumption rates for the PCE mixtures with the catalyst suggested that PCE became more reactive to MnO_4^- in the DNAPL phase.

Conclusions

Digital photographic monitoring provided a useful approach for estimating the rates of MnO_4^- utilization in test-tube experiments. This approach appears most useful when semi-quantitative results are sufficient for comparison among several alternative designs for remedial systems. Our tests showed the method to be comparable with a more rigorous standard method. This study also showed that PTCs are capable of transferring MnO_4^- into the DNAPL phase where it is available to oxidize the organic phase. In a mixture of DNAPLs, reaction rates are enhanced when one component is effectively oxidized by MnO_4^- and the other is capable of extracting the PTC from the aqueous phase. Thus, there is hope of oxidizing a compound like PCE in a mixture because apparently PCE is reactive in the DNAPL phase, if MnO_4^- can be provided.

The results of this study suggest that PTCs might be useful in field situations where contaminants occur as a mixture of DNAPLs. Although PTCs increase the effectiveness of MnO_4^- as an oxidant for organic contaminants, there is still a need for research on reaction mechanisms and pathways. The research outcome would provide a better understanding of the potential applicability of this oxidative approach for remedial actions and any potentially adverse impacts of possibly hazardous intermediate or final products.

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