



Cosolvent-enhanced chemical oxidation of perchloroethylene by potassium permanganate

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Abstract

A laboratory study was conducted to examine cosolvent-enhanced in-situ chemical oxidation (ISCO) of perchloroethylene (PCE) using potassium permanganate (KMnO₄). The conceptual basis for this new technique is to enhance permanganate oxidation of dense non-aqueous phase liquids (DNAPLs) with the addition of a cosolvent, thereby increasing DNAPL solubility while avoiding mobilization. Among 17 cosolvent candidates screened, tertiary butyl alcohol (TBA) and acetone were the most stable in the presence of KMnO₄, both of which increased PCE aqueous solubility significantly, and therefore are suitable to be used as cosolvent in this study. Batch experiments indicated that the second-order rate constant for PCE oxidation by potassium permanganate was $0.043 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$ in the purely aqueous (no cosolvent) solution. In the presence of 20% cosolvent (volume fraction = $f_c = 0.2$), the rate constant decreased to $0.036 \pm 0.003 \text{ M}^{-1} \text{ s}^{-1}$ with TBA and to $0.031 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$ with acetone. However, in the presence of free-phase PCE, chloride ion concentration from PCE oxidation in acetone/water solutions ($f_c = 0.2$) was about twice that in aqueous solutions, indicating that the increase in PCE solubility more than compensated for the decrease in reaction rate constant, such that the oxidation efficiency of PCE was increased with cosolvent. A complete chlorine mass balance was observed in the aqueous system, whereas approximately 70% was obtained in TBA/water or acetone/water ($f_c = 0.2$). In soil columns containing residual DNAPL and subjected to isocratic flushing with step-wise increases in f_c cosolvent, TBA at $f_c = 0.2$ resulted in PCE mobilization, whereas acetone at $f_c \leq 0.5$ did not. Therefore, although both TBA and acetone exhibit similar solubility enhancements, acetone may be a better solvent choice for use in in-situ remediation of DNAPL source zones.

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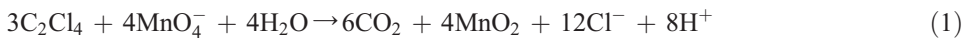
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1. Introduction

Innovative and aggressive technologies are needed for treatment of a large number of sites contaminated with chlorinated hydrocarbons in the United States (Stroo et al., 2003). Technologies that are suitable for removal or destruction of chlorinated hydrocarbons, occurring as dense non-aqueous phase liquids (DNAPLs) in source zones, include in-situ chemical oxidation (ISCO) and in-situ cosolvent flushing; both of these technologies have been tested at the lab and field scales (AATDF, 1997; USEPA, 1998). Fenton's reagent, ozone, permanganate, and persulfate have been explored as chemical reagents for ISCO with all but persulfate applied to chlorinated hydrocarbons, including chlorinated alkenes such as perchloroethylene (PCE) (Chung et al., 2002; DeHghi et al., 2002; Khan and Watts, 1996; Schnarr et al., 1998). All of these oxidants, except permanganate, are based upon non-selective free-radical mechanisms, and will react with a variety of reduced compounds in addition to the target contaminant. Permanganate, on the other hand, is selective toward the alkene functional group (C=C) in chlorinated alkenes (Singh and Lee, 2001).

Permanganate ion, (MnO_4^-) has recently been applied for in-situ oxidation of trichloroethylene (TCE) and PCE in laboratory and field studies (Hood et al., 2000a,b; Huang et al., 1999a,b, 2001, 2002; Lee et al., 2003; Li and Schwartz, 2003; MacKinnon and Thomson, 2002; Nelson et al., 2001; Schnarr et al., 1998; Siegrist et al., 1999; USEPA, 1998; Yan and Schwartz, 1999, 2000), and complete oxidation to chloride ion (Cl^-) and carbon dioxide has been observed, as described in Eq. (1).



The exact mechanisms and kinetics involved are not well established, but the reactions occur primarily in the aqueous phase (Huang et al., 1999a, 2002). Thus, the rate of oxidation is controlled by the rate at which aqueous phase PCE (or any other chlorinated alkene) reacts with permanganate ion, and the rate at which PCE in the aqueous phase is replenished by mass-transfer. Several kinetic studies concluded that PCE oxidation by potassium permanganate is second-order overall (i.e., first-order with respect to either PCE or permanganate) with a second-order rate coefficient of approximately $0.05 \text{ M}^{-1} \text{ s}^{-1}$ (Hood et al., 2000a,b; Huang et al., 2001; Seol and Schwartz, 2000; Yan and Schwartz, 1999, 2000). The oxidant concentration can be high (5% by mass) in field applications, thus PCE oxidation by permanganate in the aqueous phase may be fast (USEPA, 1998). Dissolution of DNAPL and desorption from the sorbed phase, the processes which replenish aqueous phase PCE during oxidation, are generally slow considering the low solubility of PCE (150–250 mg/L, Broholm et al., 1992; Ladaa et al., 2001; Schwarzenbach et al., 2002). Therefore, any approach that enhances the aqueous PCE concentration and the mass-transfer rate should also enhance chemical oxidation rates.

The ability of cosolvents to enhance dissolution and desorption of organic compounds is well known (Banerjee and Yalkowsky, 1988; Schwarzenbach et al., 2002; Yalkowsky et al., 1972a,b; Yalkowsky and Roseman, 1981). Cosolvent-enhanced solubility has led to the development and use of in-situ cosolvent flushing as a DNAPL source remediation technology (AATDF, 1997; ITRC, 2003). However, contaminants are not destroyed during in-situ flushing, thus requiring above ground treatment. On the other hand, a cosolvent can lower the interfacial tension (IFT) between DNAPL and the solution phase, which may lead to the DNAPL mobilization and contaminate the previously clean region (AATDF, 1997; ITRC, 2003; Reitsma and Kueper, 1997a,b). Therefore, the maximum amount of cosolvent applicable is limited by its DNAPL mobilization potential.

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