Production and accumulation of surfactants during the chemical oxidation of PAH in soil

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ABSTRACT

A soil contaminated with polycyclic aromatic hydrocarbons (PAH) was treated in laboratory slurry reactors with three chemical oxidants: (1) modified Fenton chemistry (MFC) with hydrogen peroxide (HP), (2) MFC with calcium peroxide (CP) (Cool-Ox™), and (3) sodium persulfate activated with Fe chelated using ethylenediaminetetraacetic acid (EDTA). A bioreactor served as a control. Samples of slurry filtrate were tested to quantify emulsification of PAH and concentrations of bulk surfactants, using the critical micelle dilution method. All three oxidants produced surfactants reaching levels above the critical micelle concentration (CMC), though the surfactants were removed at the end of treatment. The surfactants emulsified the PAH, and resulted in greater overall removal of 5- and 6-ring PAH than biodegradation alone. Treatment with CP-MFC resulted in the highest concentration of surfactants (four times the CMC), the most emulsification of PAH, and the highest removal of 5- and 6-ring PAH. None of the chemical treatments significantly reduced counts of culturable heterotrophic microorganisms.
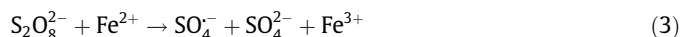
1. Introduction

In situ chemical oxidation (ISCO) is a powerful tool for the remediation of most organic contaminants (ITRC, 2005). Two of the most effective oxidants for treating petroleum hydrocarbons are: (1) modified Fenton chemistry (MFC) (also known as catalyzed peroxide propagations, or CPP), and sodium persulfate (SPS) (Osgerby, 2006). Traditional Fenton chemistry describes the catalysis by Fe^{2+} of hydrogen peroxide (H_2O_2, or HP) at low pH to form the hydroxyl radical ($\cdot OH$) (reaction (1)). Modified Fenton chemistry (MFC) produces $\cdot OH$ at quasi-neutral pH and with a greater ratio of hydrogen peroxide to iron, which is much more suitable for ISCO (ITRC, 2005). MFC also produces a weak oxidant (the perhydroxyl radical, $HO_2^\cdot$) and a reductant (superoxide, $O_2^{\cdot -}$), that also reacts with organic contaminants (ITRC, 2005; Watts and Teel, 2005; Osgerby, 2006). Liquid HP has a very short half-life (hours to days) in the subsurface (Watts and Teel, 2005). A longer-lasting source of HP is calcium peroxide (CaO_2 or CP) powder, that releases HP slowly as it dissolves in water (reaction (2)) at quasi-neutral pH (Northup and Cassidy, 2008). At a pH of 8, CP supports MFC over a period of weeks to months in the subsurface (Osgerby, 2006), although CP is exhausted within days in well-mixed laboratory reactors (Ndjou'ou and Cassidy, 2006).

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \quad (1)$$
$$CaO_{2(s)} + 2H_2O \rightarrow Ca(OH)_{2(s)} + H_2O_2 \quad (2)$$
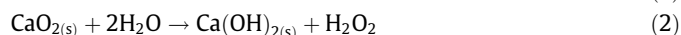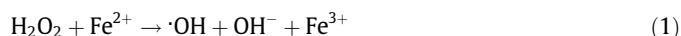
Sodium persulfate ($Na_2S_2O_8$ or SPS) is a promising new oxidant. Like CP, SPS has a half-life of weeks to months in the subsurface. Activation of the persulfate anion ($S_2O_8^{2-}$) forms the sulfate radical ($SO_4^{\cdot -}$), which is nearly as strong an oxidant as the hydroxyl radical (ITRC, 2005; Osgerby, 2006). Reaction (3) shows the activation of persulfate with Fe^{2+}. Other activation methods include high or low pH, high temperature, and hydrogen peroxide. At neutral to alkaline pH, persulfate also forms hydroxyl radicals via the reaction of the sulfate radical with water (reaction (4)) (ITRC, 2005; Liang et al., 2007).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Fe^{3+} \quad (3)$$
$$SO_4^{\cdot -} + H_2O \rightarrow \cdot OH + HSO_4^- \quad (4)$$

There is ample evidence of surfactant production accompanying the chemical oxidation of organic contaminants in soil. Chemical oxidation with MFC and SPS in laboratory and field normally results in foaming, a clear indication of surfactants. Many reports of treatment of organic contaminants in soil with MFC have made observations that could be attributed to surfactant production, though few have confirmed this with appropriate measurements. Yeh et al. (2003) reported concentrations of trichloroethylene above its aqueous solubility during treatment with MFC. Bogan et al. (2003) treated polycyclic aromatic hydrocarbons (PAH) with MFC, and found that adding vegetable oil enhanced the removal of high molecular

weight (i.e., 5- and 6-ring) PAH. They attributed this to the preferential partitioning of the high molecular weight PAH into the vegetable oil, followed by oxidation. However, an alternative explanation is that surfactants produced during oxidation of vegetable oil and/or PAH preferentially increased the presence of the 5- and 6-ring PAH in the aqueous phase, thereby enhancing their extent of oxidation. Nam et al. (2001) showed that MFC oxidation of PAH followed by biodegradation resulted in 20–60% greater removal of 5- and 6-ring PAH compared with biodegradation alone. This could be explained by increased bioavailability of high molecular weight PAH from the production of surfactants. Finally, Kakarla and Watts (1997) and Watts and Stanton (1999) observed that desorption and oxidation of petroleum hydrocarbons increased with increasing doses of HP during MFC treatment. The authors attributed this phenomenon to the production of perhydroxyl radicals from modified Fenton reactions, which they claimed promoted the desorption of hydrophic organic compounds from solid surfaces. However, they did not quantify surface tension or other indicators of surfactants, so their findings could also be attributed to surfactants produced from the MFC.

Ndjou'ou and Cassidy (2006) reported the production and temporary accumulation of surfactants accompanying the treatment of fuel oil-contaminated soil with MFC in laboratory slurry reactors. They tested both HP-based MFC (HP-MFC) and CP-based MFC (CP-MFC), using a commercially available product (Cool-Ox™). Low surface tension ($\sim$30 dynes cm^{-1} in filtrate compared with 72 dynes cm^{-1} in water) confirmed the production of surfactants. They also reported emulsification of the hydrocarbons. The authors hypothesized that the surfactants produced were the products of partial oxidation of hydrocarbons and/or native organics (e.g., carboxylic acids, aldehydes, ketones) having surfactant-like properties. The surfactants were eventually removed by further chemical oxidation and/or biodegradation.

Surfactant production during ISCO has important implications for treatment of hydrophobic compounds and non-aqueous phase liquids (NAPL). Because surfactants desorb and emulsify hydrophobic contaminants in soils, surfactant production can enhance ISCO treatment. Surfactants are sometimes added during ISCO, but added surfactants consume a significant amount of oxidant that could otherwise oxidize contaminants. Surfactant production accompanying ISCO also has the potential to mobilize contaminants in groundwater. This can be used to enhance contaminant recovery, but can also cause off-site migration. It is therefore critical that we develop a better understanding of surfactant production accompanying ISCO treatment of contaminated aquifers.

This study describes the chemical oxidation of soil contaminated with PAH in laboratory slurry reactors using; (1) HP-MFC, (2) CP-MFC (with a commercially available powder, Cool-Ox™), and (3) SPS activated with Fe chelated using ethylenediaminetetraacetic acid (EDTA). The goal of this work was to quantify surfactant production from the chemical oxidation of PAH, and its effect on the presence of hydrocarbons in the aqueous phase. The results show that surfactants were produced from partial chemical oxidation of PAH and/or native organics with all three oxidants tested, supporting the observations made by Ndjou'ou and Cassidy (2006) with fuel oil. This is the first study to show that oxidation with SPS produces surfactants.

2. Materials and methods

2.1. Materials

All chemicals used were reagent grade. Sodium persulfate, ferrous sulfate, ferric sulfate, and ethylenediaminetetraacetic acid (EDTA) were purchased from Merck (Gibbstown, New Jersey,

USA). The 18 individual PAH quantified were purchased from Aldrich (Milwaukee, WI, USA). Hydrogen peroxide (50%) was provided *gratis* by Solvay (Houston, Texas, USA). Cool-Ox™ was obtained from DeepEarth Technologies, Inc. (Alsip, IL, USA).

2.2. Contaminated soil

The soil used in these studies was collected from a former manufactured gas plant (MGP) site. The soil was first sieved to remove particles larger than 2 mm. The sieved soil was homogenized in a portable cement mixer for 2 h. Characterization of the homogenized soil was done according to methods of soil analysis (Klute, 1994), and the results of the analyses are listed in Table 1.

2.3. Slurry reactors

The slurry reactor setup was similar to that described by Ndjou'ou and Cassidy (2006). The 14 L glass vessels had a slurry volume of 10 L. Each reactor received 4 kg of soil (dry weight) and 8.5 L of water (including the oxidant solutions) for a final solids concentration of 40% (w v^{-1}). The central port in the lid housed the shaft of a mechanical mixer, which was set at 300 rpm to provide mixing throughout the reaction period. Volatile contaminant losses were quantified by collecting on powdered activated carbon (PAC) traps housed in a dedicated port in the reactor lid. The other two ports in the lid were closed, except for sampling, and the port housing the mixer was well sealed with a gasket and vacuum grease.

2.4. Doses of oxidants and nutrients

The MFC treatment with liquid HP was accomplished by adding the following to the reactor in sequence, 200 mg of EDTA, 1 g Fe(III) (as ferric sulfate), and 1 L of 50% HP. Iron is often added as Fe^{3+} instead of Fe^{2+} in MF applications to minimize the consumption of H$_2$O$_2$ according to reaction (1) and to make the process less exothermic. The EDTA chelates Fe^{3+}, which is otherwise quite insoluble at quasi-neutral pH. These doses are typical of *in situ* applications of MFC (Watts and Teel, 2005), and are similar to the doses used by Ndjou'ou and Cassidy (2006). For CP-MFC treatment, 500 g of Cool-Ox™ powder were added, which is also similar to that used by Ndjou'ou and Cassidy (2006). For persulfate oxidation, 25 g of EDTA, 125 g Fe(II) (as ferrous sulfate), and 620 g of sodium persulfate powder were added to the reactor. This resulted in a ratio of persulfate anion:EDTA:Fe(II) of 20:1:5, which is a commonly used ratio (Liang et al., 2004). The biological control was aerated with a diffuser stone to provide oxygen, and received ammonia and phosphate to provide a ratio of C:N:P of 30:10:1, which typically ensures sufficient nutrients for complete biodegradation of hydrocarbons in soil. No pH buffers were added to any of the reactors. The reactors were maintained in a temperature controlled room at 20 °C.

Table 1
Properties of the homogenized contaminated soil before treatment.

Analyte	Result	Units
Sand-sized particles	79	% (w w-1)
Silt-sized particles	20	% (w w^{-1})
Clay-sized particles	1	% (w w^{-1})
Native organic material (NOM)	0.1	% (w w^{-1})
Total carbonates	3	% (w w^{-1})
pH	7.9 ± 0.2 (12)[a]	
Culturable PAH-degrading microorganisms	6.8 ± 0.3 (6)	log CFU g^{-1} soil
Total PAH concentration	21,420 ± 360 (12)	mg kg^{-1}

[a] Mean ± standard deviation (number of measurements).