Activation of Peroxymonosulfate by Subsurface Minerals

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ABSTRACT

In situ chemical oxidation (ISCO) has become a widely used technology for the remediation of soil and groundwater. Although peroxymonosulfate is not a common oxidant source for ISCO, its chemical structure is similar to the ISCO reagents hydrogen peroxide and persulfate, suggesting that peroxymonosulfate may have the beneficial properties of each of these oxidants. Peroxymonosulfate activation in the presence of subsurface minerals was examined as a basis for ISCO, and possible reactive species (hydroxyl radical, sulfate radical, and reductants + nucleophiles) generated in the mineral-activated peroxymonosulfate systems were investigated. Rates of peroxymonosulfate decomposition and generation rates of reactive species were studied in the presence of three iron oxides, one manganese oxide, and three soil fractions. The iron oxide hematite-activated peroxymonosulfate system most effectively degraded the hydroxyl radical probe nitrobenzene. Reductants + nucleophiles were not generated in mineral-activated peroxymonosulfate systems. Use of the probe compound anisole in conjunction with scavengers demonstrated that both sulfate radical and hydroxyl radical are generated in mineral-activated peroxymonosulfate systems. In order to confirm the activation of peroxymonosulfate by subsurface minerals, one natural soil and associated two soil fractions were evaluated as peroxymonosulfate catalysts. The natural soil did not effectively promote the generation of oxidants; however, the soil organic matter was found to promote the generation of reductants + nucleophiles. The results of this research show that peroxymonosulfate has potential as an oxidant source for ISCO applications, and would be most effective in treating halogenated contaminants when soil organic matter is present in the subsurface.

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1. Introduction

In situ chemical oxidation (ISCO) has become an established technology for the treatment of contaminated soils and groundwater. Hydrogen peroxide (H_2O_2) and sodium persulfate ($Na_2S_2O_8$) are often the most effective ISCO oxidant sources for site remediation because of their robust chemistries; both oxidant sources can be activated to generate a variety of reactive oxygen species that promote the destruction of most contaminants of concern (Petri et al., 2011a, 2011b); however, both oxidant sources have limitations.

Catalyzed H_2O_2 propagations (CHP) is based on Fenton's reagent, which is the iron (II)-initiated decomposition of hydrogen peroxide to generate hydroxyl radical (OH•) (Walling, 1975):

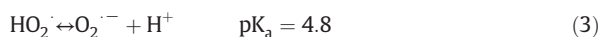$$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^{-} + Fe^{3+}. \tag{1}$$
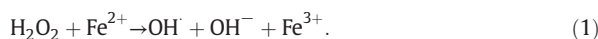
Most ISCO applications of CHP use 1 M to 4 M (3%–12%) hydrogen peroxide, which drives several propagation reactions to generate perhydroxyl radical (HO₂•), superoxide ($O_2^{\bullet-}$), and hydroperoxide anion (HO_2^-):

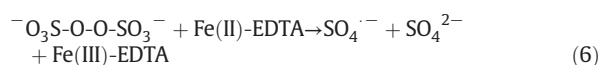$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{2}$$

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$$HO_2^{\cdot} \leftrightarrow O_2^{\cdot -} + H^+ \qquad pK_a = 4.8 \tag{3}$$

$$O_2^{\cdot -} + Fe^{3+} \rightarrow O_2 + Fe^{2+} \tag{4}$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+} \tag{5}$$

The reactive species generated in reactions 2, 3, and 5 provide a robust chemistry for CHP ISCO. Hydroxyl radical is a strong, nonspecific oxidant that reacts rapidly with a wide range of organic contaminants (Haag and Yao, 1992). Superoxide is a nucleophile and weak reductant. Although superoxide has traditionally been considered unreactive with organic contaminants in water (Asmus, 1988), recent findings demonstrate that in highly complex aqueous systems, including those containing hydrogen peroxide and solids, superoxide reactivity increases sufficiently to degrade halogenated organic compounds (Smith et al., 2004; Furman et al., 2009). Furthermore, the high flux of superoxide generated in CHP systems has surfactant properties; high concentrations of superoxide desorb hydrophobic contaminants from soils (Corbin et al., 2007) and enhance dense nonaqueous phase liquid (DNAPL) dissolution (Smith et al., 2006). Hydroperoxide is a strong nucleophile that can potentially degrade esters and halogenated contaminants (David and Seiber, 1999; Mitchell et al., 2014). Through the activity of hydroxyl radical, superoxide, and hydroperoxide anion, CHP provides a near-universal treatment matrix that degrades nearly all organic contaminants and provides enhanced contaminant desorption and DNAPL dissolution.

Persulfate is most frequently activated for ISCO by two mechanisms: transition metals and base. Many transition metals (e.g. Co^{2+}) catalyze the decomposition of persulfate to reactive oxygen species, but iron chelates, such as iron–ethylenediaminetetraacetic acid (iron–EDTA), are used most commonly because of their minimal toxicity and low potential for catalytic stalling (Liang et al., 2009). The initiation of persulfate decomposition through transition metals proceeds parallel to the Fenton initiation reaction (Ahmad et al., 2012) to generate sulfate radical ($SO_4^{\bullet -}$):

$$^-O_3S\text{-}O\text{-}O\text{-}SO_3^- + Fe(II)\text{-}EDTA \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Fe(III)\text{-}EDTA \tag{6}$$

Sulfate radical is a more selective oxidant than hydroxyl radical; it reacts readily with ring-activated aromatics (e.g., anisole) but is essentially unreactive with nitrobenzene (Buxton et al., 1988). However, sulfate radical is rapidly converted to hydroxyl radical by reactions with hydroxide and water (Hayon et al., 1972):

$$SO_4^{\cdot -} + OH^- \rightarrow OH^{\cdot} + SO_4^{2-} \tag{7}$$

$$SO_4^{\cdot -} + H_2O \rightarrow OH^{\cdot} + SO_4^{2-} + H^+ \tag{8}$$

The second and most common persulfate activation method for ISCO is base activation, which is initiated through base-catalyzed hydrolysis of persulfate (Furman et al., 2010):

$$^-O_3S\text{-}O\text{-}O\text{-}SO_3^- + H_2O \xrightarrow{OH^-} HO_2^- + 2SO_4^{2-} + H^+ \tag{9}$$
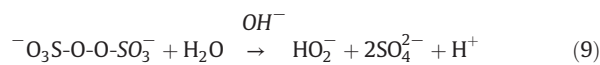
The hydroperoxide ion generated in reaction 9 then reduces another persulfate molecule to generate sulfate radical, and is itself oxidized to superoxide:

$$^-O_3S\text{-}O\text{-}O\text{-}SO_3^- + HO_2^- \rightarrow SO_4^{\cdot -} + SO_4^{2-} + O_2^{\cdot -} + H^+ \tag{10}$$
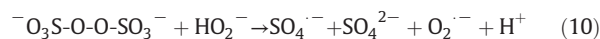
Similar to CHP, base-activated persulfate systems exhibit widespread reactivity with common contaminants due to the generation of oxidants (e.g., sulfate radical and hydroxyl radical) and reductants + nucleophiles (e.g., superoxide, alkyl radicals).

Although CHP and activated persulfate systems exhibit robust chemistries for ISCO applications, each has limitations. The primary shortcoming of CHP is the rapid decomposition of hydrogen peroxide in the presence of naturally occurring iron and manganese oxides in the subsurface (Xu and Thomson, 2010). The iron content of most soils and subsurface solids ranges from 1% to 20%, and averages 3% (Murad and Fischer, 1988). Goethite and hematite are the dominant crystalline iron oxides in temperate regions, and ferrihydrite is the primary component of amorphous iron oxides. The manganese content of soils and subsurface solids ranges from <20 mg/kg to >3000 mg/kg, with an average manganese content of 600 mg/kg (Fuller and Warrick, 1985). Birnessite is the dominant manganese oxide found in temperate regions. Although hydrogen peroxide stabilizers have recently been developed (Watts et al., 2007), the short lifetime of hydrogen peroxide in the subsurface due to activation by subsurface minerals remains a limitation in the use of CHP at many sites. Activated persulfate is limited by its often high total oxidant demand (TOD), high cost of sodium persulfate, and potential to stall, which may be caused by decreased pH as the reaction proceeds (Furman et al., 2011) or by the presence of trace minerals that appear to scavenge reactive oxygen species (Teel et al., 2007). Furthermore, activated persulfate formulations do not provide a sufficient flux of superoxide to desorb contaminants or dissolve NAPLs (Teel et al., 2009).

Peroxymonosulfate is an oxidant source that may have the beneficial properties of both hydrogen peroxide and persulfate. Peroxymonosulfate ($^-O_3S–O–O–H$) is a peroxygen that has a hydrogen moiety on one oxygen of the peroxide linkage and a sulfate moiety on the other. Peroxymonosulfate has been studied for water treatment (Anipsitakis and Dionysiou, 2003), but only one study to date has focused on peroxymonosulfate for ISCO: Rastogi et al. (2009) demonstrated that iron-catalyzed peroxymonosulfate degraded 2-chlorobiphenyl in sediment slurries. Peroxymonosulfate has potential for ISCO use because it is likely more stable than hydrogen peroxide in the presence of subsurface minerals, and it has the potential to generate more superoxide than activated persulfate. Like hydrogen peroxide and persulfate, peroxymonosulfate can be activated by transition metals, including Fe(II) and Co(II) (Anipsitakis and Dionysiou, 2004; Chan and Chu, 2009; Do et al., 2009; Rastogi et al., 2009; Ji et al., 2015). The purpose of this research was to 1) investigate