



Persulfate activation during exertion of total oxidant demand



Amy L. Teel, Farah C. Elloy, Richard J. Watts*

Department of Civil and Environmental Engineering, Washington State University, Pullman, WA, 99163-2910, USA

HIGHLIGHTS

- TOD is a standard treatability test for quantifying unproductive oxidant demand.
- Conventional wisdom: Organic matter is consumed before contaminants during ISCO.
- Contaminant destruction does occur during TOD exertion in persulfate ISCO systems.
- Contaminant loss is promoted by activation of persulfate by soil organic matter.

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ABSTRACT

Total oxidant demand (TOD) is a parameter that is often measured during in situ chemical oxidation (ISCO) treatability studies. The importance of TOD is based on the concept that the oxidant demand created by soil organic matter and other reduced species must be overcome before contaminant oxidation can proceed. TOD testing was originally designed for permanganate ISCO, but has also recently been applied to activated persulfate ISCO. Recent studies have documented that phenoxides activate persulfate; because soil organic matter is rich in phenolic moieties, it may activate persulfate rather than simply exerting TOD. Therefore, the generation of reactive oxygen species was investigated in three soil horizons of varied soil organic carbon content over 5-day TOD testing. Hydroxyl radical may have been generated during TOD exertion, but was likely scavenged by soil organic matter. A high flux of reductants + nucleophiles (e.g. alkyl radicals + superoxide) was generated as TOD was exerted, resulting in the rapid destruction of the probe compound hexachloroethane and the common groundwater contaminant trichloroethylene (TCE). The results of this research document that, unlike permanganate TOD, contaminant destruction does occur as TOD is exerted in persulfate ISCO systems and is promoted by the activation of persulfate by soil organic matter. Future treatability studies for persulfate ISCO should consider contaminant destruction as TOD is exerted, and the potential for persulfate activation by soil organic matter.

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1. Introduction

In situ chemical oxidation (ISCO) systems have become increasingly popular for treating contaminated soils and groundwater. The most common ISCO processes are catalyzed H_2O_2 propagations (CHP—modified Fenton's reagent), permanganate, and activated persulfate (Watts and Teel, 2006; Teel et al., 2011). Activated persulfate is the newest of the ISCO processes. Persulfate is relatively stable in the subsurface, and when activated, generates reactive oxygen species that can degrade most organic contaminants (Huang et al., 2005; Ahmad et al., 2012).

Oxidant sources used for ISCO (e.g., H_2O_2 , permanganate, and persulfate) do not always selectively treat hazardous contaminants because they also react with organic matter and reduced metals and minerals that are naturally present in soils and subsurface solids, which together result in an oxidant demand. A common analysis conducted for persulfate ISCO treatability studies is total oxidant demand (TOD); sodium persulfate concentrations are measured at time = 0 and time = 5 days, and TOD is defined as the mass of persulfate consumed over the 5 days per mass of soil (g/kg). Because the cost of sodium persulfate is relatively high, a TOD > 10 g/kg is considered too costly for field applications (Petri et al., 2011). Soil organic matter often comprises a significant fraction of the TOD (Haselow et al., 2003). Measurement of TOD has also been an essential first measurement in permanganate treatability studies because permanganate is rapidly consumed by soil organic

* Corresponding author. Department of Civil and Environmental Engineering, Box 2910, Washington State University, Pullman, WA, 99163-2910, USA.

E-mail address: rjwatts@wsu.edu (R.J. Watts).

matter before it oxidizes a significant mass of organic contaminants (Siegrist et al., 2001). Therefore, TOD evaluation is necessary in permanganate treatability studies to ensure the permanganate dose is sufficient to destroy contaminants. TOD evaluations for activated persulfate ISCO were adopted as an integral part of treatability studies because the consensus among practitioners was that persulfate TOD is exerted the same way as for permanganate; i.e., that persulfate preferentially oxidizes the soil organic matter, and contaminant oxidation proceeds only after the soil organic matter is consumed (Petri et al., 2011).

However, results of recent studies suggest soil organic matter may have a positive role during activated persulfate remediation rather than simply the negative effect of consuming persulfate (i.e. exerting TOD). Ahmad et al. (2010) demonstrated that soil organic matter activates persulfate at high pH regimes to generate reductants and nucleophiles. Soil organic matter is rich in phenolic moieties (Sposito, 2008), and Ahmad et al. (2010) hypothesized that the phenolic moieties of soil organic matter activate persulfate. Ahmad et al. (2013) subsequently investigated both phenol and phenoxide as activators of persulfate and concluded that only the phenoxide form activates persulfate. During persulfate activation, the phenoxide was oxidized to hydroquinones and other oxidation products. Quinones have also been found to activate persulfate to effectively degrade 2,4,4'-trichlorobiphenyl (Fang et al., 2013). Soil organic matter may activate persulfate in a manner similar to phenoxide and quinone activation, and therefore TOD may have beneficial effects on activated persulfate ISCO. The purpose of this research was to investigate the potential for contaminant destruction as TOD is exerted in activated persulfate systems over the most common testing period of 5 d.

2. Materials and methods

2.1. Materials

Ferriin indicator solution, sodium persulfate ($\geq 98\%$), and trichloroethylene ($\geq 99.5\%$) were purchased from Sigma-Aldrich (St. Louis, MO). Iron (II) sulfate (99.5%), mixed hexanes (95%, high-pressure liquid chromatography grade), nitrobenzene (99%), potassium dichromate (100%), sodium bicarbonate (100%), sodium hydroxide (98.6%), and sulfuric acid (98%) were obtained from J.T. Baker (Phillipsburg, NJ). Hexachloroethane (98%) and potassium iodide (99%) were purchased from Alfa Aesar (Ward Hill, MA). Double-deionized water (>18 M Ω cm) was obtained from a Barnstead Nanopure II Ultrapure system.

2.2. Soils

The ability to study only changes in soil organic carbon (SOC) without varying other physical characteristics cannot be achieved by collecting separate subsurface samples. Therefore, three horizons of a natural soil of low development collected from a road cut in the Palouse region of Washington state were used in the evaluation of TOD, the potential activation of persulfate, and the generation of reactive oxygen species. Although soil horizons represent different pedological strata, these different layers collected from a road cut provide an appropriate physical model of solids to evaluate the effect of SOC on persulfate activation. The Palouse loess used in this study was a soil of low development; i.e., minimal illuviation has occurred, and the three horizons sampled contained varied SOC, while the cation exchange capacity and mineralogy were essentially the same between the three horizons. The three soil horizons were collected 15 km north of Pullman, WA; each of the three horizons was air dried, and ground to pass through a 0.5 mm sieve. SOC content of the three horizons was measured using the

Walkley-Black method (Sparks, 1996). The three horizons had SOC values of 0.30% (low SOC), 0.75% (medium SOC), and 1.4% (high SOC). The soil horizons were characterized for particle size distribution by the pipette method (Gee and Bauder, 1986). The acid ammonium in darkness (AOD) method was used to analyze amorphous iron and manganese oxides (McKeague and Day, 1966). Total iron and manganese oxides were determined by citrate–bicarbonate–dithionite extraction (Jackson et al., 1986). Cation exchange capacity was determined by saturation with sodium acetate at pH 8.2 (SCS, 1986). The physical and chemical properties of the low, medium, and high SOC soil horizons are listed in Table 1. The soils for the positive controls (no SOC) were prepared by removing the SOC from the low, medium, and high SOC horizons by ignition at 400 °C for 16 h (Sparks, 1996).

2.3. Probe compounds

The probe compounds nitrobenzene and hexachloroethane (HCA) were used to detect reactive species generated in activated persulfate systems. Nitrobenzene ($k_{OH\cdot} = 3.9 \times 10^9$ M $^{-1}$ s $^{-1}$; $k_{SO_4^{\cdot-}} = \leq 10^6$ M $^{-1}$ s $^{-1}$) (Buxton et al., 1988; Neta et al., 1977) was used as a probe compound to detect hydroxyl radical (Furman et al., 2010). Hydroxyl radical (OH \cdot) is a strong, relatively nonspecific oxidant that reacts rapidly with $>98\%$ of U.S. EPA Priority Pollutants (Haag and Yao, 1992), and is the dominant oxidant in activated persulfate systems (Watts and Teel, 2006; Ahmad et al., 2010; Furman et al., 2011). HCA ($k_{e^-} = \sim 10^{10}$ M $^{-1}$ s $^{-1}$; $k_{OH\cdot} < 10^6$ M $^{-1}$ s $^{-1}$) (Afanassiev et al., 1979; Haag and Yao, 1992) was used to detect reductants + nucleophiles, such as superoxide (O $_2^{\cdot-}$), hydroperoxide anion (HO $_2^-$), and alkyl radicals (RH \cdot), without detecting oxidants such as hydroxyl radical (Furman et al., 2010). Trichloroethylene (TCE) ($k_{OH\cdot} = 4.0 \times 10^9$ M $^{-1}$ s $^{-1}$; $k_{e^-} = 1.9 \times 10^9$ M $^{-1}$ s $^{-1}$) (Haag and Yao, 1992; Buxton et al., 1988) was investigated to evaluate the destruction of a common subsurface contaminant that is reactive with hydroxyl radical and reductants + nucleophiles.

2.4. Experimental procedures

The TOD exerted by the low, medium, and high SOC soil horizons was determined by measuring the persulfate concentration in the presence of each soil horizon over 5 days:

$$\text{TOD (g/kg)} = [\text{persulfate}_{\text{Day 0}} (\text{g}) - \text{persulfate}_{\text{Day 5}} (\text{g})] / \text{mass of soil (kg)} \quad (1)$$

Table 1
Physical and chemical properties of low, medium, and high SOC soil horizons.

	Soil horizon		
	Low SOC	Medium SOC	High SOC
Sand (%)	21.2	23.8	24.4
Clay (%)	18.8	18.8	18.8
Silt (%)	60	57.5	56.9
Texture	Silt loam	Silt loam	Silt loam
Cation exchange capacity (cmol(+)/kg)	20	24	27
Organic carbon (%)	0.3	0.75	1.4
Extractable Mn (mg/kg)	330	310	300
Extractable Fe (mg/kg)	6000	5700	5600
Amorphous oxides			
Fe (mg/kg)	4720	4800	4780
Mn (mg/kg)	630	640	610
Crystalline oxides			
Fe (mg/kg)	3940	3870	3900
Mn (mg/kg)	280	250	260

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