



# Reactive oxygen species and associated reactivity of peroxymonosulfate activated by soluble iron species



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## ARTICLE INFO

### Keywords:

Peroxymonosulfate  
In situ chemical oxidation  
Soluble iron  
Chelated iron  
Hydroxyl radical  
Sulfate radical

## ABSTRACT

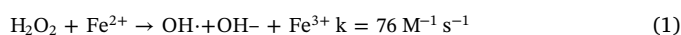
The activation of peroxymonosulfate by iron (II), iron (III), and iron (III)–EDTA for in situ chemical oxidation (ISCO) was compared using nitrobenzene as a hydroxyl radical probe, anisole as a hydroxyl radical + sulfate radical probe, and hexachloroethane as a reductant + nucleophile probe. In addition, activated peroxymonosulfate was investigated for the treatment of the model groundwater contaminants perchloroethylene (PCE) and trichloroethylene (TCE). The relative activities of hydroxyl radical and sulfate radical in the degradation of the probe compounds and PCE and TCE were isolated using the radical scavengers *tert*-butanol and isopropanol. Iron (II), iron (III), and iron (III)–EDTA effectively activated peroxymonosulfate to generate hydroxyl radical and sulfate radical, but only a minimal flux of reductants or nucleophiles. Iron (III)–EDTA was a more effective activator than iron (II) and iron (III), and also provided a non-hydroxyl radical, non-sulfate radical degradation pathway. The contribution of sulfate radical relative to hydroxyl radical followed the order of anisole > TCE > PCE > nitrobenzene; i.e., sulfate radical was less dominant in the oxidation of more oxidized target compounds. Sulfate radical is often assumed to be the primary oxidant in activated peroxymonosulfate and persulfate systems, but the results of this research demonstrate that the reactivity of sulfate radical with the target compound must be considered before drawing such a conclusion.

## 1. Introduction

The treatment of groundwater contaminated with biorefractory organic compounds remains difficult and expensive, even after decades of research and scale-up of advanced oxidation processes (AOPs). Ozone, ultraviolet light (uv)–ozone, and hydrogen peroxide–ozone have been used as ex situ processes to treat organic contaminants in industrial waste streams, dilute hazardous waste sources, and landfill leachates (Haas and Vamos, 1995). These waste streams are relatively easy to treat because of minimal mass transfer limitations. However, desorption of hydrophobic contaminants, dissolution of nonaqueous phase liquids (NAPLs), and diffusion through lower permeability strata are challenges for groundwater remediation schemes. Oxidant sources developed for the in situ chemical oxidation (ISCO) treatment of organic contaminants in soil and groundwater over the past 30 years include permanganate, hydrogen peroxide, and sodium persulfate (Watts and Teel, 2006). Each of these three oxidant sources has different reactivity with organic contaminants and longevity in the subsurface, which influences the efficacy of ISCO treatment.

Permanganate directly oxidizes organic contaminants, but is reactive only with alkenes and benzene derivatives substituted with ring-

activating groups, such as phenols and aniline (Siegrist and Urynowicz, 2001). Catalyzed H<sub>2</sub>O<sub>2</sub> propagations (CHP) is based on Fenton's reagent, in which the decomposition of hydrogen peroxide is mediated by iron (II) to generate hydroxyl radical (OH·) (Walling, 1975):



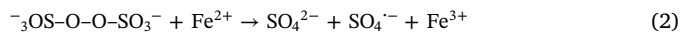
Hydroxyl radical is a strong oxidant that rapidly reacts with most organic contaminants at near diffusion-controlled rates ( $k_{\text{OH}\cdot} \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) (Haag and Yao, 1992). CHP differs from Fenton's reagent in the use of alternative catalysts and higher hydrogen peroxide concentrations, which drive propagation reactions to generate hydroperoxide anion (HO<sub>2</sub><sup>−</sup>) and superoxide (O<sub>2</sub><sup>−</sup>). Hydroperoxide anion is a strong nucleophile, and has been shown to degrade organophosphorus ester insecticides (David and Seiber, 1999) and perfluorooctanoic acid (PFOA) (Mitchell et al., 2014). Superoxide is a weak nucleophile and a reductant, and effectively degrades chloroalkanes such as hexachloroethane and carbon tetrachloride (Watts et al., 1999; Smith et al., 2004). Furthermore, superoxide exhibits surfactant properties, desorbing hydrophobic organic contaminants from soils and promoting the enhanced dissolution of NAPLs (Corbin et al., 2007; Smith et al., 2006; Smith et al., 2009). Although CHP exhibits robust

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reactivity in contaminant destruction, its use for ISCO has become less popular because of the rapid decomposition of hydrogen peroxide in the subsurface, limiting its contact with contaminants (Baciacchi et al., 2004; Xu and Thomson, 2010).

Activated persulfate is now the most common oxidant source used for ISCO (Tsitonaki et al., 2010; Petri et al., 2011). Persulfate decomposition can be initiated by transition metals, similar to the Fenton initiation reaction, to generate sulfate radical (Ahmad et al., 2012):



Sulfate radical is then rapidly converted to hydroxyl radical in aqueous systems:



Similar to CHP, numerous other activators have been investigated for persulfate activation including base (Furman et al., 2010; Furman et al., 2011), minerals (Ahmad et al., 2010; Teel et al., 2011; Liu et al., 2014), organic compounds (Ahmad et al., 2013; Fang et al., 2013a; Elloy et al., 2014), metal-treated biochar (Fang et al., 2015); iron-modified diatomite (da Silva-Rackov et al., 2016); metal-containing nanoparticles (Al-Shamsi and Thomson, 2013; Fang et al., 2013b; Ahmad et al., 2015; Sun et al., 2016; Yan et al., 2016); and carbon nanotubes (Feng et al., 2015; Cheng et al., 2016; Duan et al., 2015; Lee et al., 2015). Although activated persulfate systems are highly reactive because they contain both sulfate radical and hydroxyl radical (Hayon et al., 1972; Peyton, 1993), they are not without limitations. Activated persulfate systems do not generate sufficient fluxes of superoxide to desorb hydrophobic contaminants (Teel et al., 2009), and they are less effective than CHP systems in enhancing dense nonaqueous phase liquids (DNAPL) dissolution (Ko et al., 2012).

Peroxymonosulfate ( ${}^{-}\text{O}_3\text{S-O-O-H}$ ) is a peroxygen with a structure that is a hybrid of hydrogen peroxide and persulfate, containing one hydrogen and one sulfate group on either side of the peroxygen moiety (Ghanbari and Moradi, 2017). Similar to persulfate and hydrogen peroxide, peroxymonosulfate can be activated by transition metals and minerals (Rastogi et al., 2009; Yu et al., 2016; Oh et al., 2016). Rastogi et al. (2009) provided the first evidence of soluble iron activation of peroxymonosulfate for the destruction of 3-chlorobiphenyl. They also provided initial results of sulfate radical vs. hydroxyl radical pathways when peroxymonosulfate was activated by soluble iron species. However, their results were not based on the use of a probe compound with known reactivity with hydroxyl radical and sulfate radical. Furthermore, they did not evaluate the generation of reductants or nucleophiles in soluble iron activated peroxymonosulfate systems. Therefore, the purpose of this research was to provide a thorough investigation of the rates of peroxymonosulfate decomposition and the generation of oxidative and reductive reactive oxygen species during its activation by different forms of soluble iron.

## 2. Materials and methods

### 2.1. Chemicals

Peroxymonosulfate (triple salt), iron (III) sulfate, anisole, hexachloroethane (HCA), tetrachloroethylene (PCE), and trichloroethylene (TCE) were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide, nitrobenzene, sodium bicarbonate, acetic acid, hydrochloric acid, potassium permanganate, *tert*-butanol, isopropanol, potato starch, iron (II) sulfate, and iron ethylenediaminetetraacetic acid iron (III) sodium salt hydrate (iron [III]-EDTA) were obtained from J.T. Baker (Phillipsburg, NJ). Hexane, potassium iodide, and sodium thiosulfate were purchased from Fisher Scientific (Fair Lawn, NJ). Double-deionized water ( $> 18 \text{ M}\Omega\text{-cm}$ ) was purified using a Barnstead NANOpure II Ultrapure water purification system.

### 2.2. Activators

Activation of peroxymonosulfate was investigated using iron (II) sulfate, iron (III) sulfate, and iron (III)-EDTA. Stock solutions (5 mM) of activators were prepared in deionized water at the start of each experiment.

### 2.3. Probe compounds

Nitrobenzene, anisole, and HCA were used as reactant-specific probe compounds to investigate reactive species generated during the activation of peroxymonosulfate. All compounds surveyed that react with sulfate radical also react with hydroxyl radical; therefore, anisole was used to detect both hydroxyl radical and sulfate radical ( $k_{\text{OH}\cdot} = 5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{SO}_4^{\cdot-}} = 4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 1988; Padmaja et al., 1993). Nitrobenzene was used as a probe to detect hydroxyl radical because it is highly reactive with hydroxyl radical ( $k_{\text{OH}\cdot} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) but not with sulfate radical ( $k_{\text{SO}_4^{\cdot-}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 1988; Neta et al., 1977). HCA was used as a probe compound for reductants + nucleophiles (Smith et al., 2004; Ahmad et al., 2012). It has low reactivity with hydroxyl radical and sulfate radical ( $k_{\text{OH}\cdot} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{SO}_4^{\cdot-}} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) (Haag and Yao, 1992; Petri et al., 2011), but is readily reduced ( $k_{e^-} \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and decomposed via nucleophilic attack (Larson and Weber, 1994). TCE and PCE were used as model groundwater contaminants to further investigate the reactivity of the reactive species generated during peroxymonosulfate activation. TCE and PCE are reactive with hydroxyl radical ( $k_{\text{OH}\cdot}$  for TCE =  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{OH}\cdot}$  for PCE =  $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 1988); no rate constants are available for the reactivity of TCE and PCE with sulfate radical.

### 2.4. Hydroxyl radical and sulfate radical scavengers

*Tert*-butanol was used to scavenge hydroxyl radical but not sulfate radical ( $k_{\text{OH}\cdot} = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{SO}_4^{\cdot-}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 1988) and isopropanol was used to scavenge hydroxyl radical + sulfate radical ( $k_{\text{OH}\cdot} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{SO}_4^{\cdot-}} = 8.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al., 1988; Clifton and Huie, 1989). There are no scavengers available that are specific to sulfate radical; scavenging of sulfate radical can only be accomplished in concert with scavenging of hydroxyl radical. The molar ratio of scavenger to probe compounds was 1000:1.

### 2.5. Reaction procedures

Reactions containing probe compounds or the model contaminants TCE and PCE were conducted in triplicate at  $20 \pm 2^\circ \text{C}$  in 20 mL borosilicate reactors containing a soluble iron species and a mixture of peroxymonosulfate and sodium hydroxide solutions to produce a near-neutral pH environment (pH 7.5). The 10 mL reaction volume contained 0.5 M peroxymonosulfate and 0.5 M sodium hydroxide for a 1:1 molar ratio, and 5 mM of iron (II), iron (III), or iron (III)-EDTA. Probe compound concentrations were 1 mM for nitrobenzene, 1  $\mu\text{M}$  for HCA, and 100  $\mu\text{M}$  for PCE and TCE. The 1  $\mu\text{M}$  HCA concentration is based on the linear range of detection for its analysis by gas chromatography/electron capture detection (GC/ECD). The 100  $\mu\text{M}$  TCE and PCE concentrations are typical concentrations found in contaminated groundwater (Watts, 1998). A set of reactors was established for each time point; the entire reactor contents were extracted with hexane at selected time points, and the hexane extracts were analyzed by gas chromatography. Control experiments were conducted in parallel using deionized water in place of peroxymonosulfate and sodium hydroxide. Positive control experiments, containing peroxymonosulfate and sufficient sodium hydroxide to maintain the circumneutral pH, were also conducted in parallel using deionized water in place of the iron

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