



Persulfate activation by glucose for in situ chemical oxidation

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ABSTRACT

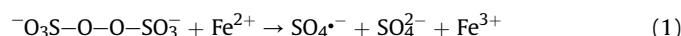
Sodium persulfate has become the most popular oxidant source for the in situ chemical oxidation (ISCO) treatment of organic contaminants in the subsurface. The most common persulfate activators, iron chelates and base, are often ineffective in initiating the generation of reactive oxygen species in field applications. In this study, glucose was investigated as a persulfate activator in systems containing varying concentrations of sodium hydroxide using nitrobenzene as a hydroxyl radical probe and hexachloroethane as a reductant + nucleophile probe. Glucose activation of persulfate increased as a function of sodium hydroxide addition, but was still effective at circumneutral pH regimes. Use of central composite rotatable experimental designs showed that hydroxyl radical and reductant + nucleophile generation rates increased as a function of persulfate at near-neutral pH regimes. Glucose activation of persulfate has the advantages over other activation pathways of more options and flexibility for effective process chemistry and of minimizing or eliminating the mass of sodium hydroxide added to the subsurface. The results of this research can be applied in the field by first evaluating glucose activation compared to base and iron chelate activation of persulfate in laboratory treatability studies.

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1. Introduction

In situ chemical oxidation (ISCO) is an increasingly popular technology for the treatment of contaminated soils and groundwater. Of the three common oxidation technologies (catalyzed H_2O_2 propagations, permanganate, and activated persulfate), activated persulfate has become the most commonly used ISCO process in field applications (Tsitonaki et al., 2010).

Similar to hydrogen peroxide, sodium persulfate must be activated to effectively destroy refractory organic contaminants (Matzek and Carter, 2016); the most common persulfate activators used for ISCO are iron chelates and base (Watts and Teel, 2006). Iron activation of persulfate is parallel to the Fenton initiation reaction for hydrogen peroxide (Teel et al., 2007); iron (II) provides an electron to initiate the decomposition of persulfate to sulfate radical ($\text{SO}_4^{\bullet-}$) and sulfate anion (Liang et al., 2004; Ahmad et al., 2012):

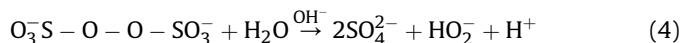


Sulfate radical then reacts with water or hydroxide to form

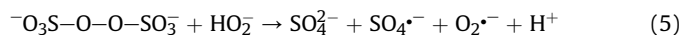
hydroxyl radical (OH^\bullet) (Hayon et al., 1972; Peyton, 1993):



In base activation, the most common method used for ISCO, base catalyzed hydrolysis of persulfate yields hydroperoxide anion (HO_2^-), the conjugate base of hydrogen peroxide, which has a pK_a of 11.8 (Furman et al., 2010):



Hydroperoxide reduces another persulfate molecule to generate sulfate radical, and is oxidized to superoxide ($\text{O}_2^{\bullet-}$) (Furman et al., 2010, 2011):



In order to maintain the system pH near the pK_a of hydrogen peroxide/hydroperoxide anion, base activated persulfate ISCO requires the addition of large masses of sodium hydroxide both to offset sulfuric acid generated during persulfate decomposition (Petri et al., 2011) and to overcome the natural buffering capacity of the subsurface. Such large masses of sodium hydroxide are

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expensive, create potential safety hazards in the field, and can leave the treated soil and groundwater at an alkaline pH (Petri et al., 2011).

Persulfate activation by naturally-occurring subsurface minerals has also been investigated. Ahmad et al. (2010) documented that the major iron oxide minerals goethite, hematite, and ferrihydrite do not activate persulfate. Manganese oxides can activate persulfate, but only at concentrations that are significantly higher than those found in native soils and subsurface solids (Ahmad et al., 2010; Liu et al., 2014). Some reduced minerals, such as pyrite, activate persulfate, but reduced minerals are not common in the subsurface. Most trace minerals do not activate persulfate, and many scavenge reactive oxygen species (Teel et al., 2011).

Several innovative heterogeneous persulfate activators have recently been investigated including metal-treated biochar (Fang et al., 2015); metal oxides, ores, and bimetallic particles (Ayoub and Ghauch, 2014; Jo et al., 2014; Zhang et al., 2014; Yuan et al., 2015); iron-modified diatomite (da Silva-Rackov et al., 2016); metal-containing nanoparticles (Al-Shamsi and Thomson, 2013; Fang et al., 2013a; Ahmad et al., 2015; Sun et al., 2016; Yan et al., 2016); and carbon nanotubes with (Feng et al., 2015; Cheng et al., 2016) and without (Duan et al., 2015; Lee et al., 2015) metal constituents. However, use of these particulate-based activators is not feasible for activated persulfate injections to the subsurface.

Activation of persulfate in field applications has been problematic to date; mineral and iron (II) activation is often ineffective, and base activation often stalls in the field when the pH drops below 10.5 (Tsitonaki et al., 2010). Soil organic matter (SOM) also activates persulfate (Teel et al., 2016), likely through the phenoxide and quinone moieties that are present in the SOM structure; organic compounds that make up SOM such as phenoxide and quinones have been shown to activate persulfate (Ahmad et al., 2013; Fang et al., 2013b). However, the SOM content of the subsurface is usually low, and cannot be relied upon for persulfate activation. Organic activation with an external carbon source may provide a pathway that is more reliable than base and transition metal activation. Preliminary results from our laboratory demonstrate that glucose, which is inexpensive and non-toxic, may activate persulfate. The purpose of this research was to investigate the potential for glucose to activate persulfate, and to evaluate the conditions that effectively promote its activation.

2. Materials and methods

2.1. Chemicals

Sodium persulfate and hexachloroethane were purchased from Sigma Aldrich (St. Louis, MO). Glucose, sodium hydroxide, potato starch, and nitrobenzene were obtained from J.T. Baker (Phillipsburg, NJ). Sodium thiosulfate, potassium iodide, and *n*-hexane were purchased from Fisher Scientific (Fair Lawn, NJ). Double-deionized water was purified to >18 M Ω ·cm using a Barnstead NANOpure II Ultrapure system.

2.2. Probe compounds and scavengers

The probe compound nitrobenzene was used to detect hydroxyl radical ($k_{OH\cdot} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{SO_4\cdot-} \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Neta et al., 1977; Buxton et al., 1988; Clifton and Huie, 1989). Hexachloroethane was used as a nucleophile + reductant probe because it has negligible reactivity with hydroxyl radical ($k_{OH\cdot} \leq 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Haag and Yao, 1992), but is reactive with superoxide and reductants ($k_{O_2\cdot-} = 400 \text{ M}^{-1} \text{ s}^{-1}$) (Afanasev, 1989). Hexachloroethane has previously been used as probe for superoxide in hydrogen peroxide and persulfate systems (Furman et al.,

2009; Ahmad et al., 2012).

2.3. General reaction procedures

Reactions were conducted in triplicate in 20 mL borosilicate vials capped with polytetrafluoroethylene (PTFE) lined septa. Each vial contained 10 mL of 0.2 M persulfate, 5 mM glucose, and a molar ratio of sodium hydroxide:persulfate ranging from 0:1 to 2:1. The initial concentration of the probe compounds was 1 mM for nitrobenzene and 2 μ M for hexachloroethane due to lower water solubility. Control experiments were conducted in parallel using deionized water in place of sodium hydroxide, persulfate, and glucose. In addition, positive control systems were established in parallel containing persulfate and sodium hydroxide without glucose to distinguish between base activation and glucose activation of persulfate. All reactions were conducted at 20 ± 2 °C. At each time point a set of vials was shake-extracted with *n*-hexane and the extracts were analyzed for nitrobenzene by gas chromatography/flame ionization detection and for hexachloroethane by gas chromatography/electron capture detection. In addition, sodium persulfate was quantified at each time point by iodometric titration.

2.4. Effect of glucose and persulfate concentrations on hydroxyl radical and reductant + nucleophile generation

Central composite rotatable designs (Cochran and Cox, 1992) were used to investigate the interactive effect of glucose and persulfate concentrations on the generation of oxidants (measured by nitrobenzene loss) or reductants + nucleophiles (measured by hexachloroethane loss) at pH 6.5 and pH 12.5. The design included two variables, each at five levels, with five center points for statistical validity (Hogg and Ledolter, 1992; Cochran and Cox, 1992) and four star points set at a factor of 1.414 on the far end of the coded scale to achieve complete rotatability (Box et al., 1978). Using the same reaction conditions described under Section 2.3, the variables were glucose concentration (10–50 mM at pH 6.5; 1–5 mM at pH 12.5) and persulfate concentration (0.1–0.5 M). Rate constants for nitrobenzene and hexachloroethane loss were calculated by plotting the natural log of concentration vs. time until 90% loss was achieved. The conditions for each trial and the resulting data are listed in Supplemental Tables S1–S4. Trials 1 through 8 were used to quantify the rate of probe compound loss, while trials 9 through 13 were replicates (center points) used to quantify precision.

The experimental data were analyzed by least squares linear regression to develop equations for nitrobenzene and hexachloroethane loss rate constants. Stepwise regression was used for the selection of response surface model terms, with all terms in the final model significant at $p < 0.05$. Response surfaces representing first order rate constants for the loss of nitrobenzene and hexachloroethane were developed using Minitab 17[®] Statistical Software.

2.5. Analytical procedures

Hexane extracts containing nitrobenzene were analyzed using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and fitted with a 15 m \times 0.53 mm SPB-5 capillary column. The injector and detector port temperatures were 200 °C and 250 °C, respectively, the initial oven temperature was 60 °C, the program rate was 30 °C/min, and the final temperature was 180 °C. For hexachloroethane analysis, the GC was equipped with an electron capture detector (ECD) fitted with a 30 m \times 0.53 mm EQUITY-5 capillary column. The injector and

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