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Review

Activated persulfate for organic chemical degradation: A review

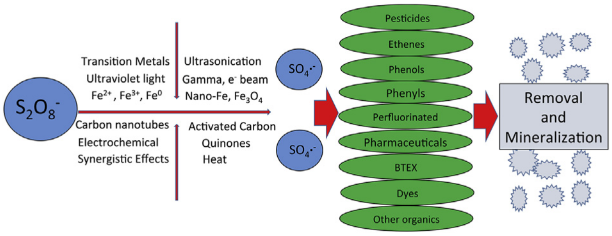
Laura W. Matzek, Kimberly E. Carter*

Department of Civil and Environmental Engineering, University of Tennessee, 325 John D. Tickle Building, Knoxville, TN 37996-2313, USA

HIGHLIGHTS

- Activated persulfate has extensive application for environmental remediation.
- Electrochemical and activated carbon persulfate activation are presented.
- Novel means of activating persulfate for removal of organic species are discussed.
- Manipulation of traditional persulfate activation for analyte removal is reviewed.
- Summarized experiments include over seventy organic compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Activated persulfate reactions have widespread application for groundwater and environmental remediation, as many of these reactions involve destruction of environmental contaminants. Within the last five years, knowledge of activated persulfate degradation reactions has grown to include novel means of activating persulfate for enhanced removal of organic species. These current studies cover a long list of organic analytes, including pharmaceuticals, pesticides, halogenated compounds and dyes. An extensive review of recently published experimental parameters and results for the destruction of organic compounds via activated persulfate is presented. Focus is placed on emerging methodologies and manipulation of traditional activation techniques. Knowledge gaps are identified and discussed, as despite the number of publications on this subject, more broad-reaching guidelines are needed for optimizing applications of activated persulfate in water treatment.

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* Corresponding author.
E-mail address: kcarte46@utk.edu (K.E. Carter).

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1. Introduction

Peroxydisulfate, or persulfate, has been investigated for its ability to degrade recalcitrant organics (Fang et al., 2013b; Zhao et al., 2014; Chen and Huang, 2015). Stable at room temperature, persulfate can be activated via heat, transition metals, ultraviolet (UV) light, or other means, forming the highly reactive sulfate radical (Equation (1)) (He et al., 2014; Zhao et al., 2014; Zhang et al., 2015a).

$$S_2O_8^{2-} + \mathit{activator} \rightarrow SO_4^{-\cdot} + \left(SO_4^{-\cdot} \text{ or } SO_4^{2-}\right) \tag{1}$$

Like the hydroxyl radical (Schwarz and Dodson, 1984), the sulfate radical has a high oxidation potential ($E^o = 2.60$ V) (Eberson, 1987), and is nonselective (Huang et al., 2002; Hao et al., 2014). Activated persulfate has widespread application for environmental remediation (Chen et al., 2014; Wang et al., 2014a; Zhao et al., 2014), as formed radicals react with organic chemicals causing either partial or complete mineralization (Paul et al., 2014; Wang and Liang, 2014; Zhang et al., 2015b). In situ remediation with activated persulfate oxidation may be preferred over peroxide based hydroxyl-radical oxidation processes, as the persulfate anion is more stable and may be transported further in the subsurface before being activated for contaminant degradation (Waldemer et al., 2007; Yan et al., 2013).

Tsitonaki et al. (2010) reviewed the use of persulfate for remediation of contaminated soil and groundwater, focusing on heat, iron and alkaline activations, effects of porous media, and in situ oxidation (Tsitonaki et al., 2010). Enhancing the effectiveness of activated persulfate includes manipulation of traditional methods and development of novel techniques (Lee et al., 2013; Hao et al., 2014; Paul et al., 2014; Sun et al., 2014; Criquet and Leitner, 2015). Recently, Zhang et al. (2015a) reviewed sulfate radical technologies, covering radicals generated from peroxymonosulfate and peroxydisulfate (Zhang et al., 2015a), photochemical and heterogeneous activation systems, in-situ remediation, hydrothermal oxidation treatment, and air pollution control technologies (Zhang et al., 2015a).

The following review provides an extensive assessment of recently published parameters and results for the destruction of various organic compounds in aqueous systems via activated persulfate. Applicable variables and impacts on activated persulfate reactions are provided. Emerging methodologies for persulfate activation, such as electrochemical and activated carbon, are highlighted, along with potential for expanding knowledge areas and obstacles that must be overcome for future practical implementation.

2. Mechanisms of persulfate reactions

2.1. Sulfate, hydroxyl, and other radical formation

Heat, UV light, and ultrasound impart energy to the persulfate anion resulting in cleavage of the peroxide bond and forming two sulfate radicals (Equation (2)) (Kolthoff and Miller, 1951; Waldemer et al., 2007). Alternately, persulfate can undergo an oxidation–reduction reaction with an electron donor from a transition metal or the radiolysis of water, generating a single sulfate radical (Equation (3)) (Hayon et al., 1972; Anipsitakis and Dionysiou, 2004a).

$$S_2O_8^{2-} + \text{energy input} \rightarrow 2SO_4^{-\cdot} \tag{2}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{-\cdot} \tag{3}$$

Enhancing the effect of activated persulfate degradation reactions are secondary radicals propagating from sulfate radical reactions (Johnson et al., 2008; Tsitonaki et al., 2010). Sulfate radicals react with water at all pHs forming hydroxyl radicals (Equation (4)) (Hayon et al., 1972), which are the primary reactive species under basic conditions (Equation (5)) (Liang and Su, 2009). At pH < 7 sulfate radicals are the dominant reactive species; however, hydroxyl and sulfate radicals participate equally in reactions at neutral pHs (Liang and Su, 2009).

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + OH\cdot + H^+ \tag{4}$$

$$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + OH\cdot \tag{5}$$

While hydroxyl radicals degrade a wide range of organic contaminants (Petri et al., 2011a), chain reactions (Equations (6) and (7)) synthesize more reactive intermediates (Waldemer et al., 2007). Likewise, peroxymonosulfate (HSO_5^-) may be activated generating sulfate radicals, as hydrogen peroxide may react with inorganic compounds producing additional free radicals. The formed radicals can subsequently participate in further reactions (Anipsitakis and Dionysiou, 2004b; Petri et al., 2011a).