EPA Public Access

Author manuscript

Environ Sci Technol. Author manuscript; available in PMC 2021 February 04.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Sci Technol. 2020 February 04; 54(3): 1955–1962. doi:10.1021/acs.est.9b06442.

Sulfate Radical Scavenging by Mineral Surfaces in Persulfate-Driven Oxidation Systems: Reaction Rate Constants and Implications

Klara Rusevova Crincoli,

Robert S. Kerr Environmental Research Center, Ada, Oklahoma

Constance Green,

East Central University, Ada, Oklahoma

Scott G. Huling

Robert S. Kerr Environmental Research Center, Ada, Oklahoma

Abstract

Activated persulfate (PS) is a common method used to generate sulfate radicals ($\text{SO}_4^{\bullet-}$), a powerful oxidant capable of degrading a broad array of environmental contaminants. The reaction of $\text{SO}_4^{\bullet-}$ with nontarget species (i.e., scavenging) contributes significantly to treatment inefficiency. Radical scavenging in this manner has been quantified for nontarget chemical species in the aqueous phase but has never been quantified for solid phase media. Kinetic analysis and laboratory methods were developed to quantify the $\text{SO}_4^{\bullet-}$ scavenging rate constant (k_{es}) for alumina, a naturally occurring mineral in soil and aquifer materials. $\text{SO}_4^{\bullet-}$ generated in UV and thermally activated persulfate (UV-APS, T-APS) batch systems, and the loss of rhodamine B (RhB) served as an indicator of $\text{SO}_4^{\bullet-}$ activity. k_{es} for alumina was 2.42×10^4 and $2.03 \times 10^4 \text{ m}^{-2} \text{ s}^{-1}$ for UV-APS and T-APS oxidative treatment systems, respectively. At $[\text{alumina}] > 5 \text{ g L}^{-1}$, the reaction of $\text{SO}_4^{\bullet-}$ with solid phase media increased over the aqueous phase reactions with RhB and aqueous scavengers. $\text{SO}_4^{\bullet-}$ scavenging by solid surfaces was orders of magnitude greater than the reaction with the target compound and scavengers in the aqueous phase, underscoring the significant role of solid surfaces in scavenging $\text{SO}_4^{\bullet-}$.

Graphical Abstract

Corresponding Author Scott G. Huling – Phone: (580) 436-8610; huling.scott@epa.gov.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b06442>.

Molecular forms of rhodamine B (RhB); X-ray diffraction patterns of commercial alumina; summary of control experiments; kinetics of RhB oxidation in alumina-amended UV-APS and T-APS oxidation systems; estimation of second-order rate constant for RhB and $\text{SO}_4^{\bullet-}$ (k_5 in this study); role of the hydroxyl radical in UV- and T-APS reaction systems; results of semicontinuous mode experiments; UV and thermal activation of PS and RhB treatment efficiency analysis; reactions of $\text{SO}_4^{\bullet-}$ consumption and $\cdot\text{OH}$ formation and consumption in UV- and T-APS reaction systems; and summary of P_{SO_4} , k_{PS} and k_{PS} for UV- and T-APS treatment systems (PDF)

The authors declare no competing financial interest.

INTRODUCTION

Inefficiency in oxidative treatment processes involving radical intermediates can be attributed to two general mechanisms, radical scavenging and nonproductive reactions (NPRs). Radical scavenging involves the reaction between radicals and nontarget chemical species; and NPR involves reactions that do not yield radicals and consequently deplete the source of oxidants, such as persulfate ($\text{S}_2\text{O}_8^{2-}$) (PS) or hydrogen peroxide (H_2O_2), which in turn diminishes radical production. PS reaction with natural media involves NPR^{1–5} and contributes to treatment inefficiency. Radical scavengers may either be soluble in the aqueous phase or may be present as a solid phase. In either case, radicals can react with scavengers found in the aqueous phase or on the surfaces of solid phase media. Radical scavenging, including sulfate radicals ($\text{SO}_4^{\bullet-}$) and/or hydroxyl radicals ($\bullet\text{OH}$) in oxidative treatment systems, has predominantly been focused on soluble constituents in the aqueous phase.^{6–9} Radical scavenging by solid phase media has not been specifically investigated. The focus of this study was to quantify radical scavenging by solid surfaces in persulfate-driven oxidation systems and to assess the relevance.

PS is a reagent utilized in chemical oxidation technologies, including in situ chemical oxidation (ISCO), for contaminant transformation and treatment of groundwater and soil.^{3,4,10} Persulfate is highly soluble and persists in subsurface environments from days to weeks,¹ allowing greater potential for oxidant distribution and contact with the targeted contaminants. PS is a relatively strong oxidant ($E^0 = 2.1 \text{ V}$), but upon activation, the more powerful reaction intermediate $\text{SO}_4^{\bullet-}$ ($E^0 = 2.6 \text{ V}$) is produced and is capable of degrading a broad spectrum of environmental contaminants.^{11–14} Several reaction pathways occur during PS activation including thermolysis^{14,15} and photolysis¹⁵ of the peroxy bond ($[\text{O}-\text{O}]^{2-}$) to generate $\text{SO}_4^{\bullet-}$ (R1 and R2; Table 1). PS reduction can be initiated by reduced transition metals,^{16–18} carbonaceous-based materials,^{15,19} or organic substrates^{15,20} (R3; Table 1).

Alkaline activation ($\text{pH} > 10.5$) is a common activation method where nucleophilic attack of $[\text{O}-\text{O}]^{2-}$ is considered a main activation pathway.¹⁵ Under basic pH conditions, the generation of $\cdot\text{OH}$ becomes significant.²¹

In treatment systems, PS also undergoes decomposition reactions without yielding $\text{SO}_4^{\bullet-}$. These NPRs undergo $2e^-$ transfer to form two sulfate anions (R4; Table 1). Such NPRs are also applicable to H_2O_2 -based oxidative treatment systems^{4,5} and are a significant source of inefficiency. The origin of NPRs involving PS has been attributed to the amorphous iron content or soil organic matter in the aquifer material.¹⁻³ Other NPRs with PS include acid-catalyzed ($\text{pH} < 3$) PS decomposition or uncatalyzed PS decomposition to hydrogen sulfate and oxygen.²³ However, these reactions occur at relatively slow rates (>80 days)¹ and are not applicable to the short-term reaction conditions used in this study.

The reaction efficiency (η) associated with the PS oxidation mechanism is the product of efficiencies associated with PS activation-dependent $\text{SO}_4^{\bullet-}$ formation (E_1), and $\text{SO}_4^{\bullet-}$ reaction with the target compound (E_2). Specifically, inefficiency in PS activation is attributed to NPRs that do not yield $\text{SO}_4^{\bullet-}$. Inefficiency in the reaction between $\text{SO}_4^{\bullet-}$ and the target compound (P) [rhodamine B (RhB), methyl-*tert* butyl ether (MTBE)] (R5 and R6; Table 1) is attributed to competing $\text{SO}_4^{\bullet-}$ reactions with aqueous (R7–R10; Table 1) and solid phase scavengers (R11; Table 1) in oxidation systems.

Radical scavenging in the aqueous phase has largely been quantified utilizing various concentrations of dissolved species and their known second-order rate constants with $\text{SO}_4^{\bullet-}$,¹⁰ whereas $\text{SO}_4^{\bullet-}$ scavenging by solid surfaces has not been quantified. In this study, competition kinetic analysis and laboratory methods were developed to quantify the $\text{SO}_4^{\bullet-}$ scavenging rate constant (k_{S}) for solid phase media. Subsequently k_{S} was used to assess the relative contribution of $\text{SO}_4^{\bullet-}$ scavenging in the aqueous and the solid phases. Further, projection of $\text{SO}_4^{\bullet-}$ scavenging by homogeneous and heterogeneous species in an ideal aquifer system was carried out using k_{S} derived from this study.

EXPERIMENTAL SECTION

Chemicals.

The chemicals used in this study were of reagent grade and used as received. RhB dye (21.33% w/w) was from Turner Designs, and sodium persulfate, methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol, alumina (α -phase), and ascorbic acid were from Aldrich. All glassware and containers were acid-washed and rinsed with deionized water (DIW) before use. Stock solutions and dilutions of PS and probes (RhB, MTBE) were prepared using DIW prior to each experiment.

Solid Selection and Characterization.

In the development of the kinetic analysis model, three reaction conditions were considered where: (1) the solid phase media does not react with PS, (2) the solid phase media reacts with PS but does not produce $\text{SO}_4^{\bullet-}$ (i.e., NPR), and (3) the solid phase media reacts with PS, forms $\text{SO}_4^{\bullet-}$, and may also include NPRs.²⁴ Here, methods of kinetic analysis were developed to estimate k_{S} for condition 1, where alumina (Al_2O_3), a naturally occurring

mineral in soil and aquifer systems,²⁵ was selected as the model mineral and tested. Laboratory testing of alumina indicated no reaction with PS.

The specific surface area (SSA) of alumina was determined by the BET method using N₂ adsorption–desorption isotherms measured on Quantachrome NOVA 4200e (Boynton Beach, FL). Metal impurities in alumina were determined by inductively coupled plasma, optical emission spectroscopy (ICP–OES) using PerkinElmer Optima 8300DV ICP–OES, based on the EPA Method 200.7. Filtered solutions of alumina (50 g L⁻¹) were analyzed for Cl⁻ and Br⁻ using Lachat flow injection analyzers. The alumina composition was confirmed by the Rigaku MiniFlex X-ray diffractometer, which provides a qualitative identification of minerals present in solid matrices and is based on a comparison to reference diffraction data for known compounds.

Batch Experiments.

Selection of a Probe and PS Activation.—RhB (Supporting Information S.1, Figure S1) was selected as a probe because of the favorable properties that allow rapid analysis and processing of samples, thus eliminating the quenching step of the remaining oxidant (PS). RhB is nonvolatile, hydrophilic, and adsorbs poorly to alumina surfaces at pH conditions applied in the study, which minimizes nonoxidative losses and simplifies the kinetic analysis. Various methods are available for PS activation. However, thermal- and UV-activated PS are most efficient in terms of SO₄^{•-} formation. Metal activation (e.g., Fe²⁺) of PS was ruled out because of possible physicochemical changes of Fe²⁺ in solution and potential effects on the fate of PS (e.g., by initiation of NPRs). Base-activated PS introduces a pool of potential reactive species including [•]OH, which would compete for the species present in the reaction mixture, thus complicating the kinetic analysis.

UV and Thermally Activated PS.—UV activation of PS (UV-APS) was conducted in 40 mL borosilicate VOA vials under a UV Lamp (High-Performance UVP Transilluminator, Model TFM-20) containing four UV-A tube bulbs (25 W bulbs, 115 V, 60 Hz, 2.0 amps, 365 nm). The base case homogeneous oxidation test system was comprised of a RhB probe ([RhB]₀ = 5 mg L⁻¹; 0.01 mM) and PS ([PS]₀ = 500 mg L⁻¹; 2.1 mM) and involved a total volume of 25 mL. The heterogeneous test system was prepared in the same manner but was amended with alumina (1–50 g L⁻¹). Uncovered test reactors were then placed on a 10-spot magnetic stirrer (500 rpm) under a UV light lamp to insure a complete mixed system during the experiments. Thermal activation of PS (T-APS) was carried out as a second method to estimate and validate the surface scavenging rate for alumina. Solutions of RhB ([RhB]₀ = 5 mg L⁻¹; 0.01 mM) and/or suspensions of alumina ([alumina] = 1–10 g L⁻¹) were adjusted to an elevated temperature (40 °C) and then spiked with PS ([PS]₀ = 500 mg L⁻¹; 2.1 mM) to initiate the reaction. At selected time intervals, samples were collected and analyzed immediately for RhB and PS.

Prior to analyses, aqueous samples were separated from the suspended alumina solid phase media by centrifugation (Eppendorf MiniSpin; 3000 rpm; 2 min). The starting reaction pH was set to pH 6 and together with temperature was monitored throughout all the experiments. No buffers were introduced to avoid additional reactions with SO₄^{•-}, as most

of the frequently used buffers react at appreciable rates with the sulfate radical.⁹ Data shown in the figures and tables are the mean values of at least two experiments. Unless stated otherwise, the reported error represents the deviation of the mean value.

Semicontinuous Mode Experiment.—Subsequent amendments (in three cycles) of freshly prepared reaction solution (RhB + PS) to the alumina was performed to assess whether the alumina scavenging changes over time. After each cycle, the suspension was decanted to eliminate the aqueous solution, and the remaining alumina was air-dried overnight. RhB (5 mg L⁻¹) and PS (500 mg L⁻¹) were added to create another suspension of the original alumina particles (10 g L⁻¹). The reaction vessels were placed under UV light on the magnetic stirrer (500 rpm) to initiate the reaction. The experiment was carried out in duplicate.

Estimation of the Second-Order Rate Constant for RhB with SO₄^{•-} (k₅).—

Because of the lack of kinetic data published in the scientific literature involving RhB oxidation by SO₄^{•-}, competition kinetic experiments were carried out to determine $k_{\text{SO}_4^{\bullet-}, \text{RhB}}$, which was used as k_5 in this study. MTBE, a structurally distinct compound, served as the reference probe with a well-established rate constant with SO₄^{•-}, $k_6 = 3.13(\pm 0.02) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.²² The relative losses of RhB and MTBE were used to estimate $k_5 \text{ (M}^{-1} \text{ s}^{-1})$. Batch reactors ($n = 2$) containing a mixed aqueous solution of RhB ([RhB]₀ = 5 mg L⁻¹; 0.01 mM) and MTBE ([MTBE]₀ = 15 mg L⁻¹; 0.17 mM) were spiked with PS ([PS]₀ = 1000 mg L⁻¹; 4.2 mM). The reactors were sealed to avoid volatile losses of MTBE and placed inversely in the UV chamber on the magnetic stirring plate (500 rpm) to uniformly expose the vials to the UV-light source. The initial reaction pH was 3.9. At selected time intervals, samples were collected for MTBE and RhB analyses. RhB was measured immediately using a spectrophotometric method. Diluted samples of MTBE were preserved using ascorbic acid (moles PS/moles ascorbic acid = 1/4)²⁶ prior the gas chromatography (GC)–mass spectrometry (MS) measurements.

Controls.

Control experiments were designed to evaluate the fate mechanisms of the RhB probe, PS, and SO₄^{•-}. The potential for a direct reaction between RhB (5 mg L⁻¹) and persulfate (500 mg L⁻¹) was tested in 40 mL VOA vials in the dark. The impact of the UV irradiation and elevated temperature on the stability of RhB was tested in PS-free systems. The possible impact of radical scavenging by dissolved species originating from alumina amendments to the test reactors was also investigated. The filtrate (25 mL) derived from 1 g L⁻¹ ($n = 2$) and 10 g L⁻¹ ($n = 2$) alumina batches was amended with RhB and PS and the [RhB] was measured over time under UV-APS conditions. The potential for light scattering by alumina particles and impact on UV-APS was investigated. The [PS] was measured over time and contrasted with results involving an alumina-free system (i.e., the homogeneous base case system).

Analytical Methods.

RhB was determined spectrophotometrically ($\lambda_{\text{max}} = 556 \text{ nm}$) on the Jenway 6505. A spectrophotometric method was used for analyzing the persulfate concentration ($\lambda_{\text{max}} = 450$

nm) as described elsewhere.²⁷ MTBE analysis was performed via the headspace GC–MS method using Thermo Scientific Trace GC Ultra coupled with Thermo DSQ II MS. Regression analysis of the spectrophotometric response and the concentrations of these analytes yielded linear calibration curves ($r^2 = 0.99$). The pH was measured using the Orion Star A215 pH meter.

Kinetic Analyses.

The development of the kinetic analysis method used to estimate $\text{SO}_4^{\bullet-}$ scavenging by alumina surfaces is based on the kinetic analysis previously reported.^{24,28} The rate of $\text{SO}_4^{\bullet-}$ accumulation is calculated as the difference between the rates of $\text{SO}_4^{\bullet-}$ production ($P_{\text{SO}_4^{\bullet-}}$) and $\text{SO}_4^{\bullet-}$ consumption ($C_{\text{SO}_4^{\bullet-}}$) (eq 1). $\text{SO}_4^{\bullet-}$ are highly reactive and a quasi-steady-state approximation for $\text{SO}_4^{\bullet-}$ is assumed where $d[\text{SO}_4^{\bullet-}]/dt \approx 0$, and $C_{\text{SO}_4^{\bullet-}} \approx P_{\text{SO}_4^{\bullet-}}$ (eq 2). RhB was used as a probe and the loss of RhB in alumina-amended and alumina-free test reactors served as a quantitative metric to estimate the $\text{SO}_4^{\bullet-}$ surface scavenging rate constant (k_{SS}). The overall rate $\text{SO}_4^{\bullet-}$ consumption (eq 3) is the sum of rates of $\text{SO}_4^{\bullet-}$ reaction with the probe (R_p) (eqs 4 and 5), scavengers in the aqueous phase, R_s (eqs 6 and 7), and scavengers in the solid phase, R_{SS} (eqs 8 and 9). The individual aqueous and solid phase scavengers are grouped into terms k_s and k_{SS} , respectively. eqs 4 and 5 were combined and used to estimate $[\text{SO}_4^{\bullet-}]_{\text{SS}}$ (eq 10), where k_5 was established based on competition kinetics, and k_{RhB} is the pseudo-first-order rate constant determined from laboratory data in this study. $[\text{SO}_4^{\bullet-}]$ was assumed to be at a steady state (i.e., $[\text{SO}_4^{\bullet-}]_{\text{SS}}$) as semilogarithmic plots of $[\text{RhB}]$ versus time were linear, indicating that $[\text{SO}_4^{\bullet-}]$ did not appreciably change over the course of the experiment.

$$d[\text{SO}_4^{\bullet-}]/dt = P_{\text{SO}_4^{\bullet-}} - C_{\text{SO}_4^{\bullet-}} \quad (1)$$

$$C_{\text{SO}_4^{\bullet-}} \approx P_{\text{SO}_4^{\bullet-}} \quad (2)$$

$$C_{\text{SO}_4^{\bullet-}} = R_p + R_s + R_{\text{SS}} \quad (3)$$

$$R_p = k_5[\text{RhB}][\text{SO}_4^{\bullet-}]_{\text{SS}} \quad (4)$$

$$R_p = k_{\text{RhB}}[\text{RhB}] \quad (5)$$

$$R_s = \sum_{i=1}^n k_i[S_i][\text{SO}_4^{\bullet-}]_{\text{SS}} \quad (6)$$

$$R_s = k_s[\text{SO}_4^{\bullet-}]_{\text{SS}} \quad (7)$$

$$R_{\equiv S} = \sum_{i=1}^n k_{\equiv, i} [S_{\equiv, i}] S_A m_S [\text{SO}_4^{\bullet -}]_{\text{SS}} \quad (8)$$

$$R_{\equiv S} = k_{\equiv S} S_A m_S [\text{SO}_4^{\bullet -}]_{\text{SS}} \quad (9)$$

$$[\text{SO}_4^{\bullet -}]_{\text{SS}} = k_{\text{RhB}} / k_5 \quad (10)$$

where $P_{\text{SO}_4^{\bullet -}}$ and $C_{\text{SO}_4^{\bullet -}}$ are rates of $\text{SO}_4^{\bullet -}$ production and consumption, respectively (M s^{-1}); R_p , R_s , and $R_{\equiv S}$ are the $\text{SO}_4^{\bullet -}$ reaction rates with the probe (RhB), scavengers in the aqueous phase (S_i) and surface scavengers ($S_{\equiv, i}$), respectively (M s^{-1}); $[\text{SO}_4^{\bullet -}]_{\text{SS}}$ is the steady-state sulfate radical concentration (M); $[\text{RhB}]$ is the rhodamine B concentration (M); k_5 is the second-order degradation rate constant of the RhB probe and $\text{SO}_4^{\bullet -}$ ($\text{M}^{-1} \text{s}^{-1}$); k_{RhB} is the pseudo-first-order degradation rate constant for the RhB probe (s^{-1}); k_S is the sum of products of individual aqueous phase scavengers (S_i) and respective $\text{SO}_4^{\bullet -}$ reaction rate constants (k_i) ($\text{M}^{-1} \text{s}^{-1}$); k_i is the second-order rate constant of an individual aqueous phase scavenger ($\text{M}^{-1} \text{s}^{-1}$); $[S_i]$ is the individual aqueous phase scavenger concentration (M); $k_{\equiv S}$ is the surface scavenging rate constant, sum of products of individual solid phase scavengers ($S_{\equiv, i}$) and respective $\text{SO}_4^{\bullet -}$ reaction rate constants ($k_{\equiv, i}$) ($\text{m}^{-2} \text{s}^{-1}$); $k_{\equiv, i}$ is the specific second-order rate constant of an individual solid phase scavenger ($\text{M}^{-1} \text{s}^{-1}$); $[S_{\equiv, i}]$ is the individual specific solid phase scavenger concentration (M m^{-2}); S_A is the surface area of the solid phase media (i.e., mineral) ($\text{m}^2 \text{g}^{-1}$); and m_S is the mass of the solid phase mineral (g).

The kinetic analysis method used to estimate $k_{\equiv S}$ involved contrasting results between a solid-free, homogeneous system and a solid-amended, heterogeneous system. Alumina was incrementally amended to the test reactors to determine whether it played a role in scavenging $\text{SO}_4^{\bullet -}$. Equations R1–R10 formed the basis to solve for $P_{\text{SO}_4^{\bullet -}}$ (eq 11) (e.g., amended with 10 g L^{-1} alumina). In an oxidative system without surface scavenging (i.e., mineral-free), the surface scavenging term in eq 11 is eliminated and results in eq 12. The subscripts in eqs 11 and 12 represent 0 and 10 g L^{-1} alumina, respectively.

$$P_{\text{SO}_4^{\bullet -}, 10} = k_5 [\text{RhB}] [\text{SO}_4^{\bullet -}]_{\text{SS}, 10} + k_S [\text{SO}_4^{\bullet -}]_{\text{SS}, 10} + k_{\equiv S} S_A m_{S, 10} [\text{SO}_4^{\bullet -}]_{\text{SS}, 10} \quad (11)$$

$$P_{\text{SO}_4^{\bullet -}, 10} = k_5 [\text{RhB}] [\text{SO}_4^{\bullet -}]_{\text{SS}, 0} + k_S [\text{SO}_4^{\bullet -}]_{\text{SS}, 0} \quad (12)$$

The experimental method used to differentiate between $\text{SO}_4^{\bullet -}$ scavenging in the solid phase and aqueous phase required two identical test conditions where one reactor was mineral-free (i.e., homogeneous base case) and the other was amended with alumina. The mineral-free, base case system contained $[\text{RhB}]_0 = 5 \text{ mg L}^{-1}$ and $[\text{PS}]_0 = 500 \text{ mg L}^{-1}$, and the mineral-amended system contained the same concentrations of these reactants, and alumina ($1\text{--}50 \text{ g}$

L^{-1}). The $[PS]_0$ and $[RhB]_0$ were identical in all test reactors used in the UV-APS and T-APS testing systems indicating favorable conditions for $PSO_4^{\bullet-}$ and k_S to be approximately equal. The pseudo-first-order degradation rate constant for PS (k_{PS} (s^{-1})) and the PS (M) over the duration of the experiments were approximately equal between the base case and alumina-amended treatment systems. Therefore, time-dependent differences in $[RhB]$ were attributed to surface scavenging effects in the alumina-amended system. The steady-state $SO_4^{\bullet-}$ $[SO_4^{\bullet-}]_{SS,0}$, $[SO_4^{\bullet-}]_{SS,10}$, were determined experimentally (eq 10); and the pseudo-first-order reaction rate constants for RhB in alumina-free ($k_{RhB,0}$ (s^{-1})) and alumina-amended systems ($1-50 \text{ g L}^{-1}$, where $k_{RhB,10}$ (s^{-1}) contained 10 g L^{-1}) were determined via semi-log plots of $[RhB]$ versus time. On this basis, the rate of $SO_4^{\bullet-}$ production was similar between systems, allowing eqs 11 and 12 to be equated and permitting the surface scavenging rate constant, $k_{\equiv S}$, to be determined (eq 13).

$$k_{\equiv S} = \frac{([SO_4^{\bullet-}]_{SS,0}(k_5[RhB] + k_S)) - ([SO_4^{\bullet-}]_{SS,10}(k_5[RhB] + k_S))}{S_{AmS,10}[SO_4^{\bullet-}]_{SS,10}} \quad (13)$$

RESULTS & DISCUSSION

Alumina Characterization.

The SSA of alumina is low ($1.5 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$; $n = 8$), the pH point of zero charge (pH_{PZC}) is 8.5,²⁵ and the XRD patterns were consistent with the diffraction patterns found in the library of available mineral (Supporting Information S.2, Figure S.2). ICP-OES analysis indicated low concentrations of total Fe (19 mg kg^{-1} ; $n = 3$), and total Mn and other metals detected were below quantitation limits (8.0 mg kg^{-1} ; $n = 3$).

Summary of Controls.

Control experiments were conducted to evaluate potential fate mechanisms for RhB, PS, and $SO_4^{\bullet-}$ and confirmed that oxidative $SO_4^{\bullet-}$ was the only significant fate mechanism (Supporting Information S.3, Figures S.3–S.6). The PS decomposition rate was similar between the base case alumina-free homogeneous and the alumina-amended systems in both UV-APS and T-APS. This indicated that UV irradiation or elevated temperature were the only activators of PS, and that light scattering did not play a role in PS activation. The pseudo-first-order degradation rate of PS (k_{PS}) in alumina-amended reactors was $2.47(\pm 0.21) \times 10^{-5} \text{ s}^{-1}$ ($n = 4$) and $2.02(\pm 0.45) \times 10^{-5} \text{ s}^{-1}$ ($n = 4$) in UV-APS and T-APS, respectively. In the mineral-free, homogeneous base case system, k_{PS} was $2.59(\pm 0.36) \times 10^{-5} \text{ s}^{-1}$ ($n = 2$) and $1.80(\pm 0.11) \times 10^{-5} \text{ s}^{-1}$ ($n = 2$), for UV-APS and T-APS, respectively. As k_{PS} was not statistically distinguishable between alumina-free and alumina-amended reactors, the rates of $SO_4^{\bullet-}$ production ($PSO_4^{\bullet-}$) were determined to be approximately equal in these treatment systems (Table S.1). Concentrations of Cl^- and Br^- in the control reactor amended with alumina were measured and were below the method detection limit (i.e., 0.574 mg L^{-1} for Cl^- , and 0.048 mg L^{-1} for Br^-). This indicated that $SO_4^{\bullet-}$ scavenging in the treatment system was because of solid surfaces and not because of dissolved constituents derived from the alumina.

Impact of Alumina on RhB Oxidation.

semi-log plots of RhB concentration versus time were linear for both the UV-APS and T-APS systems (Supporting Information S.4, Figure S.7a,b), indicating that RhB degradation was pseudo-first-order and that the $\text{SO}_4^{\bullet-}$ concentration was at steady-state ($[\text{SO}_4^{\bullet-}]_{\text{SS}}$) (i.e., the quasi-steady-state assumption is valid). In the alumina-amended UV-APS and T-APS reaction systems, RhB oxidative losses were inversely proportional to alumina solids, and k_{RhB} declined with increasing alumina concentration (Table 2), indicating that alumina was competing with RhB for $\text{SO}_4^{\bullet-}$. k_5 was determined to be $3.02(\pm 0.03) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Supporting Information S.5, Figure S.8) and used in conjunction with k_{RhB} to estimate the $[\text{SO}_4^{\bullet-}]_{\text{SS}}$ (eq 10) (Table 2). Previously, a second-order rate constant for $\text{SO}_4^{\bullet-}$ and methylene blue dye reaction was determined and ranged from 0.34×10^8 to $2.20 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, depending on the reaction conditions.²⁹ Methylene blue and RhB exhibit similar molecular characteristics that suggest similar reaction mechanisms of $\text{SO}_4^{\bullet-}$ attack (e.g., electron-rich aromatic ring(s) for initial e^- transfer or methyl/ethyl groups for hydrogen abstraction). Consequently, similar values in the approximated rate constant were anticipated.

k_S , the sum of products of individual aqueous phase scavengers $[S_i]$ and respective $\text{SO}_4^{\bullet-}$ reaction rate constants (k_i) (eq 7), was estimated as $k_7 \times [\text{PS}]$ (R7, Table 1), as $\text{SO}_4^{\bullet-}$ reaction with PS was significantly greater than all other aqueous phase scavenging reactions. A negligible contribution of OH^- (R8; Table 1) was determined, as $k_8 \times [\text{OH}^-]$ at pH_{start} 6 and pH_{final} 4.5 was 3 and 4 orders of magnitude lower, respectively, than $k_7 \times [\text{PS}]$. Further, an overall critical analysis of the potential role of $\cdot\text{OH}$ indicated that $\cdot\text{OH}$ did not play a role in the oxidative transformation of RhB or MTBE in this study (Supporting Information S.6, Figure S.9).

In semicontinuous oxidation mode, the solution was decanted and the remaining alumina (10 g L^{-1} , $n = 2$) was re-amended with fresh RhB and PS for a total of three sequential oxidations of the RhB. Upon treatment with UVAPS, the rate of RhB transformation increased by approximately 30% in the second and third cycles. In comparison to the base case homogeneous reaction system ($k_{\text{RhB}} = 0.0280 \text{ min}^{-1}$), k_{RhB} resulting from the first, second, and third oxidations was 0.011, 0.016, and 0.0165 min^{-1} , respectively. The total amount of PS applied to the alumina (three applications; 50 g PS kg^{-1} alumina; total 150 g PS kg^{-1} alumina) would be considered a very high dosage in ISCO deployment. This outcome indicated that alumina scavenging of $\text{SO}_4^{\bullet-}$ continued to play an important role in limiting RhB transformation and that this source of treatment inefficiency is not easily eliminated after multiple treatment cycles (Supporting Information S.7, Figure S.10).

Estimated Surface Scavenging Rate Constant.

k_{ES} was calculated by contrasting laboratory-derived kinetic parameters between the base case, alumina-free, homogenous system, and the alumina-amended heterogeneous systems (eq 13). The average values of k_{ES} for alumina derived from the UV-APS and T-APS treatment systems were similar, $2.42 \times 10^4 \text{ m}^{-2} \text{ s}^{-1}$ ($n = 13$) and $2.03 \times 10^4 \text{ m}^{-2} \text{ s}^{-1}$ ($n = 8$), respectively (Table 2). The initial rates of $\text{SO}_4^{\bullet-}$ reaction with RhB, PS, and alumina (eqs 4, 7, and 9, respectively) represent the relative fate of $\text{SO}_4^{\bullet-}$ in the reaction system (Figure 1).

UV activation of PS resulted in the formation of $\text{SO}_4^{\bullet-}$ in the aqueous phase. In the complete-mix, alumina-amended test reactors, the reaction of $\text{SO}_4^{\bullet-}$ can occur with species in the aqueous phase or on the surface of the alumina solids. At low [alumina] ($1\text{--}5 \text{ g L}^{-1}$), RhB was the predominant reactant. At [alumina] $>5 \text{ g L}^{-1}$, alumina became the major reactant with $\text{SO}_4^{\bullet-}$ in the system. Overall, these results indicate that alumina mineral surfaces scavenge $\text{SO}_4^{\bullet-}$ and play a significant role in the fate of $\text{SO}_4^{\bullet-}$, and that the surface scavenging represents a major source of treatment inefficiency in PS-based treatment systems.

Treatment Efficiency.

The impact of radical scavenging by aqueous and solid phase surfaces can be examined in the context of treatment efficiency (η). The efficiency (E_1) (eq 14) of PS activation-dependent $\text{SO}_4^{\bullet-}$ formation is the ratio of the rate of $\text{SO}_4^{\bullet-}$ formed, defined here as the overall rate of $\text{SO}_4^{\bullet-}$ consumption (eq 3), and the rate of PS reaction (i.e., $k_{\text{PS}} \times [\text{PS}]$). The efficiency (E_2) (eq 15) of $\text{SO}_4^{\bullet-}$ reaction with the target compound relative to other reactants is defined here as the ratio of the rate of probe (P) oxidation by $\text{SO}_4^{\bullet-}$, and the overall rate of $\text{SO}_4^{\bullet-}$ consumption (eq 3). The product of E_1 and E_2 simplifies to the ratio of the rate of probe oxidation and the rate of PS reaction. Experimentally determined rates of RhB (Table 2) and PS (Table S.2) reaction were used to quantify η (eqs 16 and 17).

$$E_1 = \frac{[\text{SO}_4^{\bullet-}]k_{\text{SO}_4^{\bullet-}, P}[P] + ([\text{SO}_4^{\bullet-}]\sum_{i=1}^n k_i[S_i]) + ([\text{SO}_4^{\bullet-}]\sum_{i=1}^n k_{\equiv, i}[S_{\equiv, i}])}{k_{\text{PS}}[\text{PS}]} \quad (14)$$

$$E_2 = \frac{[\text{SO}_4^{\bullet-}]k_{\text{SO}_4^{\bullet-}, P}[P]}{[\text{SO}_4^{\bullet-}]k_{\text{SO}_4^{\bullet-}, P}[P] + ([\text{SO}_4^{\bullet-}]\sum_{i=1}^n k_i[S_i]) + ([\text{SO}_4^{\bullet-}]\sum_{i=1}^n k_{\equiv, i}[S_{\equiv, i}])} \quad (15)$$

$$\eta = E_1 \times E_2 = [\text{SO}_4^{\bullet-}] \times k_{\text{SO}_4^{\bullet-}, P} \times [P] / k_{\text{PS}} \times [\text{PS}] \quad (16)$$

$$\eta = k_P \times [P] / k_{\text{PS}} / [\text{PS}] \quad (17)$$

where k_{PS} is the experimentally determined pseudo-first-order degradation rate of PS (s^{-1}) and k_P is the experimentally determined pseudo-first-order degradation rate of RhB (s^{-1}).

Results indicate that the role of E_1 , and therefore NPR remains generally constant (0.13) with increasing alumina concentration (Supporting Information S.8, Figure S.11). The reaction between PS and alumina was negligible (Supporting Information S.3, Figure S.4), indicating that the source of NPRs cannot be attributed to this reaction. A minor source of NPRs in the system was due to the reaction between $\text{SO}_4^{\bullet-}$ and PS (R7, Table 1). Specifically, the rate of PS reaction attributed to $\text{SO}_4^{\bullet-}$ scavenging (i.e., rate of $\text{SO}_4^{\bullet-}$ scavenging by PS) was small relative to the overall reaction rate of PS (i.e., $k_7 \times [\text{PS}] \times [\text{SO}_4^{\bullet-}]_{\text{SS}} / k_{\text{PS}} \times [\text{PS}] \approx 0.037\text{--}0.006$; $0\text{--}50 \text{ g L}^{-1}$ alumina, respectively). It is also noted that

the rate of $\text{SO}_4^{\bullet-}$ scavenging by PS, relative to the overall rate of $\text{SO}_4^{\bullet-}$ consumption (eq 3), was significant (0.29–0.04; 0–50 g L⁻¹ alumina, respectively). This indicates that whereas PS may be a significant scavenger of $\text{SO}_4^{\bullet-}$, the impact of $\text{SO}_4^{\bullet-}$ on the PS reaction rate was limited and did not constitute a major source of NPRs. Other sources of NPRs played a role and are presently undifferentiated. The efficiency of $\text{SO}_4^{\bullet-}$ reaction with RhB (E_2) declined significantly and was correlated with an increase in the concentration of alumina amended to the test systems (Supporting Information S.8, Figure S.11). Under ideal conditions, that is, in the absence of NPR and $\text{SO}_4^{\bullet-}$ scavenging, the ideal efficiency would be 2.0 for both UV-APS and T-APS oxidative treatment systems, where 2 mol $\text{SO}_4^{\bullet-}$ are formed/mol PS (i.e., R1 and R2, Table 1). On this basis, the overall ideal efficiency (η_{ideal}), defined as $E_1 \times E_2/2 = (k_{\text{RhB}} \times [\text{RhB}]/k_{\text{PS}} \times [\text{PS}]/2)$, ranged from 0.044 to 0.007 (0–50 g L⁻¹ alumina, respectively) (Supporting Information S.8, Figure S.11). In natural soil systems where PS reacts directly with reduced aquifer solids and does not form $\text{SO}_4^{\bullet-}$, NPRs would play a greater role and the range in η_{ideal} is projected to be lower. It is evident that the reduction in treatment efficiency as a result of alumina amendment to the oxidative treatment system underscores the role of solid surfaces in scavenging radicals in PS-based oxidation treatment systems.

The mechanism of surface scavenging is beyond the scope of this study; however, some speculation is warranted. The alumina mineral (α -phase) used here was highly crystalline (calcined at $T \approx 1000^\circ\text{C}$) and is considered to be less catalytically active than low-temperature calcined alumina and exhibited low surface area.²⁵ The dehydration step during calcination causes formation of surface defects^{25,30} that may be responsible for $\text{SO}_4^{\bullet-}$ scavenging. Also, the (protonated) hydroxyl groups (OH) on the surface of alumina are known reactants with $\cdot\text{OH}$ ³¹ ($1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)³² and could serve as potential H donors to form HSO_4^- . It is not proposed that Al ion in alumina (Al_2O_3) specifically scavenges $\text{SO}_4^{\bullet-}$, as it occurs at its highest oxidation state.

Environmental Implications.

In subsurface systems, the solids to water ratio is much greater than in the dilute suspensions used during the laboratory testing in this study. This suggests that the rate of $\text{SO}_4^{\bullet-}$ scavenging by mineral surfaces could be much greater in aquifer and soil systems during ISCO deployment than in dilute solid suspensions. To explore this further, $\text{SO}_4^{\bullet-}$ scavenging rates were calculated using the experimentally derived value of k_{SS} for alumina (Table 2) and contrasted with $\text{SO}_4^{\bullet-}$ reaction rates with aqueous phase species. In this simplified analysis, assumed conditions and parameter values included an ideal representative volume of unconsolidated porous media (1 m³) containing 7 wt % of alumina, 1 pore volume mixture of 1,4-dioxane ($1.13 \times 10^{-5} \text{ M}$; 1 mg L⁻¹), and PS ($4.2 \times 10^{-2} \text{ M}$; 10 g L⁻¹) with instantaneous mixing, no 1,4-dioxane sorption or NPR, and $[\text{SO}_4^{\bullet-}]_{\text{SS}} = 5 \times 10^{-12} \text{ M}$. The rate of $\text{SO}_4^{\bullet-}$ reaction with alumina surfaces ($t = 0 \text{ h}$) dominated the fate of $\text{SO}_4^{\bullet-}$ by approximately 5 and 7 orders of magnitude over PS and 1,4-dioxane, respectively (Figure 2). These results emphasize the dominant role of $\text{SO}_4^{\bullet-}$ scavenging by mineral surfaces during PS-driven oxidative treatment in aquifer and soil systems.

Previously, perchloroethylene (PCE) oxidation was evaluated using heat-activated PS in the presence of 10 different solids including clays, sands, and a field soil.³³ In batch systems containing illite or montmorillonite, approximately the same amount of PS was reacted as in the solids-free system, but rates of PCE oxidation were significantly diminished in comparison to the solids-free system. This suggests that the reduction in treatment efficiency outcome was predominantly attributed to surface scavenging (i.e., E_2). Further, the PCE loss was greater in illite than montmorillonite, which suggests that the role of k_{S} is mineral-specific.

The kinetic analysis method developed in this study involved the quasi-steady-state assumption where $d[\text{SO}_4^{\bullet-}]/dt \approx 0$ and $C_{\text{SO}_4^{\bullet-}} \approx P_{\text{SO}_4^{\bullet-}}$ (eq 2), in conjunction with the condition that $P_{\text{SO}_4^{\bullet-}}$ was similar between the solids-free and solids-amended systems.

Alumina was found to be unreactive with the PS (Supporting Information S.3, Figure S.4), making it an ideal mineral solid to test in these experiments. Given the identical test conditions used for the solids-free and solids-amended systems, and that the pseudo-first-order degradation rate constant for PS (k_{PS} (s^{-1})), and the PS (M) were found to be approximately equal, the time-dependent differences in [RhB] were attributed to surface scavenging allowing $k_{\text{S,alumina}}$ to be estimated.

Under the condition where the solid phase media reacts with PS and does not produce $\text{SO}_4^{\bullet-}$ (i.e., NPR), the kinetic analysis method presented here would yield an estimate of k_{S} that represents a maximum value (i.e., eq 13) and therefore must be reported with a qualifier (i.e., k_{S}). Under the condition where solid phase media react with PS and produce $\text{SO}_4^{\bullet-}$, as is most often the case (i.e., natural activation), the kinetic analysis method developed here becomes unstable because $P_{\text{SO}_4^{\bullet-}}$ cannot be equated between the solids-free and solids-amended systems which served as the basis for eq 13. For example, in studies involving PS reaction in soil and mineral oxidative treatment systems, contaminant transformation rates were contrasted between solids-free and solids-amended (i.e., Fe- and Mn-based minerals, including goethite, birnessite, soils, and aquifer materials) to assess PS activation.³⁴ The PS reacted with the solid phase media and consequently, results could not be used to definitively assess whether the changes in probe oxidation rates were attributed to (1) changes in PS activation efficiency (E_1) where $\text{SO}_4^{\bullet-}$ production ($P_{\text{SO}_4^{\bullet-}}$) changed (i.e., the mineral species is a better/worse activator), (2) NPR, or (3) $\text{SO}_4^{\bullet-}$ oxidation efficiency (E_2) where there was a change in the $\text{SO}_4^{\bullet-}$ scavenging rate by the solids amended to the treatment system, or perhaps by the soluble constituents imparted by the solids. Conversely, where illite–smectite was amended to a thermally activated PS treatment system, a decrease in the PCE degradation rate was measured relative to the solids-free, base-case system, despite similar rates of PS reaction.³³ This result suggested proof of concept that solid surfaces were responsible for scavenging radicals and reducing PCE degradation.

The total oxidant demand test was developed as a diagnostic tool to generally measure the mass of oxidant needed to significantly reduce background soil oxidant demand, improve contaminant oxidation, and to quantify how much oxidant is needed for ISCO design purposes.^{35,36} Others have reported that repeated persulfate treatments did not improve the rate of contaminant oxidation in some soils and minerals.³³ One possible explanation for

these seemingly opposing results may lie in the role of radical scavenging. Solid phase radical scavenging occurs during and after persulfate treatments, where significant reductions in background oxidant demand and NPR may be achieved. Specifically, elimination of the background oxidant demand does not preclude aggressive surface radical scavenging by some solid phase media, including alumina. Results from our study indicate that repeated and aggressive persulfate treatments of the alumina (i.e., 50 g PS/kg alumina ($\times 3$); 150 g PS/kg alumina) did not significantly diminish the rate of $\text{SO}_4^{\bullet-}$ scavenging, suggesting that this source of treatment inefficiency is not easily eliminated for some solid phase media. Rather, these results suggest that surface radical scavenging extends beyond the depletion of oxidant demand, and contaminant transformation is controlled by competing $\text{SO}_4^{\bullet-}$ reactions between the target contaminant(s) and nontarget species, including aqueous species and solid phase surfaces as per eq 15.

In this study, kinetic analysis and laboratory methods were developed to account for the reaction of $\text{SO}_4^{\bullet-}$ in both the aqueous and solid phases for the first time. By accounting for the significant reaction of $\text{SO}_4^{\bullet-}$ at solid surfaces, it is evident that $\text{SO}_4^{\bullet-}$ production is likely much greater than currently being credited in PS-driven ISCO systems, and possibly advanced oxidation technology water treatment systems. Given the predominant role of $\text{SO}_4^{\bullet-}$ scavenging by solid surfaces in environmental oxidative treatment systems, it is evident that methods to mitigate this form of scavenging would have a high potential to improve the treatment efficiency.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

This research was performed while K.R.C. held an NRC Research Associateship award with the U.S. Environmental Protection Agency at the Robert S. Kerr Environmental Research Center, Ada, OK 74820. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

REFERENCES

- (1). Sra KS; Thomson NR; Barker JF Persistence of persulfate in uncontaminated aquifer materials. *Environ. Sci. Technol* 2010, 44, 3098–3104. [PubMed: 20205387]
- (2). Johnson RL; Tratnyek PG; Johnson ROB Persulfate persistence under thermal activation conditions. *Environ. Sci. Technol* 2008, 42, 9350–9356. [PubMed: 19174915]
- (3). Liang C; Lee I-L; Hsu I-Y; Liang C-P; Lin Y-L Persulfate oxidation of trichloroethylene with and without iron activation in porous media. *Chemosphere* 2008, 70, 426–435. [PubMed: 17692892]
- (4). Huling SG; Pivetz B. In Situ Chemical Oxidation-Engineering Issue, EPA/600/R-06/072, 2006.
- (5). Rusevova K; Kopinke F-D; Georgi A. Nano-sized magnetic iron oxides as catalysts for heterogeneous Fenton-like reactions - influence of Fe(II)/Fe(III) ratio on catalytic performance. *J. Hazard. Mater* 2012, 241–242, 433–440.
- (6). Grebel JE; Pignatello JJ; Mitch WA Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. *Environ. Sci. Technol* 2010, 44, 6822–6828. [PubMed: 20681567]

- (7). Lipczynska-Kochany E; Sprah G; Harms S. Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction. *Chemosphere* 1995, 30, 9–20. [PubMed: 22454978]
- (8). Huie RE; Clifton CL Temperature dependence of the rate constants for the reaction of sulfate radical, $\text{SO}_4^{\cdot-}$, with anions. *J. Phys. Chem* 1990, 94, 8561–8567.
- (9). Waldemer RH; Tratnyek PG; Johnson RL; Nurmi JT Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products. *Environ. Sci. Technol* 2007, 41, 1010–1015. [PubMed: 17328217]
- (10). Tsitonaki A; Petri B; Crimi M; Mosbæk H; Siegrist RL; Bjerg PL In situ chemical oxidation of contaminated soil and groundwater using persulfate: A review. *Crit. Rev. Environ. Sci. Technol* 2010, 40, 55–91.
- (11). Wacławek S; Lutze HV; Grubel K; Padil VVT; Cernik M; Dionysiou DD Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J* 2017, 330, 44–62.
- (12). Neta P; Huie RE; Ross AB Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* 1988, 17, 1027–1284.
- (13). Matta R; Tlili S; Chiron S; Barbat S. Removal of carbamazepine from urban wastewater by sulfate radical oxidation. *Environ. Chem. Lett* 2011, 9, 347–353.
- (14). Huang K-C; Zhao Z; Hoag GE; Dahmani A; Block PA Degradation of volatile organic compounds with thermally activated persulfate oxidation. *Chemosphere* 2005, 61, 551–560. [PubMed: 16202809]
- (15). Wang J; Wang S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging pollutants. *Chem. Eng. J* 2018, 334, 1502–1517.
- (16). Zhang B-T; Zhang Y; Teng Y; Fan M. Sulfate radical and its application in decontamination technologies. *Crit. Rev. Environ. Sci. Technol* 2015, 45, 1756–1800.
- (17). Anipsitakis GP; Dionysiou DD Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol* 2004, 38, 3705–3712. [PubMed: 15296324]
- (18). Xu X-R; Li X-Z Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion. *Sep. Purif. Technol* 2010, 72, 105–111.
- (19). Dua X.; S C.; Zho L.; Su H.; Suvorov A.; Odeair T.; Zh Z.; Sha Z.; Wan S. Surface controlled generation of reactive radicals from persulfate by carbocatalysis on nanodiamonds. *Appl. Catal., B* 2016, 194, 7–15.
- (20). Fang G; Gao J; Dionysiou DD; Liu C; Zhou D. Activation of persulfate by quinones: free radical reactions and implication for the degradation of PCBs. *Environ. Sci. Technol* 2013, 47, 4605–4611. [PubMed: 23586773]
- (21). Ike IA; Linden KG; Orbell JD; Duke M. Critical review of the science and sustainability of persulfate advanced oxidation processes. *Chem. Eng. J* 2018, 338, 651–669.
- (22). George C; Rassy HE; Chovelon J-M Reactivity of selected volatile organic compounds (VOCs) toward the sulfate radical ($\text{SO}_4^{\cdot-}$). *Int. J. Chem. Kinet* 2001, 33, 539–547.
- (23). Kolthoff IM; Miller IK The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. *J. Am. Chem. Soc* 1951, 73, 3055–3059.
- (24). Rusevova Crincoli K; Huling SG Hydroxyl radical scavenging by solid mineral surfaces in oxidative treatment systems: rate constants and implications. *Water Res.* 2020, 169, 115240.
- (25). Kasprzyk-Hordern B. Chemistry of alumina, reactions in aqueous solution and its application in water treatment. *Adv. Colloid Interface Sci* 2004, 110, 19–48. [PubMed: 15142822]
- (26). Ko S, Huling SG, Pivetz B. Ground water sample preservation at in-situ chemical oxidation sites—recommended guidelines. EPA Ground Water Issue Paper EPA/600/R-12/049; US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center: Ada, OK, 2012.
- (27). Huling SG; Ko S; Park S; Kan E. Persulfate oxidation of MTBE- and chloroform-spent granular activated carbon. *J. Hazard. Mater* 2011, 192, 1484–1490. [PubMed: 21782339]
- (28). Huling S; Arnold RG; Sierka RA; Miller MR Influence of peat on Fenton oxidation. *Water Res.* 2001, 35, 1687–1694. [PubMed: 11329670]

- (29). Liang CJ; Huang SC Kinetic model for sulfate/hydroxyl radical oxidation of methylene blue in a thermally-activated persulfate system at various pH and temperatures. *Sustainable Environ. Res* 2012, 22, 199–208.
- (30). Flockhart BD; Leith IR; Pink RC Electron-transfer at alumina surfaces. Part 3. Reduction of aromatic nitro-compounds. *Trans. Faraday Soc* 1970, 66, 469–476.
- (31). Suh M; Bagus PS; Pak S; Rosynek MP; Lunsford JH Reactions of hydroxyl radicals on titania, silica, alumina, and gold surfaces. *J. Phys. Chem. B* 2000, 104, 2736–2742.
- (32). Buxton GV; Greenstock CL; Helman WP; Ross AB Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\bullet\text{OH}/\text{O}\bullet^-$) in aqueous-solution. *J. Phys. Chem. Ref. Data* 1988, 17, 513–886.
- (33). Costanza J; Otaño G; Callaghan J; Pennell KD PCE oxidation by sodium persulfate in the presence of solids. *Environ. Sci. Technol* 2010, 44, 9445–9450. [PubMed: 21070044]
- (34). Ahmad M; Teel AL; Watts RJ Persulfate activation by subsurface minerals. *J. Contam. Hydrol* 2010, 115, 34–45. [PubMed: 20439128]
- (35). Haselow JS; Siegrist RL; Crimi M; Jarosch T. Estimating the total oxidant demand for in situ chemical oxidation design. *Remediat. J* 2003, 13, 5–16.
- (36). Johnson RL; Tratnyek PG; Johnson ROB Persulfate persistence under thermal activation conditions. *Environ. Sci. Technol* 2008, 42, 9350–9356. [PubMed: 19174915]

Figure 1. Initial SO_4^{2-} reaction rates with RhB (5 mg L^{-1} ; 0.01 mM), PS (500 mg L^{-1} ; 2.94 mM), and alumina ($0\text{--}50 \text{ mg L}^{-1}$), $\text{pH}_{\text{start}} = 6.0$, $\text{pH}_{\text{end}} = 4.5$.

Figure 2.

Calculated $\text{SO}_4^{\bullet-}$ reaction and scavenging rates in aquifer material where k_{ss} was derived from this study; aquifer and reaction parameters: total volume = 1 m^3 , $\rho_{\text{bulk}} = 1.6 \text{ g cm}^{-3}$, porosity (η) = 0.3, [alumina] = 7 wt %, $k_{\text{ss}} = 4.42 \times 10^4 \text{ m}^{-2} \times \text{s}^{-1}$, $[\text{PS}]_0 = 4.2 \times 10^{-2} \text{ M}$, $k_6 = 6.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $[1,4\text{-dioxane}]_0 = 1.13 \times 10^{-5} \text{ M}$, $k_{\text{SO}_4^{\bullet-}, 1,4\text{-dioxane}} = 4.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $[\text{SO}_4^{\bullet-}]_{\text{SS}} = 5 \times 10^{-12} \text{ M}$ (assumed).

Table 1.

Summary of Persulfate Activation, Related Reactions, and Rate Constants

persulfate activation	
Heat (>35 °C)	
$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ (R1)	
UV Irradiation (<400 nm)	
$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ (R2)	
e^- Transfer	
$S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-}$ (R3)	
$S_2O_8^{2-} \rightarrow 2SO_4^{2-}$ (R4)	
sulfate radical reaction	
$SO_4^{\bullet-} + RhB \rightarrow$ products (R5)	$k_5 = 3.02(\pm 0.03) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (this study)
$SO_4^{\bullet-} + MTBE \rightarrow$ products (R6)	$k_6 = 3.13(\pm 0.02) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (ref 22)
$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$ (R7)	$k_7 = 6.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (ref 12)
$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-}$ (R8)	$k_8 = 7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (ref 12)
$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \bullet OH + H^+$ (R9)	$k_9 = 6.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (ref 12)
$SO_4^{\bullet-} + \sum_{i=1}^n [S_i] \rightarrow$ products (R10)	
$SO_4^{\bullet-} + S_j^- \rightarrow$ products (R11)	$k_{\text{SSi,alumina}}$ (this study)

Table 2.

Estimates of the Surface $\text{SO}_4^{\bullet-}$ Scavenging Rate Constant (k_{SS}) for Alumina Derived from UV-APS and T-APS Treatment Systems

[alumina] (g L ⁻¹)	k_{RhB}^a (s ⁻¹)	$[\text{SO}_4^{\bullet-}]_{\text{SS}}^a$ (M)	k_{SS} (m ⁻² s ⁻¹)
UV-APS^b			
0 (<i>n</i> = 3)	4.67×10^{-4}	1.55×10^{-12}	
1 (<i>n</i> = 3)	3.22×10^{-4}	1.07×10^{-12}	5.27×10^5
5 (<i>n</i> = 2)	2.52×10^{-4}	8.35×10^{-13}	2.04×10^4
10 (<i>n</i> = 4)	1.88×10^{-4}	6.25×10^{-13}	1.81×10^4
30 (<i>n</i> = 2)	1.55×10^{-4}	5.14×10^{-13}	8.14×10^a
50 (<i>n</i> = 2)	7.08×10^{-5}	2.35×10^{-13}	1.35×10^4
			avg. 2.42×10^4
T-APS^c			
0 (<i>n</i> = 3)	9.92×10^{-5}	3.50×10^{-13}	
1 (<i>n</i> = 2)	8.17×10^{-5}	2.88×10^{-13}	2.52×10^4
5 (<i>n</i> = 3)	5.89×10^{-5}	2.08×10^{-13}	1.63×10^4
10 (<i>n</i> = 3)	3.72×10^{-5}	1.31×10^{-13}	2.12×10^4
			avg. 2.03×10^4

^a Average k_{RhB} and $[\text{SO}_4^{\bullet-}]_{\text{SS}}$ for alumina concentrations 0–50 g L⁻¹; k_{RhB} in the UV-APS system 0.92 ± 0.99 ; k_{RhB} in the T-APS system 0.94 ± 0.99 .

^b UV-APS system: average k_{SS} (*n* = 13) using 1–50 g L⁻¹ alumina (95% C.I. = 1.57×10^4 to 3.27×10^4 m⁻² s⁻¹).

^c T-APS system: average k_{SS} (*n* = 8) using 1–10 g L⁻¹ alumina (95% C.I. = 1.58×10^4 to 2.48×10^4 m⁻² s⁻¹).