

Chemistry of persulfates for the oxidation of organic contaminants in water

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Abstract. Persulfates (i.e., peroxymonosulfate and peroxydisulfate) are capable of oxidizing a wide range of organic compounds via direct reactions, as well as by indirect reactions by the radical intermediates. In aqueous solution, persulfates undergo self-decomposition, which is accelerated by thermal, photochemical and metal-catalyzed methods, which usually involve the generation of various radical species. The chemistry of persulfates has been studied since the early twentieth century. However, its environmental application has recently gained attention, as persulfates show promise in *in situ* chemical oxidation (ISCO) for soil and groundwater remediation. Persulfates are known to have both reactivity and persistence in the subsurface, which can provide advantages over other oxidants inclined toward either of the two properties. Besides the ISCO applications, recent studies have shown that the persulfate oxidation also has the potential for wastewater treatment and disinfection. This article reviews the chemistry regarding the hydrolysis, photolysis and catalysis of persulfates and the reactions of persulfates with organic compounds in aqueous solution. This article is intended to provide insight into interpreting the behaviors of the contaminant oxidation by persulfates, as well as developing new persulfate-based oxidation technologies.

Keywords: persulfate; peroxymonosulfate; peroxydisulfate; *in situ* chemical oxidation (ISCO); soil and groundwater remediation; oxidation; sulfate radical

1. Introduction

Chemical oxidation is a rapid and strong method that is capable of transforming a wide spectrum of contaminants into less toxic and more biodegradable products. A number of oxidation technologies employing chemical oxidants, sometimes in combination with catalysts, have been developed for water treatment and soil remediation and many of them have already been put into practical use in treatment plants and contaminated sites. The chemical oxidants commonly used are ozone, hydrogen peroxide, chlorines and permanganate. The fundamental chemistry of these oxidants and the technical information for their applications are well documented (Siegrist *et al.* 2001, von Gunten 2003a, b, Pignatello *et al.* 2006, Deborde and von Gunten 2008, Huh and Ahn 2017, von Gunten 2018).

Persulfates (i.e., peroxymonosulfate and peroxydisulfate) are relatively new oxidants that have recently attracted interest. Anipsitakis and Dionysiou (2003) first proposed the use of peroxymonosulfate (PMS) for environmental remediation as an oxidant for the cobalt-catalyzed Fenton-like system. The traditional Fenton system (i.e., hydrogen peroxide in combination with iron) is available only under acidic pH conditions, due to the precipitation of iron and the mechanistic alteration of the Fenton reaction under neutral pH conditions (Hug and

Leupin 2003, Pignatello *et al.* 2006), whereas the cobalt-catalyzed system using PMS exhibits constant activity regardless of pH. Although several undefined issues related to cost and process design still limit the practical application of PMS, significant research is being conducted to develop various PMS-based oxidation technologies and optimize their efficiency.

On the other hand, peroxydisulfate (PDS) has attracted attention for the purpose of *in situ* chemical oxidation (ISCO) for soil and groundwater remediation (Huling and Pivetz 2006). PDS is a unique oxidant that exhibits both the properties of reactive oxidants (e.g., hydrogen peroxide and ozone) and persistent ones (e.g., permanganate). The decomposition of PDS forms reactive radical intermediates that can non-selectively oxidize a variety of organic compounds with high reaction rates. At the same time, PDS is known to remain stable for several weeks in the subsurface, allowing sufficient time for the oxidants to diffuse in the targeted area. Many PDS-based ISCO technologies have been suggested for the past ten years and some of them are currently being used in field scale applications (Tsitonaki *et al.* 2010).

The chemistry of persulfates and related compounds has been sporadically studied for the past century. The chemistries of PMS and PDS are closely related to each other, because these oxidants are interconvertible under certain conditions and share many radical intermediates formed during their decomposition. With the recent advances in persulfate-based remediation technologies, there has been an increasing need to review the chemistry of persulfates from the viewpoint of environmental

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application. In recent years, several papers have reviewed the chemistry and applications of persulfate-based oxidation systems (Tsitonaki *et al.* 2010, Matzek and Carter 2016, Zhao *et al.* 2017, Ghanbari and Moradi 2017, Waclawek *et al.* 2017, Ike *et al.* 2018, Wang and Wang 2018). However, the focus of these reviews was mainly on the activation of persulfates (i.e., the conversion of persulfates into more reactive species) and the application of activated-persulfates to the oxidation of organic contaminants.

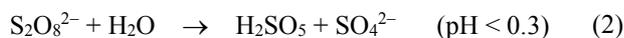
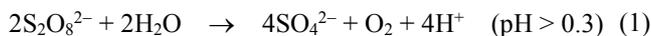
The purposes of this review article are to improve understanding of the fundamental chemistry of persulfates and to provide new perspectives for interpreting the persulfate-based remediation systems. This article presents an overview of the basic chemistry associated with the thermal, photochemical and metal-catalytic decomposition of persulfates (both PMS and PDS), as well as the reactions of persulfates with organic compounds. The details of persulfate activation using a variety of approaches reported in many recent papers (mainly using heterogeneous catalysts) are beyond the scope of this review.

2. Aqueous chemistry of persulfates

2.1 Thermal decomposition

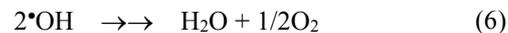
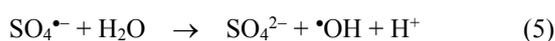
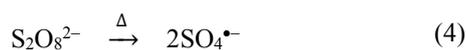
2.1.1 Peroxydisulfate

Peroxydisulfate (PDS) undergoes thermal decomposition in aqueous solution (i.e., hydrolysis) and its chemistry has been mainly studied before the 1960s (Palme 1920, Smith and Campbell 1947, Bartlett and Nozaki 1948, Bartlett and Cotman 1949, Kolthoff and Miller 1951). The mechanism for the hydrolysis of PDS depends on the solution pH. Under dilute acidic, neutral and alkaline pH conditions (pH > 0.3), PDS oxidizes water into oxygen (four-electron oxidation), with the overall reaction represented by Reaction 1. However, in strong acidic solution (pH < 0.3), PDS is hydrolyzed into peroxymonosulfuric acid (H₂SO₅) (Reaction 2), which can be further decomposed into hydrogen peroxide (H₂O₂) via two-electron oxidation of water (Reaction 3).



In order to determine the source of oxygen released from Reaction 1, Kolthoff and Miller (1951) performed the experiments with O¹⁸-labelled water over the pH range from (0.3 to 13). They found that the oxygen is mainly from water molecules at approximately pH > 1.5, whereas at the lower pH values, PDS itself serves as the major oxygen source, with an increasing degree as the pH decreases. From these observations, the following mechanism was proposed, depending on the solution pH:

At pH > 1.5 (Reactions 4-6):



At pH < 1.5 (Reactions 7 and 8):

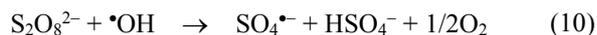


At pH < 0.3 (Reaction 9):

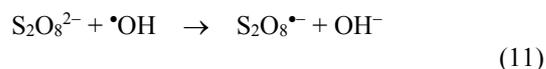


According to the mechanism, at pH > 1.5, the decomposition of PDS is initiated by the homolytic fission of the O-O bond to form two sulfate radical anions (SO₄^{•-}) (Reaction 4). SO₄^{•-} is converted into hydroxyl radical (•OH) (Reaction 5), which subsequently goes through the disproportionation to oxygen (Reaction 6; this reaction is composed of many elementary reactions involving free radicals, of which the details will be discussed below). At pH < 1.5, the PDS hydrolysis is initiated via the heterolytic fission of the O-O bond to form sulfur tetraoxide (SO₄), which subsequently releases oxygen (Reactions 7 and 8). In strong acidic solution (pH < 0.3), SO₄ is hydrolyzed to H₂SO₅ (Reaction 9).

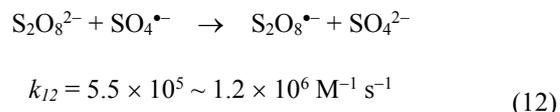
Although not included in the mechanism suggested by Kolthoff and Miller (1951), the radical species produced by Reactions 4 and 5 (i.e., SO₄^{•-} and •OH) can be further used in the decomposition of PDS. An earlier study proposed the reaction of •OH with PDS (Reaction 10, Bartlett and Cotman 1949). House (1962) also pointed out that a chain decomposition mechanism including Reaction 10 is more suitable for explaining the behavior of PDS hydrolysis in the presence of organic substrates:



The rate constants determined in the later studies indicate that the reaction of S₂O₈²⁻ with SO₄^{•-} is also responsible for the chain decomposition of PDS (Reaction 12).



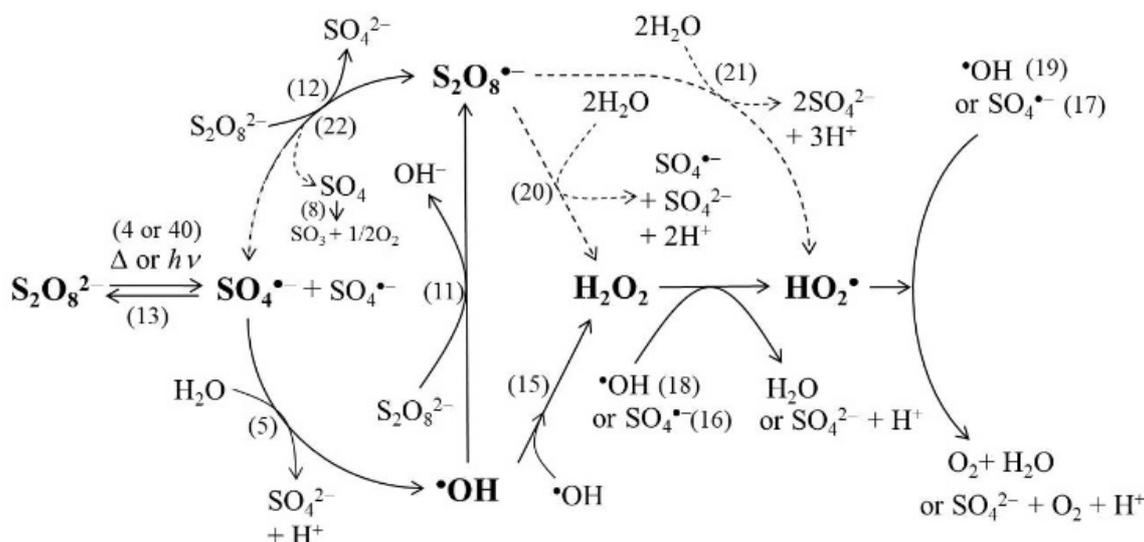
$$k_{11} < 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{Roebke } et al. \text{ 1969})$$



(Schuchmann *et al.* 1987, McElroy and Waygood 1990, Jiang *et al.* 1992, Herrmann *et al.* 1995, Yu *et al.* 2004)

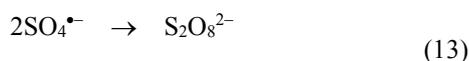
No researchers since Kolthoff and Miller (1951) have focused on the chemistry of PDS hydrolysis in particular. However, many research groups have extensively studied the reactions of free radicals containing sulfur and oxygen using pulsed radiation and spectroscopic techniques (Hayon *et al.* 1972, Bielski *et al.* 1985, Buxton *et al.* 1988, Neta *et al.* 1988). Based on those reactions and their determined rate constants, the mechanism of the PDS hydrolysis at pH > 3 can be reorganized as follows.

SO₄^{•-} produced from the initiation (Reaction 4) oxidizes

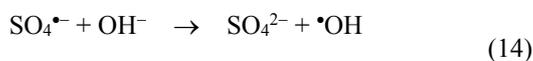


Scheme 1 Overall mechanism of the thermal ($3 < \text{pH} < 13$) and the photolytic decomposition of PDS: The dashed lines indicate the reactions postulated in this article, the numbers in parentheses represent the reaction numbers in the text.

either $\text{S}_2\text{O}_8^{2-}$ into $\text{S}_2\text{O}_8^{\bullet-}$ (Reaction 12) or water into $\bullet\text{OH}$ (Reaction 5), unless it is reversed to $\text{S}_2\text{O}_8^{2-}$ (Reaction 13). Many researchers has reported the k_{12} values ranging from 5.5×10^5 to $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Schuchmann *et al.* 1987, McElroy and Waygood 1990, Jiang *et al.* 1992, Herrmann *et al.* 1995, Yu *et al.* 2004), although a few have suggested lower values ($< 10^4 \text{ M}^{-1} \text{ s}^{-1}$, Bao and Barker 1996, $5.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, Ivanov *et al.* 2000). The rate constant for Reaction 5 (k_5) reported in the literature ranges from 7.9 to $170 \text{ M}^{-1} \text{ s}^{-1}$ (Hayon *et al.* 1972, Herrmann *et al.* 1995, Bao and Barker 1996, Ivanov *et al.* 2000, Yu *et al.* 2004). As calculated with maximum values for k_5 and k_{12} from the literature, Reaction 12 is more favored than Reaction 5 when the concentration of $\text{S}_2\text{O}_8^{2-}$ is approximately more than 8 mM. However, in alkaline solution, the oxidation of water into $\bullet\text{OH}$ by $\text{SO}_4^{\bullet-}$ can be accelerated (Reaction 14).



$$k_{13} = (3.8 \times 10^8 - 1.8 \times 10^9) \text{ M}^{-1} \text{ s}^{-1} \text{ (Neta *et al.* 1988)}$$

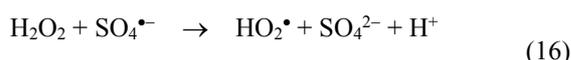


$$k_{14} = (4.6 \times 10^7 - 8.3 \times 10^7) \text{ M}^{-1} \text{ s}^{-1} \text{ (Neta *et al.* 1988)}$$

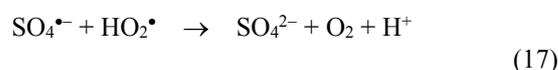
The self-combination of $\bullet\text{OH}$ (Reaction 15) produces hydrogen peroxide (H_2O_2), which is further oxidized into hydroperoxyl radical (HO_2^{\bullet}) and oxygen in a series of reactions with $\text{SO}_4^{\bullet-}$ (Reactions 16 and 17).



$$2k_{15} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton *et al.* 1988)}$$

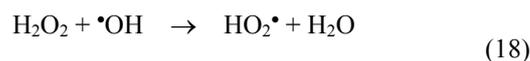


$$k_{16} = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (Maruthamuthu and Neta 1978)}$$

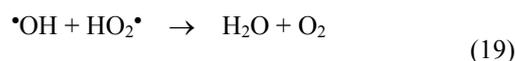


$$k_{17} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (Yu *et al.* 2004)}$$

The stepwise oxidation of H_2O_2 into oxygen can also take place via the reactions with $\bullet\text{OH}$ (Reactions 18 and 19).

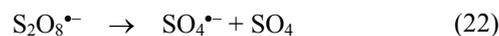
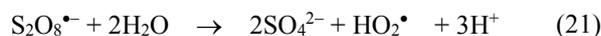
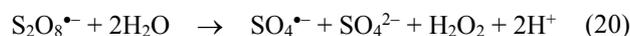


$$k_{18} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton *et al.* 1988)}$$



$$k_{19} = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton *et al.* 1988)}$$

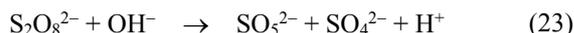
On the other hand, the fate of $\text{S}_2\text{O}_8^{\bullet-}$, the one-electron oxidation product of $\text{S}_2\text{O}_8^{2-}$ (from Reaction 12) is not well known. However, $\text{S}_2\text{O}_8^{\bullet-}$ may be used in the water oxidation, most likely through two or three-electron transfer (Reactions 20 and 21). It is also possible that $\text{S}_2\text{O}_8^{\bullet-}$ is self-decomposed into $\text{SO}_4^{\bullet-}$ and SO_4 , followed by Reaction 8 to release oxygen.



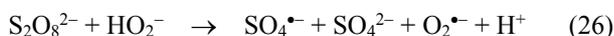
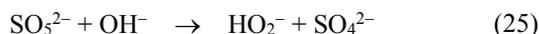
Based on the reactions discussed above, Scheme 1 summarizes the overall pathways of the PDS hydrolysis via a radical mechanism. The described pathways suggest that during the process, H_2O_2 occurs as an intermediate. However, the steady-state concentration of H_2O_2 may be low due to its fast consumption by the reactions with radical species (i.e., $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$): The rate constants for reactions of H_2O_2 with $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ are higher than those

of $S_2O_8^{2-}$ by more than one order of magnitude (compare k_{I1} vs. k_{I8} and k_{I2} vs. k_{I6}).

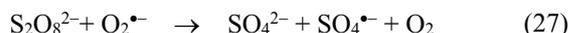
On the other hand, in strong alkaline solution (ca. pH > 13), PDS is known to undergo the base-catalyzed hydrolysis, according to which PDS is transformed into SO_5^{2-} and further decomposes to SO_4^{2-} and oxygen (Reactions 23 and 24, Singh and Venkatarao 1976).



However, a recent study has proposed that the decomposition of SO_5^{2-} (Reaction 24) consists of a series of elementary reactions that involve radical intermediates (Furman *et al.* 2010). The proposed mechanism indicates that SO_5^{2-} produces hydroperoxide anion (HO_2^- , the conjugate base of H_2O_2) (Reaction 25), which further reacts with $S_2O_8^{2-}$ to form $SO_4^{\bullet-}$ and $O_2^{\bullet-}$ (Reaction 26).



$SO_4^{\bullet-}$ initiates the radical chain reactions, as described in Scheme 1. $O_2^{\bullet-}$ may also be used in reducing PDS to produce another $SO_4^{\bullet-}$ (Reaction 27).



The hydrolysis of PDS follows the first-order kinetics with the rate law given in Eq. 28 (Kolthoff and Miller 1951, House 1962, Wilmarth *et al.* 1983). The observed rate constant for the decomposition of PDS ($k_{obs,PDS}$) does not significantly change with pH in neutral and weak alkaline solutions ($3 < \text{pH} < 13$). However, the $k_{obs,PDS}$ value increases in acidic solution ($\text{pH} < 3$) or in strong alkaline solution ($\text{pH} > 13$), where the acid-catalyzed (Reactions 7-9) or base-catalyzed mechanism (Reactions 23-26) is involved.

$$-d[S_2O_8^{2-}]/dt = k_{obs,PDS}[S_2O_8^{2-}] \quad (28)$$

In order to explain the pH dependence of the $k_{obs,PDS}$ value at $\text{pH} < 13$, Kolthoff and Miller (1951) divided $k_{obs,PDS}$ into two terms, consisting of the individual rate constants that account for the uncatalyzed and acid-catalyzed mechanisms, respectively (i.e., k_I and k_{II} , Eq. 29).

$$K_{obs,PDS} = k_I + k_{II}[H^+] \quad (29)$$

The rate of the PDS hydrolysis strongly depends on temperature. The activation energy of $k_{obs,PDS}$ reported in the previous studies ranges from 28 to 31 kcal mol⁻¹ under neutral pH conditions and more specifically, k_I has a slightly higher activation energy (i.e., 32-34 kcal mol⁻¹) than k_{II} (i.e., 24-28 kcal mol⁻¹) (House 1962). By fitting the temperature-dependent k_I and k_{II} values obtained by Kolthoff and Miller (1951) into the Arrhenius equation, k_{obs} can be expressed as a function of pH and temperature.

$$k_{obs,PDS} = k_I + k_{II}[H^+] = A_I \exp(-E_{aI}/(RT)) + A_{II} \exp(-E_{aII}/(RT)) \times 10^{-\text{pH}} \quad (30)$$

Where, $A_I = 1.200 \times 10^{17} \text{ s}^{-1}$, $A_{II} = 6.168 \times 10^{13} \text{ s}^{-1}$, $E_{aI} =$

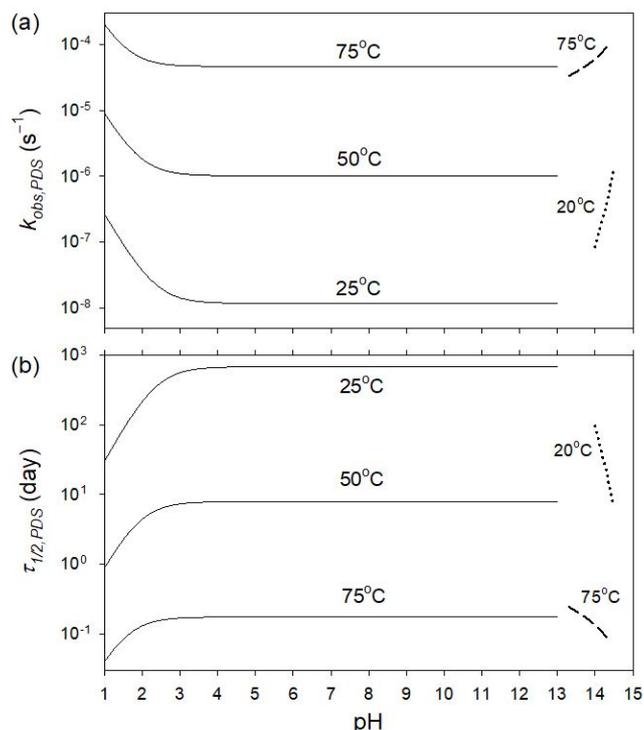


Fig. 1 (a) First-order rate constants and (b) half-lives for the hydrolysis of PDS as a function of pH: The solid lines are calculated based on the results by Kolthoff and Miller (1951) and the dashed and dotted lines are experimental data from Singh and Venkatarao (1976) and Furman *et al.* (2010), respectively.

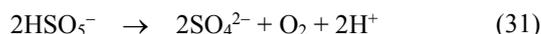
34.08 kcal mol⁻¹, $E_{aII} = 26.42 \text{ kcal mol}^{-1}$, R (gas constant) = $1.986 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$ and T is temperature (K). The k_{obs} value as a function of temperature and pH was calculated by Eq. 30 and presented with the estimated half-life ($\tau_{1/2,PDS}$) (Fig. 1).

The initial concentration of PDS ($[S_2O_8^{2-}]_0$) and ionic strength also have a slight influence on the rate of the PDS hydrolysis. The $k_{obs,PDS}$ value increases by approximately 30-40% when $[S_2O_8^{2-}]_0$ decreases by one order of magnitude (Schumb and Rittner 1940, Kolthoff and Miller 1951, House 1962). Increasing ionic strength suppresses the acid-catalyzed decomposition by lowering the pK_a of $HS_2O_8^-$. The $k_{obs,PDS}$ value measured in 0.1 M HClO_4 solution decreased by half when 0.9 M NaClO_4 was added (Kolthoff and Miller 1951).

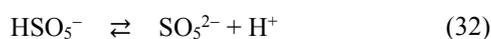
In strong alkaline solution ($\text{pH} > 13$), the rate of the PDS decomposition increases with the concentration of OH^- due to the base-catalyzed mechanism (Singh and Venkatarao 1976, Furman *et al.* 2010). According to the earlier study by Singh and Venkatarao (1976), $k_{obs,PDS}$ increased from 3.3×10^{-5} to $9.0 \times 10^{-5} \text{ s}^{-1}$ when $[\text{OH}^-]$ varied from 0.2 to 2 M (pH 13-14.3) at 75°C, which appears to reasonably extrapolate the values in the lower pH range (the dashed line in Fig. 1). However, the recent values reported by Furman *et al.* (2010) were much higher than those that can be predicted from the lower pH values (the dotted line in Fig. 1).

2.1.2 Peroxymonosulfate

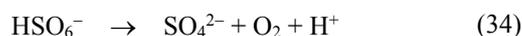
Peroxymonosulfuric acid (Caro's acid; H₂SO₅) has pK_a values of 0.4 and 9.3 (Elias *et al.* 1994, Evans and Upton 1985) and thereby HSO₅⁻ is the predominant species of peroxymonosulfate (PMS) under neutral pH conditions. The mechanism for the hydrolysis of PMS suggested in the literature is much simpler than that of PDS, because it does not involve free radical reactions. In strong acidic solution, PMS oxidizes water into H₂O₂ (two-electron oxidation) (Reaction 3). However, PMS in neutral and alkaline solutions is decomposed into SO₄²⁻ and oxygen with the overall reaction presented in Reaction 31.



Ball and Edwards (1956) observed that the rate of PMS decomposition under neutral and alkaline pH conditions follows second-order kinetics with the optimum value at around pH 9.3 (pK_a of HSO₅⁻) and proposed the following mechanism (Reactions 32-34).



$$k_{33} = 0.392 \text{ M}^{-1} \text{ s}^{-1} \text{ (Ball and Edwards 1956)}$$



The reaction of HSO₅⁻ with its deprotonated form, SO₅²⁻ (Reaction 33) is the rate-determining step and Eq. 35 gives the rate law for the PMS decomposition as a function of pH.

$$-\text{d}[\text{PMS}]/\text{dt} = k_{33}[\text{HSO}_5^-][\text{SO}_5^{2-}] = k_{obs,PMS}[\text{PMS}]_t^2 \quad (35)$$

$$(k_{obs,PMS} = \frac{k_{33}K_{a,HSO_5^-}10^{-\text{pH}}}{(K_{a,HSO_5^-} + 10^{-\text{pH}})^2})$$

Where, $k_{obs,PMS}$ is the observed second-order rate constant for the PMS hydrolysis, $[\text{PMS}]_t$ is the total concentration of PMS (i.e., $[\text{HSO}_5^-] + [\text{SO}_5^{2-}]$) and K_{a,HSO_5^-} is the acidity constant of HSO₅⁻ (i.e., 10^{-9.3} M).

The temperature dependence of the PMS hydrolysis can be quantified by the temperature-dependent k_{33} and K_{a,HSO_5^-} values. The k_{33} and K_{a,HSO_5^-} can be represented as a function of temperature using the Arrhenius equation and Van't Hoff equation, respectively (Eqs. 36 and 37).

$$k_{33}(T) = k_{33}(25^\circ\text{C})\exp\left[-\frac{E_{a,33}}{R}\left(\frac{1}{T(\text{K})} - \frac{1}{298}\right)\right] \quad (36)$$

$$K_{a,HSO_5^-}(T) = K_{a,HSO_5^-}(25^\circ\text{C})\exp\left[-\frac{\Delta H^\circ}{R}\left(\frac{1}{T(\text{K})} - \frac{1}{298}\right)\right] \quad (37)$$

Where, $E_{a,33}$ is the activation energy for Reaction 33 and ΔH° is the enthalpy change for the dissociation of HSO₅⁻ (Reaction 27). $E_{a,33}$ and ΔH° are known to be 13 and 5 kcal mol⁻¹, respectively (Ball and Edwards 1956). The $k_{obs,PMS}$ values at several temperatures were calculated as a function of pH using Eqs. 35-37 (Fig. 2a).

As is the case of PDS, PMS also undergoes the base-catalyzed hydrolysis in strong alkaline solution (ca. pH > 13). It has been evidenced that the oxygen evolving during the hydrolysis originates from both water and PMS

molecules and hydroxyl radical may form as an intermediate (Lunenok-Burmakina and Aleeva 1972). However, the detailed reaction mechanism is not clearly elucidated.

The kinetics of the base-catalyzed decomposition of PMS is the first-order with respect to both the PMS and OH⁻ concentrations with the rate law given by Eq. 38 (Lunenok-Burmakina and Aleeva 1972).

$$-\text{d}[\text{PMS}]/\text{dt} = k_{38}[\text{OH}^-][\text{SO}_5^{2-}] \quad (38)$$

$$k_{38} = 6.9 \times 10^8 \exp(-17.3 \text{ kcal mol}^{-1}/RT) \text{ M}^{-1} \text{ s}^{-1}$$

The observed first-order rate constants for the base-catalyzed hydrolysis of PMS ($k_{b,obs,PMS}$, Eq. 39) were calculated as a function of pH at several different temperatures (dashed lines in Fig. 2a).

$$-\text{d}[\text{PMS}]/\text{dt} = k_{b,obs,PMS}[\text{SO}_5^{2-}] \quad (k_{b,obs,PMS} = k_{38}[\text{OH}^-]) \quad (39)$$

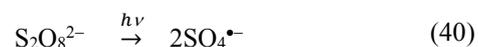
The half-lives ($\tau_{1/2,PMS}$) of PMS as a function of pH were calculated using the observed rate constants (i.e., $k_{obs,PMS}$ and $k_{b,obs,PMS}$) and were plotted under several conditions of temperature and the initial concentration of PMS (Figs. 2b and c).

The effect of ionic strength on the rate of PMS hydrolysis has not been clearly quantified. However, a slight negative salt effect has been reported, probably due to the influence on the K_{a,HSO_5^-} value (Ball and Edwards 1956). In addition, little is known about the kinetics of the acid-catalyzed hydrolysis of PMS in strong acidic solution (Reaction 3). Mariano (1968) observed that 80 μM PMS in 5 M sulfuric acid is decomposed into H₂O₂ with a half-life of approximately 170 h.

2.2 Photolytic decomposition

2.2.1 Peroxydisulfate

PDS is photolyzed into SO₄²⁻ and oxygen upon ultraviolet (UV) irradiation (Crist 1932, Heidt 1942, Dogliotti and Hayon 1967). The UV absorbance of PDS has a band centered at 215 nm (i.e., $\epsilon_{215} = 220 \text{ M}^{-1} \text{ cm}^{-1}$) and gradually decreases as the wavelength increases (e.g., $\epsilon_{248} = 26 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{266} = 9.6 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{308} = 1.2 \text{ M}^{-1} \text{ cm}^{-1}$). As with the thermal decomposition, the photolysis of PDS is initiated by the homolytic dissociation of PDS into SO₄^{•-} (Reaction 40), which subsequently propagates the radical chain reactions described in Scheme 1.



The kinetics of the SO₄^{•-} production by Reaction 40 follows the Beer-Lambert law (Eq. 41).

$$\text{d}[\text{SO}_4^{\bullet-}]/\text{dt} = -I_0\phi_{\text{SO}_4^{\bullet-}}(1-10^{-\epsilon b[\text{PDS}]}) \quad (41)$$

Where, I_0 is the incident light intensity (Einstein L⁻¹ s⁻¹), $\phi_{\text{SO}_4^{\bullet-}}$ is the quantum yield for the production of SO₄^{•-} (i.e., moles of SO₄^{•-} produced per moles of photons absorbed by PDS), ϵ is the molar absorption coefficient of PDS (M⁻¹ cm⁻¹) and b is the optical path length of the photochemical reactor (cm). I_0 , ϕ_{PDS} and ϵ depend on the

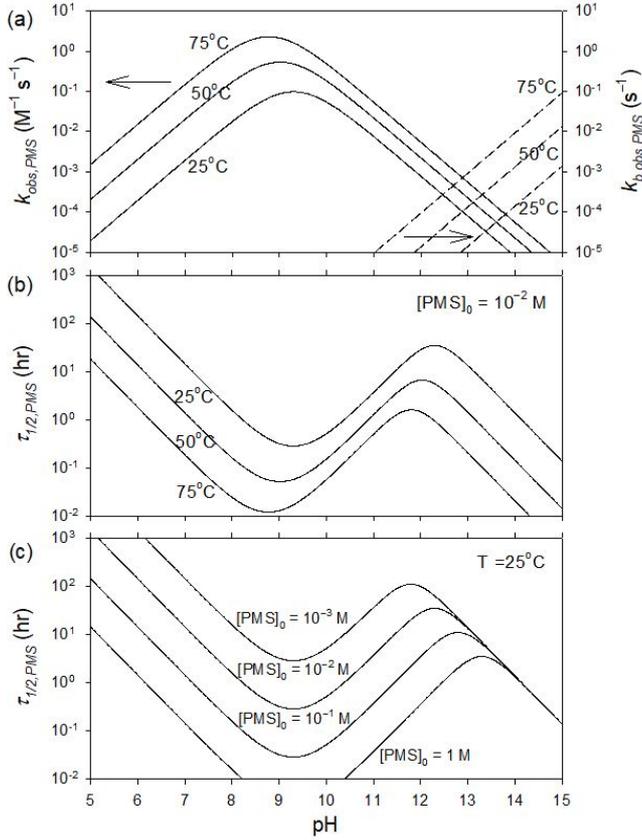


Fig. 2 (a) Rate constants and (b) and (c) half-lives for the hydrolysis of PMS as a function of pH: The solid lines in (a) are the second-order rate constants calculated based on the results by Ball and Edwards (1956), while the dashed lines are the first-order rate constants for the base-catalyzed hydrolysis reported by Lunenok-Burmakina and Aleeva (1972).

wavelength of the light. When PDS absorbs almost the entire light ($\epsilon b[\text{PDS}] > 2$), the rate of the PDS decomposition is almost constant, regardless of the concentration of PDS (i.e., $d[\text{PDS}]/dt \approx -I_0 \phi_{\text{PDS}}$). However, when the light absorption by PDS is insignificant ($\epsilon b[\text{PDS}] < 0.01$), the rate law follows the first-order kinetics (i.e., $d[\text{PDS}]/dt \approx -2.303 I_0 \phi_{\text{PDS}} \epsilon b[\text{PDS}]$).

The primary quantum yield for Reaction 40 is known to be unity in the UV-C region (i.e., $\phi_{\text{SO}_4^{\bullet-}} = 2$ at 248, 254 and 266 nm, Heidt 1942, Tang *et al.* 1988, Wine *et al.* 1988, Hynes and Wine 1988), but a lower value was reported at a longer wavelength (i.e., $\phi_{\text{SO}_4^{\bullet-}} = 0.55$ at 308 nm, Ivanov *et al.* 2000).

On the other hand, the quantum yield based on the PDS decomposition (ϕ_{PDS} , Eq.42) usually shows the values lower than unity ($\phi_{\text{PDS}} < 1$), even in the UV-C region (Crist 1932, Heidt 1942), indicating that the regeneration of PDS by the recombination of $\text{SO}_4^{\bullet-}$ (Reaction 13) is favored, compared to its secondary decomposition by the radical reactions (Reactions 11 and 12).

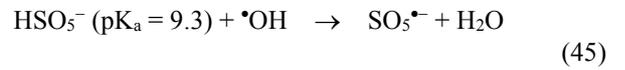
$$d[\text{PDS}]/dt = -I_0 \phi_{\text{PDS}} (1 - 10^{-\epsilon b[\text{PDS}]}) \quad (42)$$

2.2.2 Peroxymonosulfate

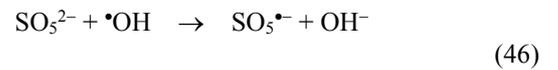
Similar to PDS, PMS absorbs UV light mostly below 300 nm. The molar absorption coefficients of HSO_5^- and SO_5^{2-} are approximately 200 and 700 $\text{M}^{-1} \text{cm}^{-1}$ at 220 nm, respectively and the values exponentially decrease with increasing wavelength (Elias *et al.* 1994). The UV irradiation results in the photolysis of PMS into SO_4^{2-} and oxygen (McGinniss and Kah 1979, Kanakaraj and Maruthamuthu 1983). According to the proposed mechanism, the primary process of the PMS photolysis is the O-O bond scission to liberate $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ (Reaction 43).



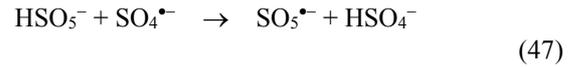
The produced radical species can recombine into the parent molecule (Reaction 44) or propagate the chain reactions by oxidizing another PMS into peroxymonosulfate radical ($\text{SO}_5^{\bullet-}$, Reactions 45-47).



$$k_{45} = 1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton } et al. \text{ 1988)}$$

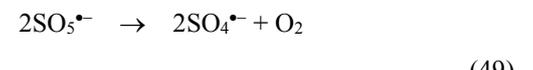
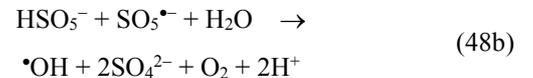
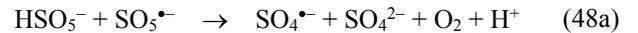


$$k_{46} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton } et al. \text{ 1988)}$$



$$K_{47} < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \text{ (Neta } et al. \text{ 1988)}$$

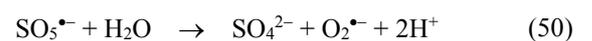
$\text{SO}_5^{\bullet-}$ further accelerates the chain reactions, serving as a reductant in the reaction with PMS. The one-electron reduction of PMS results in the heterolytic scission of the O-O bond to produce either $\text{SO}_4^{\bullet-}$ (Reaction 48a) or $\bullet\text{OH}$ (Reaction 48b) (Maruthamuthu and Neta 1977, Kanakaraj and Maruthamuthu 1983). The disproportionation of $\text{SO}_5^{\bullet-}$ proceeds via various pathways, among which the one generating $\text{SO}_4^{\bullet-}$ (Reaction 49) is dominant (Brandt and Eldik 1995).

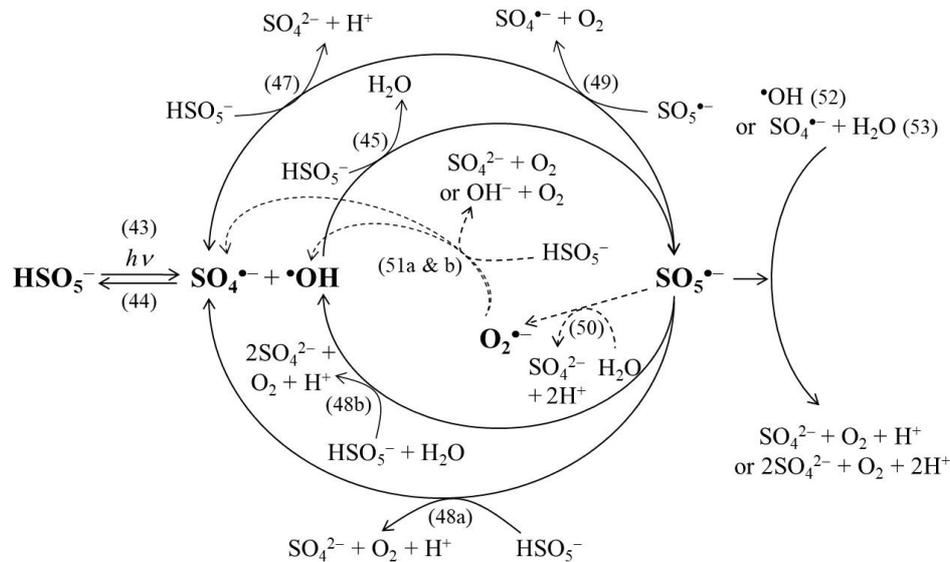


$$2k_{49} = 1.1 \times 10^7 \sim 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

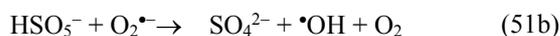
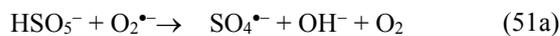
(Brandt and Eldik 1995)

$\text{SO}_5^{\bullet-}$ may also go through hydrolysis to produce superoxide radical ($\text{O}_2^{\bullet-}$, Reaction 50), which subsequently leads to one-electron reduction of PMS (Reactions 51a and 51b).

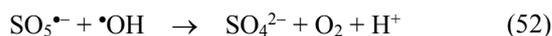




Scheme 2 Overall mechanism of the PMS photolysis: The dashed lines indicate the reactions postulated by Maruthamuthu and Neta (1977), the numbers in parentheses represent the reaction numbers in the text.



The radical chain reactions can be terminated as follows (Reactions 52 and 53).



Scheme 2 summarizes the reactions involved in the PMS photolysis.

The overall quantum yields for the PMS decomposition at 254 nm (ϕ_{PMS} , Eq. 54) reportedly range 0.68 to 1.18, depending on the initial concentration of PMS, $[\text{PMS}]_0$ (Kanakaraj and Maruthamuthu 1983). The increasing ϕ_{PMS} value with increasing $[\text{PMS}]_0$ was observed due to the chain decomposition of PMS.

$$d[\text{PMS}]/dt = -I_0\phi_{\text{PMS}}(1 - 10^{-\epsilon b[\text{PMS}]}) \quad (54)$$

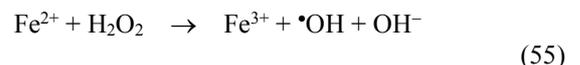
Later studies reported the primary quantum yield for the production of $\text{SO}_4^{\bullet-}$ (Reaction 43) as $\phi_{\text{SO}_4^{\bullet-}} = 0.12$ at 248 nm (Herrmann 2007) and $\phi_{\text{SO}_4^{\bullet-}} = 0.52$ at 254 nm (Guan *et al.* 2011). Guan *et al.* (2011) claimed that the discrepancy between the two reported values was because Herrmann's study did not take the sink of $\text{SO}_4^{\bullet-}$ into consideration.

2.3 Metal-catalyzed decomposition

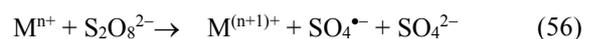
2.3.1 Peroxydisulfate

The decomposition of PDS is catalyzed by several transition metals through the mechanism analogous to the Fenton reaction (Reaction 55). The metal ion ($\text{M}^{\text{n+}}$) transfers one electron to PDS, splitting the molecule into $\text{SO}_4^{\bullet-}$ and SO_4^{2-} (Reaction 56). Fe(II), Ag(I), Cu(I), Ti(III) and V(V) are known to have the catalytic activity (House

1962, Thompson 1981, Fürholz and Haim 1987, Gilbert *et al.* 1988, Anipsitakis and Dionysiou 2004, Fang *et al.* 2017). Ruthenium(II) amine complexes have also shown to lead to the catalytic decomposition of PDS (Fürholz and Haim 1987).

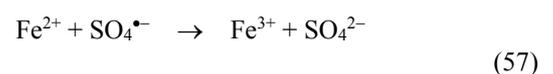


$$k_{55} = 63 \text{ M}^{-1} \text{ s}^{-1} \text{ (Walling and Goosen 1973)}$$

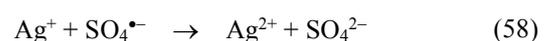


The rate constants for Reaction 56 are known for several metal ions, such as Fe^{2+} ($26 \text{ M}^{-1} \text{ s}^{-1}$, Fürholz and Haim 1987), Cu^+ ($\approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$, Gilbert *et al.* 1988), Ag^+ ($\approx 0.1 \text{ M}^{-1} \text{ s}^{-1}$, estimated from the results by Srivastava *et al.* 1984) and Ti^{3+} ($\approx 200 \text{ M}^{-1} \text{ s}^{-1}$, Gilbert *et al.* 1988). These rate constants can increase with increasing pH, as the metal ions are hydrolyzed to form their hydroxy complexes that are stronger electron donors than the uncomplexed species. For example, the rate constant for the Fenton reaction (k_{55}) increases from 63 to $2.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ when the solution pH increases from 2 to 7 (King *et al.* 1995). In addition, the rate constants can also be higher when the metal ions are coordinated with electron-donating organic ligands.

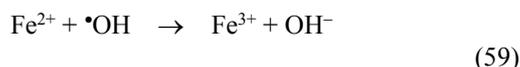
$\text{SO}_4^{\bullet-}$ induces the formation of other radical species such as $\bullet\text{OH}$, $\text{S}_2\text{O}_8^{\bullet-}$ and $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$, as shown in Scheme 1. These radicals participate in the redox reactions of the metal ion couple ($\text{M}^{\text{(n+1)+}}/\text{M}^{\text{n+}}$), affecting the kinetic chain length of the catalytic decomposition of PDS. $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ inhibit the chain reactions by oxidizing $\text{M}^{\text{n+}}$ into $\text{M}^{\text{(n+1)+}}$ (Reactions 57-60).



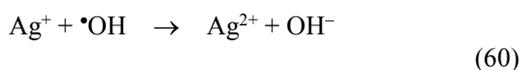
$$k_{57} = 9.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ (Neta et al. 1988)}$$



$$k_{58} = 1.8 \times 10^9 - 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (Neta et al. 1988)}$$

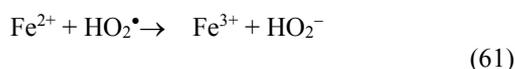


$$k_{59} = 2.3 \times 10^8 - 4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton et al. 1988)}$$

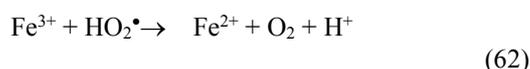


$$k_{60} = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ (Buxton et al. 1988)}$$

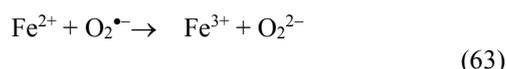
$\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ can play a role as both an oxidant and a reductant. However, $\text{HO}_2\bullet$ has a higher potential as an oxidant than as a reductant ($E_H^\circ[\text{HO}_2\bullet/\text{H}_2\text{O}_2] = +1.51 \text{ V}$; $E_H^\circ[\text{O}_2/\text{HO}_2\bullet] = -0.125 \text{ V}$; Bard *et al.* 1985), whereas $\text{O}_2^{\bullet-}$ is the opposite ($E_H^\circ[\text{O}_2^{\bullet-}/\text{HO}_2^-] = +0.20 \text{ V}$; $E_H^\circ[\text{O}_2/\text{O}_2^{\bullet-}] = -0.33 \text{ V}$; Bard *et al.* 1985). These trends are shown in the rate constants for the reactions with metal ions. For example, $\text{HO}_2\bullet$ is more likely to oxidize Fe^{2+} rather than to reduce Fe^{3+} ($k_{61} > k_{62}$; Reactions 61 and 62), but $\text{O}_2^{\bullet-}$ is more favored to reduce Fe^{3+} ($k_{63} < k_{64}$; Reactions 63 and 64).



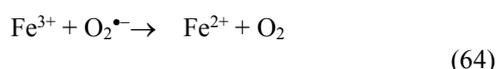
$$k_{61} = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ (Jayson and Parsons 1972)}$$



$$k_{62} < 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \text{ (Rush and Bielski 1985)}$$



$$k_{63} = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (Rush and Bielski 1985)}$$

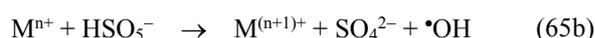
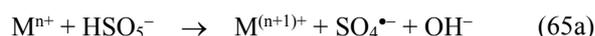


$$k_{64} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \text{ (Rothschild and Allen 1958)}$$

$\text{O}_2^{\bullet-}$ can also produce $\text{SO}_4^{\bullet-}$ by the reaction with PDS (Reaction 27).

2.3.2 Peroxymonosulfate

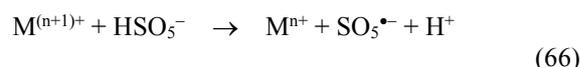
The catalytic decomposition of PMS by transition metals proceeds via one-electron transfer from the metal ion to PMS. Many transition metals, such as Co(II), Fe(II), Ru(III), Ti(III), Ce(III), Mn(II) and Ni(II), mainly produce $\text{SO}_4^{\bullet-}$ (Reaction 59a), but V(III) is known to produce both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Reactions 65a and 65b) (Gilbert and Stell 1990, Marsh *et al.* 1990, Zhang and Edwards 1992, Anipsitakis and Dionysiou 2004, Lente *et al.* 2009). The rate constants for Fe^{2+} and Ti^{3+} have been reported to be 3.7×10^4 (Lente *et al.* 2009) and $7.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (Gilbert and Stell 1990), respectively.



As is the case for the catalytic decomposition of PDS, the radical species formed during the PMS decomposition,

such as $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $\text{SO}_5^{\bullet-}$ and $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ (Scheme 2), can be involved in the redox reactions of the metal ion couple ($\text{M}^{(n+1)+}/\text{M}^{n+}$). All these radical species, except for $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$, may serve as an oxidant for the reactions with metal ions.

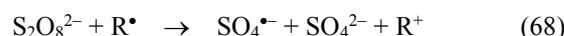
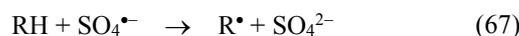
On the other hand, it has been reported that several metal ions, such as cobalt, iron and cerium, can be directly reduced by the reaction with PMS (Reaction 66) (Marsh *et al.* 1990, Kim and Edwards 1995, Anipsitakis and Dionysiou 2004). In particular, for the cerium redox couple, the reduction of Ce(IV) is more favored than the oxidation of Ce(III) in the reactions with PMS (i.e., $k_{65a} < k_{66}$).



3. Oxidation of organic compounds by persulfates

3.1 Peroxydisulfate

Numerous studies have shown that PDS oxidizes a broad spectrum of organic compounds via indirect reaction with $\text{SO}_4^{\bullet-}$ as discussed later in Section 3.3. However, the direct reactions of organic compounds with PDS are not established and the mechanisms are disputed. A few early studies showed that the thermal decomposition of PDS is greatly accelerated by the presence of alcohols, suggesting direct reactions between PDS and alcohols via radical (Bartlett and Cottman 1949) and non-radical mechanisms (Levitt *et al.* 1962). However, these observations were also explained by the indirect mechanism mediated by $\text{SO}_4^{\bullet-}$ in radical chain reactions (Kolthoff *et al.* 1953, Gallopo and Edwards 1971), in which the oxidation of alcohols is initiated by $\text{SO}_4^{\bullet-}$ (Reaction 67) generated by thermal decomposition of PDS (Reaction 4). Subsequently, the resulting organo radical (R^\bullet) reduces another PDS molecule to generate $\text{SO}_4^{\bullet-}$, propagating the chain reactions (Reaction 68).



A later study supported this radical chain mechanism via experiments using radical scavengers for the oxidation of alcohols and aldehydes (Beylerian and Khachatryan 1984).

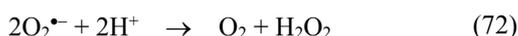
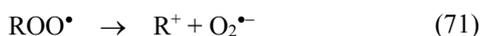
The inhibitory effect of dissolved oxygen on the oxidation of alcohols by PDS (McIsaac and Edwards 1969, Gallopo and Edwards 1971), appears to be attributed to chain termination via formation of peroxy radical (ROO^\bullet) (Reactions 69 and 70). ROO^\bullet is known to rapidly dissociate into various products via a tetraoxide intermediate (Reaction 70) or produce $\text{O}_2^{\bullet-}$ that further generates O_2 and H_2O_2 (Reactions 71 and 72) (Schuchmann and von Sonntag 1979, Neta *et al.* 1990).



Table 1 Standard reduction potentials of various oxidants for ISCO and related radical species

Oxidant	Reaction	Electrode potential (V vs. NHE)
Hydroxyl radical (pK _a = 11.9)	•OH + H ⁺ + e ⁻ → H ₂ O	2.813 ^a , 2.59 ^b , 2.72 ^c , 2.74 ^d
	•OH + e ⁻ → OH ⁻	1.985 ^a , 1.77 ^b , 1.89 ^c , 1.91 ^d
	•O ⁻ + H ₂ O + e ⁻ → 2OH ⁻	1.59 ^a , 1.64 ^b , 1.76 ^c , 1.78 ^d
Ozone	O ₃ + 2H ⁺ + 2e ⁻ → O ₂ + H ₂ O	2.075 ^a
	O ₃ + 2H ₂ O → O ₂ + 2OH ⁻	1.246 ^a
Hydrogen peroxide (pK _a = 11.6)	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O	1.763 ^a
	HO ₂ ⁻ + H ₂ O + 2e ⁻ → 3OH ⁻	0.867 ^a
	HO ₂ • + 3H ⁺ + 3e ⁻ → 2H ₂ O	1.65 ^a
Hydroperoxyl/ Superoxide radical (pK _a = 4.8)	HO ₂ • + H ⁺ + e ⁻ → H ₂ O ₂	1.44 ^a
	O ₂ • ⁻ + 2H ₂ O + 3e ⁻ → 4OH ⁻	0.645 ^a
	O ₂ • ⁻ + H ₂ O + e ⁻ → HO ₂ ⁻ + OH ⁻	0.20 ^a
	SO ₄ • ⁻ + e ⁻ → SO ₄ ²⁻	2.43 ^e , 2.5–3.1 ^f
Sulfate radical anion	SO ₃ • ⁻ + H ⁺ + e ⁻ → HSO ₃ ⁻	≈1.1 at pH 7 ^g
	S ₂ O ₈ ²⁻ + 2H ⁺ + 2e ⁻ → 2HSO ₄ ⁻	2.08 ^a
Peroxydisulfate	S ₂ O ₈ ²⁻ + 2e ⁻ → 2SO ₄ ²⁻	1.96 ^a
	HSO ₅ ⁻ + 2H ⁺ + 2e ⁻ → HSO ₄ ⁻ + 2H ₂ O	1.81 ^h , 1.82 ⁱ
Peroxymonosulfate (pK _a = 9.3)	HSO ₅ ⁻ + H ⁺ + 2e ⁻ → SO ₄ ²⁻ + H ₂ O	1.75 ^h
	SO ₃ ²⁻ + H ₂ O + 2e ⁻ → SO ₄ ²⁻ + 2OH ⁻	1.22 ^h
	MnO ₄ ⁻ + 4H ⁺ + 3e ⁻ → MnO _{2(s)} + 2H ₂ O	1.70 ^a
Permanganate	MnO ₄ ⁻ + 2H ₂ O + 3e ⁻ → MnO _{2(s)} + 4OH ⁻	0.60 ^a

a: Bard *et al.* 1985; b: Koppenol and Liebman 1984; c: Schwarz and Dodson 1984; d: Klaning *et al.* 1985; e: Huie *et al.* 1991; f: Ebersson 1982; g: Huie and Neta 1984; h: Spiro 1979; i: Steele and Appelman 1982



The oxygen effect is influenced by the branching ratio between Reactions 69 and 70. The reaction of R[•] with oxygen (Reaction 69) is nearly diffusion-controlled ($k_{69} \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Schuchmann and von Sonntag 1979), whereas the rate constants for reactions of R[•] with PDS (Reaction 68) range approximately from 10^4 to $10^6 \text{ M}^{-1} \text{ s}^{-1}$ for aliphatic radicals (Gilbert and Stell 1990). Therefore, the kinetic chain length depends on the organic compound species and the concentrations of PDS and dissolved oxygen.

Several studies reported the oxidation of aromatic compounds via direct reaction with PDS. Phenol is known to be oxidized via a nucleophilic attack of phenoxide ion on PDS, generating sulfate-substituted compounds at ortho and para positions as the primary products (Behrman and Walker 1962, Ogata and Akada 1970). This bimolecular reaction was supported by the second-order kinetics of the PDS decomposition with respect to the concentrations of phenol and PDS. A similar non-radical mechanism has also been suggested for the oxidation of aromatic amines (Boylard *et al.* 1953, Behrman 1967). However, other aromatic compounds, such as benzaldehydes, appear to be oxidized by a radical mechanism involving SO₄•⁻ (Srivastava *et al.* 1974).

By contrast, recent studies reported that the direct reactions of organic compounds, such as quinones (Fang *et al.* 2013), phenols (Ahmad *et al.* 2013) and glucose (Watts *et al.* 2018), with PDS generate SO₄•⁻ and •OH, by reducing PDS via the single-electron transfer pathway.

3.2 Peroxymonosulfate

In contrast to PDS, PMS appears to oxidize organic compounds mainly via direct non-radical mechanism, via transfer of an oxygen atom to the substrates (Gallop and Edwards 1981, Ando *et al.* 1983, Manivannan and Maruthamuthu 1986, Renganathan and Maruthamuthu 1986, Zhu and Ford 1991, Meenakshisundaram and Sarathi 2007). Evidence suggests non-radical mechanisms such as lack of polymer formation, absence of effect of oxygen and second-order kinetics (Manivannan and Maruthamuthu 1986). The oxidation of aliphatic and aromatic ketones by PMS (the so-called Baeyer-Villiger oxidation) leads to the formation of corresponding esters (Manivannan and Maruthamuthu 1986). The reaction mechanism involves the nucleophilic addition of PMS to the carbonyl group to form a tetrahedral intermediate, which subsequently undergoes rearrangement to release the corresponding ester and sulfuric acid (i.e., a concerted migration of the adjacent carbon group to the oxygen from PMS). The reaction rate increases with decreasing pH, due to the acid-catalyzed decomposition of the tetrahedral intermediate.

The oxidation of benzaldehydes by PMS proceeds via a similar mechanism (Renganathan and Maruthamuthu 1986). Similar to ketones, the first step is the nucleophilic addition of PMS to the carbonyl group. However, depending on the rearrangement step, either the corresponding benzoic acids or phenols are produced: The hydride migration leads to the formation of benzoic acids, whereas the aryl migration results in the formation of phenols. The unsubstituted benzaldehyde produces only benzoic acid and the substitution with electron-donating functional groups favors the formation of phenols.

Oxidation of alkenes (Zhu and Ford 1991),

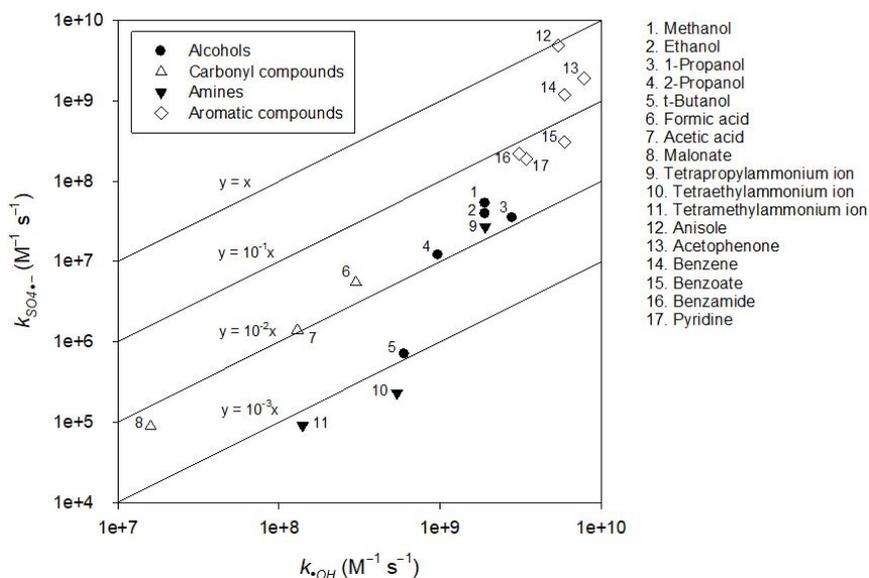
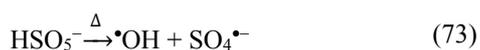


Fig. 3 Comparison between the $k_{\text{SO}_4^{\bullet-}}$ and the $k_{\bullet\text{OH}}$ values for several groups of organic compounds: The $k_{\text{SO}_4^{\bullet-}}$ and the $k_{\bullet\text{OH}}$ values are adopted from Neta *et al.* (1988) and Buxton *et al.* (1988), respectively

benzoquinone (Ando *et al.* 1983) and indole (Meenakshisundaram and Sarathi 2007) is also initiated via nucleophilic addition of PMS and results in various products, depending on the secondary mechanism. In addition, the oxidation of pyridine by PMS is catalyzed by the presence of ketones (Gallop and Edwards 1981). The PMS oxidation of many other organic compounds, such as alcohols, amines and halogen compounds, has been discussed (Kennedy and Stock 1960). More recent studies (Zhou *et al.* 2015, 2017) reported generation of singlet oxygen via PMS oxidation of benzoquinone and phenols (via the benzoquinone intermediate). Singlet oxygen can also be generated by self-decomposition of PMS, but its role in oxidation of organic compounds is only minor (Yang *et al.* 2018). In addition, Chen *et al.* (2018) reported the PMS oxidation of β -lactam antibiotics by non-radical pathways.

Although the PMS oxidation of organic compounds has been mostly explained by the non-radical mechanism and little is known about the formation of radical species via PMS hydrolysis (see section 2.1.2), the possibility of indirect oxidation by radical species cannot be completely excluded. Kennedy and Stock (1960) found that the free radical polymerization of vinyl monomers is initiated by PMS, even if PDS was a stronger initiator than PMS suggesting that PMS may be thermally decomposed to produce $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Reaction 73), which leads to further radical reactions with organic compounds. These radical species facilitate oxidation of recalcitrant organic compounds that are hardly decomposed by the direct reaction with PMS.



3.3 Reactions of radical intermediates

Among the free radical species generated during the

decomposition of persulfates (i.e., $\text{SO}_4^{\bullet-}$, $\text{SO}_5^{\bullet-}$, $\bullet\text{OH}$ and $\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$), $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ are particularly strong oxidants with high reduction potentials (Table 1). These two radical species oxidize a broad range of organic compounds via electron abstraction, hydrogen abstraction and addition. $\bullet\text{OH}$ reacts rapidly with organic compounds (Buxton *et al.* 1988, Neta *et al.* 1988). The reaction mechanism of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ includes electron abstraction via the three mechanisms, whereas $\text{SO}_4^{\bullet-}$ favors electron abstraction, rather than hydrogen abstraction and addition.

$\text{SO}_4^{\bullet-}$ is a more selective oxidant than $\bullet\text{OH}$ and therefore, the second-order rate constants for $\text{SO}_4^{\bullet-}$ ($k_{\text{SO}_4^{\bullet-}}$) are usually lower than those for $\bullet\text{OH}$ ($k_{\bullet\text{OH}}$) by up to three orders of magnitude, depending on the target compound (Fig. 3). The $k_{\text{SO}_4^{\bullet-}}$ values for aromatic compounds are approximately one order of magnitude lower than the corresponding $k_{\bullet\text{OH}}$ values. The difference between the $k_{\text{SO}_4^{\bullet-}}$ and the $k_{\bullet\text{OH}}$ values is approximately two to three orders of magnitude for alcohols and carbonyl compounds and for *t*-butanol and some quaternary ammoniums, respectively. Meanwhile, a quantitative structure-activity relationship approach has been studied for the oxidation of organic compounds by $\text{SO}_4^{\bullet-}$ (Xiao *et al.* 2015).

$\text{SO}_5^{\bullet-}$ and HO_2^{\bullet} are much less reactive species than $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Table 1) and highly selective in their reactions with organic compounds (Bielski *et al.* 1985, Neta *et al.* 1988). However, as stated in section 2.3, $\text{SO}_5^{\bullet-}$ and $\text{O}_2^{\bullet-}$ act as reducing agents for reactions with PDS and PMS (reactions 48a and b, 51a and b) or with metal ions (reactions 62, 64), accelerating the decomposition of PDS and PMS by the chain propagation.

4. Use of persulfates for contaminant oxidation

Persulfates can be used for the oxidative degradation of

organic contaminants present in water and soil, with potential applications in wastewater treatment and ISCO for soil and groundwater remediation. In particular, the PDS-based ISCO technologies for soil and groundwater remediation have already been used at several contaminated sites (Tsitonaki *et al.* 2010). As described in the previous chapter, organic compounds are oxidized by direct and indirect reactions of persulfates. However, for most of the organic contaminants, the indirect oxidation by radical intermediates, such as $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, is more important than the direct oxidation by persulfates themselves. Although limited information is available pertaining to the rate constants for the direct reactions of persulfates with organic compounds, persulfates may be significantly less reactive and more selective than $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$.

Several methods to accelerate the decomposition of persulfates into radical species have been suggested to improve the oxidation rate of contaminants. These methods include thermal, photochemical, metal-catalyzed and alkaline activation techniques (refer to Chapter 2), among which thermal and metal-catalyzed methods have been studied most extensively.

ISCO is performed by injecting the solution of persulfate salts (i.e., $\text{Na}_2\text{S}_2\text{O}_8$ for PDS and $2\text{KHSO}_5\text{-KHSO}_4\text{-K}_2\text{SO}_4$, Oxone[®] for PMS) into the contaminated subsurface, occasionally in combination with metal catalysts. The ISCO system using PMS usually employs metal catalysts, as it does not favor the formation of radical species during the thermal decomposition of PMS (see sections 2.1.2 and 3.2). In contrast, PDS is often used without catalysts. The PDS oxidation of several contaminants, such as chlorinated ethenes and ethanes, diphenylamine and methyl *tert*-butyl ether (MTBE), has been studied at ambient and elevated temperatures (Huang *et al.* 2002, Liang *et al.* 2003, Liang *et al.* 2007a, Waldemer *et al.* 2007, Liang and Bruell 2008, Li *et al.* 2009). At ambient temperatures, PDS is quite stable in aqueous solution ($\tau_{1/2} \approx 2$ yr at 25°C, Fig. 1b) and lowers the degradation of contaminants by radical intermediates. However, the PDS decomposition in the subsurface is much faster than in pure water, due to the catalytic roles of minerals or natural organic matters (NOM) present in the soil matrix. Various transition metals in soil catalyze the decomposition of persulfates into radical species (see section 2.3). In addition, the reaction of NOM with $\text{SO}_4^{\bullet-}$ may initiate the radical chain reactions of PDS decomposition by the intermediate organo radicals (see section 3.1). Indeed, the decomposition rate of PDS increased by approximately one order of magnitude in the presence of 1 g soil per ml of water (Johnson *et al.* 2008) and the degradation of contaminants was also enhanced in soil slurry (Liang *et al.* 2008b). This catalytic effect is diminished after the oxidant demand is met.

Elevating temperature is one of the methods to enhance the thermal decomposition of PDS into reactive radical species ($\tau_{1/2} \approx 4$ hr at 75°C, Fig. 1b). This thermal activation is accomplished in combination with *in situ* thermal remediation (ISTR) techniques, such as electrical heating, steam (or hot air) injection and radio frequency heating (Hinchee and Smith 1992), although it requires additional

cost for installation and operating the equipment for ISTR.

The use of metal catalysts may be a more efficient method to activate persulfates than heating. Several recent studies have demonstrated ISCO systems using the metal-catalyzed decomposition of persulfates. In particular, the cobalt(II)-catalyzed decomposition of PMS (i.e., the Co(II)/PMS system) and the iron(II)-catalyzed decomposition of PDS (i.e., the Fe(II)/PDS system) have been most extensively studied by two research groups (i.e., Dionysiou's and Liang's group, respectively, Anipsitakis and Dionysiou 2003, Anipsitakis and Dionysiou 2004, Liang *et al.* 2004a, b, Anipsitakis *et al.* 2005, Anipsitakis *et al.* 2006, Liang *et al.* 2007b, Liang and Bruell 2008, Liang *et al.* 2008b, Liang and Lee 2008a). The oxidized Co(III) is recycled to Co(II) directly by the reaction with PMS, whereas Fe(III) is hardly reduced to Fe(II) (see section 2.3.2). As a result, the Co(II)/PMS system results in higher activity via oxidation of 2,4-dichlorophenol than the Fe(II)/PDS system (Anipsitakis and Dionysiou 2004). However, iron may exhibit a few advantages compared with other metals, in terms of cost and toxicity. Earlier studies investigating these metal-catalyzed systems mainly focused on the various factors affecting system efficiency, but later works developed modified systems using chelating agents (Liang *et al.* 2004b, Liang *et al.* 2007b) and heterogeneous catalysts (Anipsitakis *et al.* 2005, Yang *et al.* 2009).

The Fe(II)-catalyzed decomposition of PMS (i.e., the Fe(II)/PMS system) has been also demonstrated for the degradation of organic contaminants including polychlorinated biphenyls (Rastogi *et al.* 2009), Rhodamine B (Wang and Chu 2011) and lindane (Khan *et al.* 2016). Several studies demonstrated that the Fe(II)/PMS system exhibited better activity than the Fe(II)/PDS system (Anipsitakis and Dionysiou 2004, Rastogi *et al.* 2009, Kurukutla *et al.* 2015).

Meanwhile, the additional use of UV, electricity and a reducing agent in the Fe(II)/persulfates systems can further enhance the generation of radical species, by accelerating the reduction of Fe(III) to Fe(II) (Khan *et al.* 2013, Zou *et al.* 2013, Govindan *et al.* 2014).

An increase in the decomposition rate of persulfates usually leads to enhanced degradation of contaminants by radical intermediates. However, the rapid consumption of persulfates limits the diffusive transport of these oxidants in the contaminated zone for the ISCO application. Therefore, determination of optimal conditions or oxidant injection methods that balance these two issues is needed for the effective application of persulfate-based ISCO systems.

5. Conclusions

In order to better understand the chemistry of persulfate and effectively apply the persulfate-based oxidation systems to the field, additional studies are needed from both scientific and engineering perspectives.

Despite extensive investigation into the chemistry of persulfate decomposition, it still remains unclear whether the thermal decomposition of PMS occurs via a radical mechanism directly generating $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (reaction 73) or indirectly via the reaction with organic compounds.

Although early studies suggested a non-radical mechanism for the thermal decomposition of PMS (see section 2.1.2), specific behaviors observed in the PMS oxidation of organic compounds support the generation of radical species (see section 3.2).

Fundamental analysis is also needed to identify the reactive oxidants produced by the decomposition of persulfates under various conditions. $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ are interconverted during the thermal and photolytic decomposition of persulfates (Schemes 1 and 2) and the steady-state concentrations of these radical species vary depending on pH and the concentrations of persulfates. Liang and Su (2009) have investigated the pH dependence of the formation of $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ during the thermal decomposition of PDS at high concentrations (> 50 mM); however, the result varied at a relatively low concentration of PDS (e.g., $[\text{PDS}] < 8 \text{ mM}$; see section 2.1.1).

Additional research is required to improve our understanding of the roles that the soil and groundwater composition plays in the decomposition of persulfates. There is a lack of understanding of the effects of various soil minerals and organic compounds with different functional groups on the decomposition of persulfates. Soil constituents are believed to decompose persulfates via both the radical and nonradical mechanisms. In particular, the interactions of persulfates with NOM have yet to be established. The natural oxidant demand due to direct and indirect reactions of persulfates with NOM requires investigation followed by quantitatively comparison with those of other ISCO systems. The kinetics and mechanism underlying the reaction of $\text{SO}_4^{\bullet-}$ with NOM need to be studied, focusing on the roles of NOM as a promoter and an inhibitor of the contaminant oxidation. In addition, further research into the reactions of organo radicals with persulfates and the effect of dissolved oxygen on the radical chain reactions (see section 3.1) is needed to establish the basis for interpretation of the oxidative behavior of NOM, as well as organic contaminants, during the decomposition of persulfates.

Comparative studies of the ISCO systems are needed to systematically investigate the advantages and disadvantages of persulfates compared with other oxidants, such as ozone, H_2O_2 and permanganate. A comparison may be based on the rate of reactive radical generation, oxidant utilization efficiency, effects of reaction factors on system efficiency and other parameters. Synergistic effects of mixed oxidants enhance the application of persulfate-based ISCO systems. The mixed use of PDS and PMS in the presence of Ag^+ led to enhanced decomposition of the oxidants, possibly enhancing the generation of reactive radical species (Thompson 1981). Minor reactions of a single oxidant may promote the generation of reactive radical species by other oxidants and vice versa.

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