

Article

Role of Borate Buffer in Organic Degradation by Peroxymonosulfate in the Presence of Metal Oxides

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Abstract: The effects of borate ions on the reactivity of peroxymonosulfate (PMS) during organic degradation in the presence of metal oxides were examined. The metal oxides exhibited catalytic abilities for the degradation of carbamazepine (CBZ) but not for phenol (PN). Scavenging experiments revealed the absence of radical generation during PN degradation in the presence of the various metal oxides and borate buffer. This indicated that the borate buffer hindered the catalytic abilities of the metal oxides for producing radicals via the PMS oxidant, especially during the faster degradation of compounds such as PN. Various concentrations of borate ions were assessed for enabling pH control and permitting catalytic activity. Fe₂O₃ was found to accelerate and inhibit PN degradation at borate-ion concentrations of 2 mM and 5–20 mM, respectively. Only the 20 mM borate-ion solutions were successful at maintaining the initial pH for 2 d. Phosphate buffer, which was examined as an alternative, also disrupted radical formation but not as considerably as that of the borate ions with metal oxides. This study demonstrates the significance of enabling pH control and permitting the catalytic activity for ensuring the effective use of oxyanions as buffers.

Keywords: borate ions; peroxymonosulfate; metal oxides; radicals; buffer solution



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1. Introduction

Advanced oxidation processes (AOPs) which use potent reactive oxygen species such as hydroxyl radicals and sulfate radicals have been widely applied in water treatments to destroy various contaminants [1,2]. AOPs are classified as hydroxyl radical-based, ozone-based, UV-based, Fenton-related, sulfate radical-based, and others [1,3]. Since the 1980s, hydroxyl radical-based AOPs have been actively investigated due to their high efficiency in destroying organic and inorganic contaminants. However, recently, sulfate radical-based AOPs such as using peroxymonosulfate (PMS) or peroxydisulfate (PDS) have received a great attention due to their higher oxidation potential (SO₄^{•−}; E° = 2.5–3.1 V, OH[•]; E° = 1.9–2.7 V) and longer lifetime than hydroxyl radicals (SO₄^{•−}; t_{1/2} = 30–40 μs, OH[•]; t_{1/2} ≤ 1 μs) [4–6]. Also, a more liberal approach towards operating parameters such as pH, dosage of oxidants, and constituents of environmental matrices due to their reactive selectivity, leads to a wide range of applications [5,7,8].

Among the sulfate radical-based AOPs, PMS oxidants have been actively utilized for in situ subsurface remediation owing to their high solubility and reactivity, decent stability, and sustainability [9–13]. PMS can be activated by external energy (e.g., heat, UV radiation, and ultrasound) [9], chemicals [14–16], transition metals [17], and carbon-based catalysts [18,19] to produce free sulfate and/or hydroxyl radicals; these radicals are highly reactive toward most organic compounds such as acids, alcohols, aldehyde, aromatics, amines, ethers, and ketones [20–22]. Recent studies have proposed that PMS can

independently generate the reactive species such as $\text{SO}_4^{\bullet-}$, OH^{\bullet} , superoxide ($\text{O}_2^{\bullet-}$), and singlet oxygen ($^1\text{O}_2$) via self-degradation and without activation, especially under slightly alkaline pH conditions [23–25].

Several studies have used borate ions as a typical buffer solution to mimic groundwater-relevant pH conditions (6.0–8.5) owing to their pH buffering capacity being in a range of 8.0–10.0 [26,27]. Borate ions were recently found to stimulate PMS activity or induce PMS depletion resulting in accelerating or decelerating the degradation of target compounds depending on its concentrations [24,28].

The in situ presence of naturally occurring minerals such as Fe(II/III)- (1–20%, avg. 3%) and Mn(IV)-containing oxides (20–3000 mg/kg, avg. 600 mg/kg) [29–31] in subsurface systems can presumably enable the activation of injected PMS [32,33]. Although the effects of borate buffer on PMS activation in the absence of catalysts have been systematically investigated, the interactions between borate buffer and PMS in the presence of catalysts such as metal oxides have not yet been explored. Therefore, the present study was aimed at investigating the effects of borate buffer on organic degradation by the PMS oxidant in the presence of various metal oxides, identifying the major reactive species of PMS oxidation in the presence of metal oxides and borate ions, and optimizing the concentration of borate buffer solution to maintain a target pH and ensure indifference toward PMS reactivity.

2. Materials and Methods

2.1. Reagents

Chemicals such as carbamazepine (CBZ; $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$; $\geq 99.0\%$), phenol (PN, $\text{C}_6\text{H}_5\text{OH}$; $\geq 99.0\%$), nitrobenzene (NB; $\text{C}_6\text{H}_5\text{NO}_2$; 99%), benzoic acid (BZA; $\text{C}_6\text{H}_5\text{COOH}$; $\geq 99.5\%$), iron(II) sulfate heptahydrate ($\text{Fe}(\text{II})\text{SO}_4 \cdot 7\text{H}_2\text{O}$; $\geq 99.0\%$), sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$; 99.998%), boric acid (H_3BO_3 ; $\geq 99.5\%$), OXONE[®] monopersulfate compound ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$; >4.0% active oxygen basis), and sodium carbonate (Na_2CO_3 ; 99.999%) were purchased from Sigma-Aldrich. Four types of pure metal oxides, iron(III) oxide (hematite, Fe_2O_3 ; <5 μm , $\geq 99\%$), iron(II/III) oxide (magnetite, Fe_3O_4 ; <5 μm , 95%), ferric hydroxide oxide (goethite, FeOOH ; 30–63% Fe), and manganese(IV) oxide ($\text{MnO}_2(\text{s})$; 10 μm , $\geq 90\%$) were obtained from Sigma-Aldrich. In addition, isopropanol (IPA, $(\text{CH}_3)_2\text{CHOH}$; 99.7%) and tert-butanol (TBA, $(\text{CH}_3)_3\text{COH}$; $\geq 99.5\%$), which were used as quenching agents, were purchased from Sigma-Aldrich. Hydrochloric acid (HCl; 37%) and sodium hydroxide (NaOH; 10.0 N standardized solution) obtained from Sigma-Aldrich and Thermo Fisher Scientific, respectively, were used for pH adjustment.

2.2. Experimental Procedure

The sample preparation and treatments were all conducted using 125-mL crimped amber bottles with airtight butyl-rubber stoppers in an anaerobic chamber (>95% N_2 , <5% H_2) to mimic the anaerobic conditions of aquifer systems. All solutions were purged with N_2 gas for 1 h prior to use. The pH of borate buffer solution (~25 mM) was adjusted to 7.5–8.0 using 0.1 M HCl and 0.1 M NaOH, accordingly, and 25 mL of the borate buffer solution (25 mM) was added to separate vessels containing 0.006 g of the respective metal oxides. In addition, 15 mL of CBZ (90 μM) or phenol (90 μM) solution was added in accordance with the specific experiments. Finally, the addition of PMS stock solution (20 mL, 600 μM) initiated the experiments. Additionally, the effects of borate buffer concentration on PMS reactivity were examined by varying the borate-ion concentration. Moreover, the identification of the predominant reactive species during PMS oxidation in the presence of the borate buffer solution and the metal oxides was conducted using 0.5 mL of scavengers such as TBA (10.46 M) and IPA (13.07 M), which are known to eliminate $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, respectively, with a 500:1 molar ratio of the scavenger to the PMS oxidant [34]. In addition, NB (9.71 M) was used to detect $\bullet\text{OH}$ ($k_{\bullet\text{OH}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [35]. The effect of the borate buffer solution on PMS reactivity in the presence of catalysts was elucidated using $\text{Fe}(\text{II})\text{SO}_4$ as a positive control instead of the metal oxides. Triplicate samples were mixed using an end-over-end rotary shaker (45 rpm) during the reaction. Seven milliliters

of the samples were periodically drawn using a syringe and filtered using 0.22 µm nylon filter and stored prior to analysis.

The degradation rates of each target compound were described using the pseudo-first-order reaction or second-order reaction, with the reaction rate constant (k) being determined using Equation (1) or (2), respectively.

$$k[\text{target compound}] = -\frac{d[\text{target compound}]}{dt} \quad (1)$$

$$k_{obs}[\text{target compound}][\text{PMS}] = -\frac{d[\text{target compound}]}{dt} \quad (2)$$

2.3. Analytical Methods

The concentrations of CBZ, PN, and NB were quantified using an ultra-performance liquid chromatography apparatus (Agilent Technologies-1260 Infinity) equipped with a UV detector (UPLC/UV). Samples were diluted with MeOH (1:1, v/v) to quench the reactions and reduce the matrix effects. Ultrapure water (18 MΩ water, solvent A) and MeOH (solvent B) were used as mobile solutions, with chromatographic separation being achieved using an Eclipse XDB-C18 column (5 µm, 4.6 × 150 mm) at an injection volume of 20 µL. For CBZ analysis, the gradient was initiated at 20% of solvent A, ramped to 70% in 12 min, maintained for 8 min, returned to 20% at 25 min, and maintained for 30 min at a flow rate of 1.0 mL min⁻¹ under 286-nm UV radiation. PN and NB were analyzed using an isocratic mobile phase with 45% and 40% of solvent A at wavelengths of 254 nm and 275 nm, respectively, and a flow rate of 0.8 mL min⁻¹.

The analysis of SO₄²⁻ ions generated via PMS oxidation was conducted using an ion chromatography system (DIONEX ICS-1000, Dionex/Thermo Scientific, Waltham, MN, USA) equipped with Dionex IonPacTM AS9-HC RFICTM (4 × 250 mm) and Dionex IonPacTM AG9-HC RFICTM (4 × 50 mm) columns. Na₂CO₃ solution (9 mM) was used as the mobile phase at a flow rate of 1 mL min⁻¹.

3. Results and Discussion

3.1. Organic Degradation by the Peroxymonosulfate (PMS) Oxidant in the Presence of Metal Oxides and Borate Buffer

The effects of borate buffer on organic degradation by PMS were assessed in the presence of various metal oxides. Two different organic compounds, CBZ and PN, were individually applied, and their degradation rates were quantified. The contents of the metal oxides were optimized by conducting CBZ degradation experiments in the range of 0.1–100 g L⁻¹ of metal oxides (Figure 1). The metal oxides appear to exhibit the highest removal of CBZ at 0.1 g L⁻¹ among the investigated concentrations (1–100 g L⁻¹), which contradicts the results obtained in the previous studies that revealed a positive effect of metal oxides on the degradation of target compounds in a concentration range of 0.1–2.0 g L⁻¹ which showed the accelerated degradation of contaminants as the dosage of metal oxides increased [36,37]. This is presumably because of agglomeration of the excess metal-oxide catalysts, which decreases the number of active sites and consequently reduces the catalytic activity. In addition, a large quantity of catalysts can possibly reduce the amount of PMS available for the reactions [38–41]. Therefore, a metal-oxide concentration of 0.1 g L⁻¹ was selected for the subsequent experiments. The degradation rates of CBZ and PN can be adequately described using the first- and second-order kinetics models, respectively; the rapid degradation reaction of PN enabled the latter (Figure 2). Figure 2a shows that the presence of metal oxides accelerates CBZ degradation rates, with FeOOH exhibiting the fastest degradation, followed by Fe₃O₄, Fe₂O₃, and MnO₂. The Fe(III) component of FeOOH possibly exhibits enhanced catalytic activity for PMS activation compared to that of the other metal oxides, and/or the surface-hydroxylated FeOOH may

be readily accessible for reacting with PMS by generating radicals in accordance with Equations (3)–(7), because of their crystalline structures [42,43].

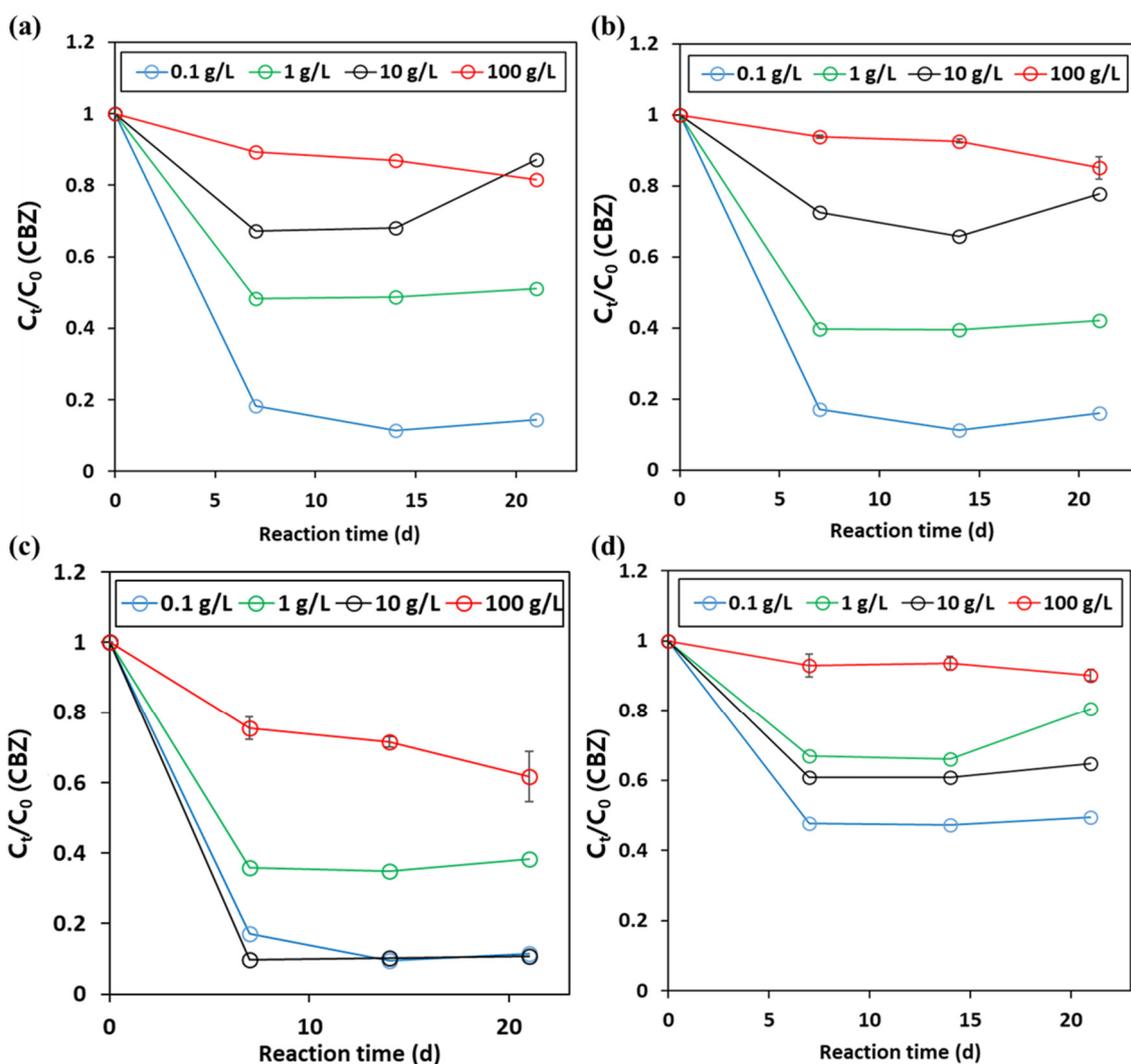
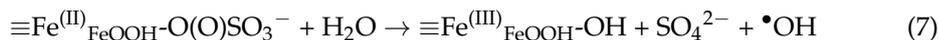
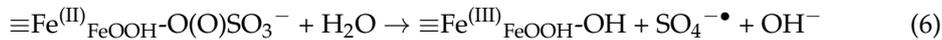
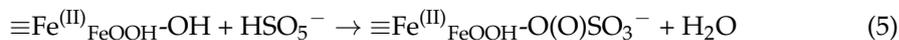
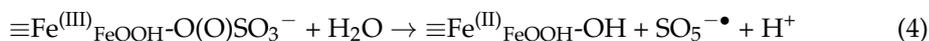
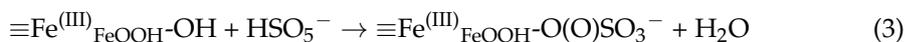


Figure 1. The effects of the concentration of metal oxides on carbamazepine (CBZ) degradation by peroxymonosulfate (PMS) oxidant (a) Fe_2O_3 -PMS treatment, (b) Fe_3O_4 -PMS, (c) FeOOH -PMS, and (d) MnO_2 -PMS ([CBZ] = 10 μM , [PMS] = 200 μM , [borate buffer] = 18.75 mM, [pH] = 7.5~8.0, sampling time = 0, 7, 14, and 21 d).

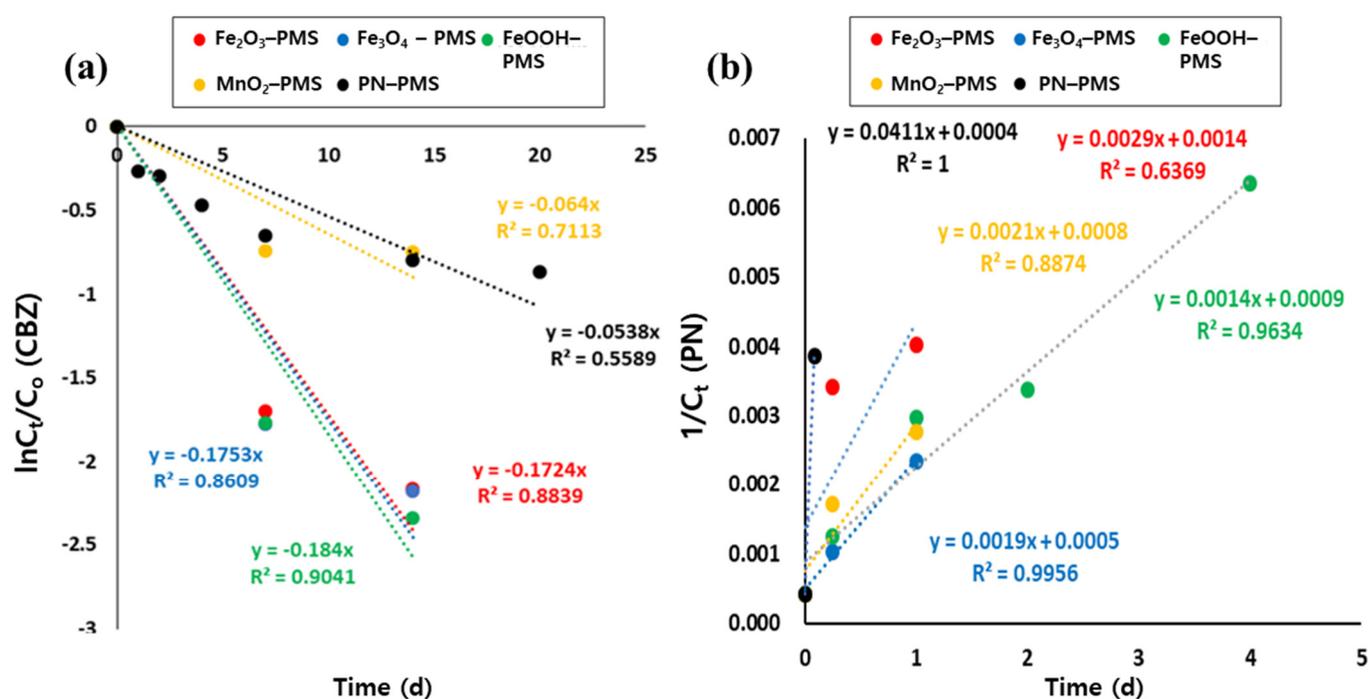


Figure 2. The rates of CBZ and phenol (PN) decomposition by PMS oxidant in the presence of different metal oxides (a) CBZ decomposition and (b) PN decomposition ([CBZ] = 10 μ M, [PN] = 10 μ M, [PMS] = 200 μ M, [metal oxide] = 0.1 g/L, [borate buffer solution] = 18.75 mM, [pH] = 7.5–8.0, sampling time = 0, 7, 14 and 21 d for CBZ decomposition, 0, 0.25, 1, 2, 4 and 7 d for PN decomposition).

However, optimal PN degradation was found to occur in the absence of metal oxides, with values of 0.29, 0.21, 0.19, and 0.14 $\times 10^{-2} \text{ M}^{-1} \text{ d}^{-1}$ corresponding to Fe₂O₃, MnO₂, Fe₃O₄, and FeOOH, respectively (Figure 2b). This indicates the potential of metal oxides as PMS activators for CBZ treatment, and their insignificant catalytic capability for PN degradation. Figure 3 suggests that the FeOOH-PMS treatment for CBZ degradation yields the highest concentration of SO₄²⁻ ions, indicating the ability of FeOOH to effectively activate PMS by producing SO₄²⁻ ions as products of PMS oxidation. Given that PN can be degraded relatively faster than CBZ by PMS-based technologies owing to its selective reactivity toward phenolic compounds [23], the amount of PMS added in the present study is presumed to be sufficient for independently decomposing PN, thereby not requiring additional catalytic assistance. Alternatively, this result indicates that the presence of borate buffer possibly obscures the capability of metal oxide catalysts during the relatively easier/faster PN degradation by the PMS-metal oxide systems.

3.2. Identification of the Major Reactive Species in PMS Oxidation Systems in the Presence of Metal Oxides and Borate Buffer

The predominant reactive species during PN degradation by the PMS-metal oxide systems in borate buffer were determined by conducting scavenging experiments to clarify the role of borate buffer (Figure 4). The addition of TBA, which is known to efficiently eliminate $\bullet\text{OH}$ radicals ($k_{\bullet\text{OH}} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), does not affect PN degradation, except with FeOOH (Figure 4a–d); moreover, no NB degradation occurs in any of the metal oxide systems (Figure 4e), which implies the lack of $\bullet\text{OH}$ radical generation in the assessed systems. Figure 4a–d suggest that the spiking of IPA, a scavenger for both $\bullet\text{OH}$ and SO₄^{•-} radicals ($k_{\bullet\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{SO}_4^{\bullet-}} = 8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [20,21], also does not cause any changes with respect to the PN degradation rates achieved without IPA. Therefore, the scavenging experiments reveal that the $\bullet\text{OH}$ and SO₄^{•-} radicals are not the primary reactive species produced in the PN-PMS systems with four different metal oxides and borate buffer. This observation contradicts previous studies that have confirmed

$\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ to be the significant reactive species participating in PN degradation by the PMS oxidant with additional catalysts such as CeVO_4 , coal-fly-ash-supported Co_3O_4 , and $\alpha\text{-Mn}_2\text{O}_3$ [44–46]. This discrepancy can be attributed to the inhibition of the catalytic capability of metal oxides owing to the presence of borate buffer solution. This was confirmed by conducting a positive-control scavenging experiment using an Fe(II)SO_4 catalyst instead of the metal oxides. Figure 5 shows a clear difference in the degrees of PN degradation achieved in systems without the scavenger and the samples with TBA/IPA without the borate buffer system; however, the impact of the scavengers on the degree of PN degradation in the borate-buffered systems is insignificant. According to previous studies [24,28], it has been known that borate ions can stimulate PMS reactivity accelerating the degradation of target compounds at certain range of borate concentration (<100 mM) [28]. However, above 200 mM of borate ions hindered the degradation of contaminants since borate ions function as a consumer of PMS rather than a catalyst of PMS [24,28]. Based on the results in this study, it is hypothesized that borate ions ($\text{XO}_n^{\text{m-}}$) may react with Lewis acid of metal oxides ($\text{M}^{\text{n+}}$) instead of reacting with PMS [47]. Thus, when borate ions and metal oxides co-exist, metal oxides disable to exhibit its catalytic capability due to the interaction of metal oxides with borate ions.

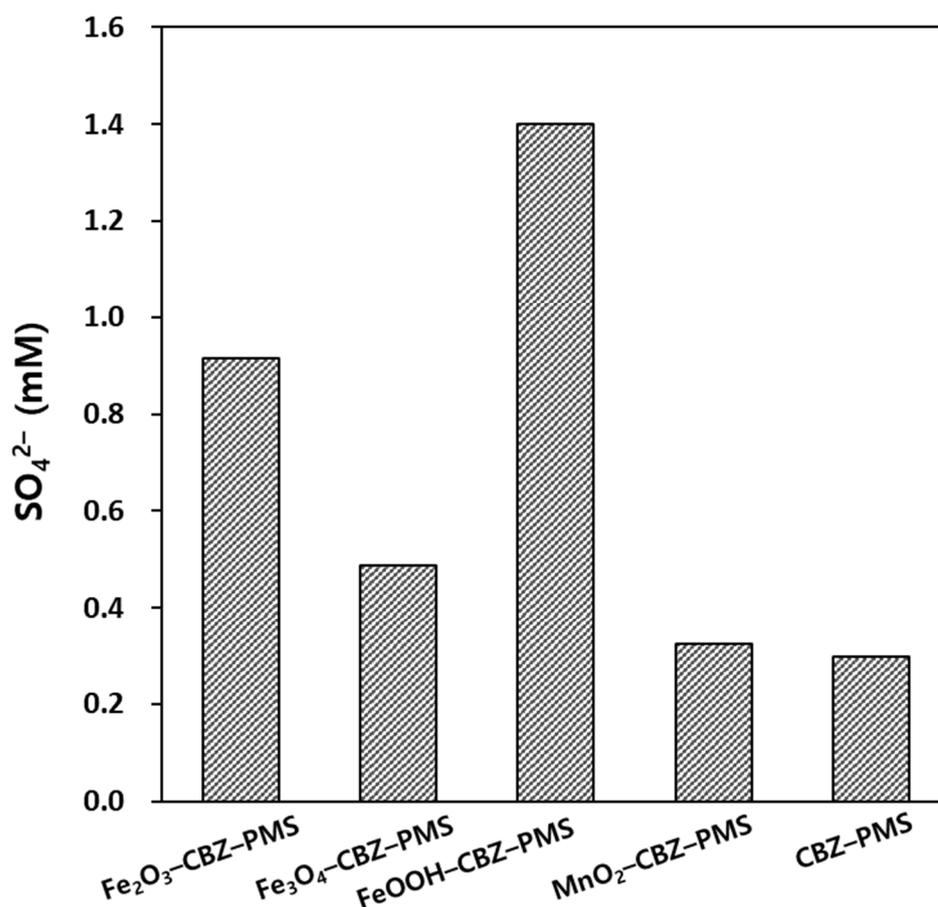


Figure 3. The concentration of SO_4^{2-} generated from PMS in CBZ decomposition experiments ([CBZ] = 10 μM , [PMS] = 200 μM , [metal oxide] = 0.1 g/L, [borate buffer solution] = 18.75 mM, [pH] = 7.5–8.0, reaction time = 7 d).

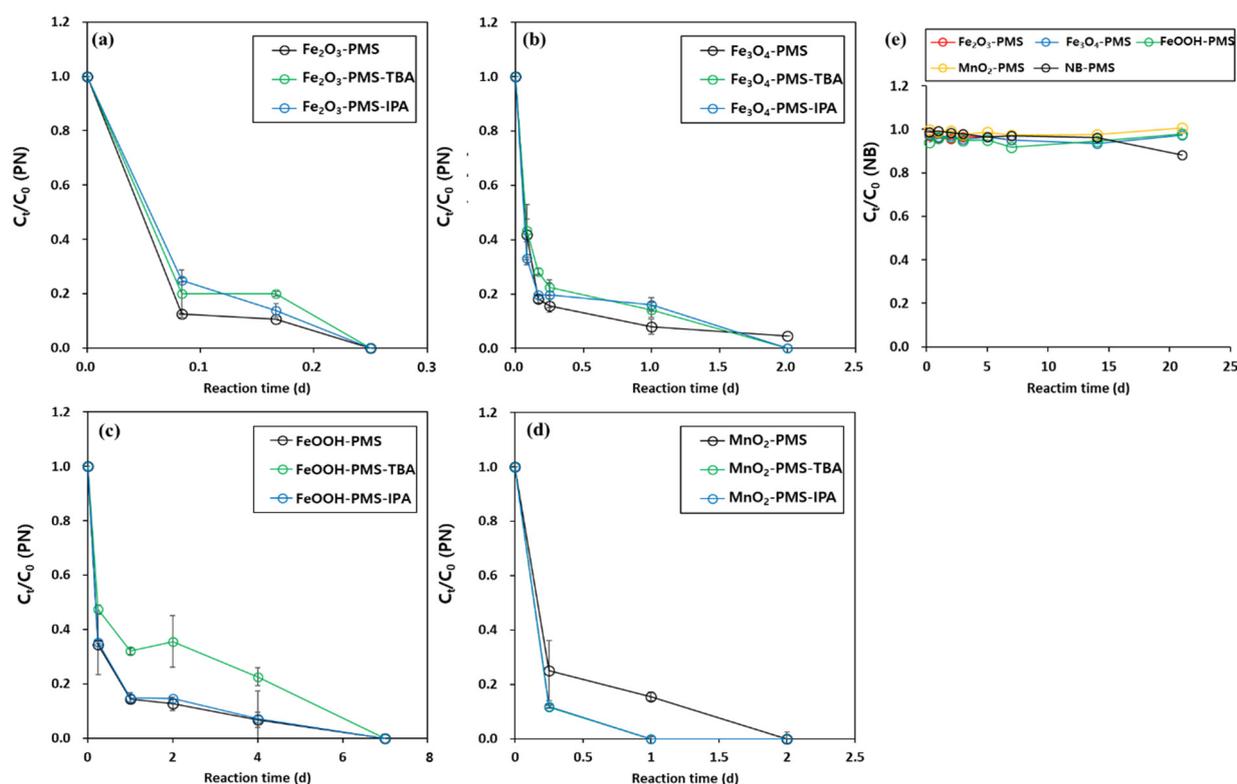


Figure 4. Quenching experiments to identify the reactive species in PN decomposition by PMS oxidant in the presence of diverse metal oxides (a) Fe_2O_3 metal oxide, (b) Fe_3O_4 , (c) $FeOOH$, (d) MnO_2 , and (e) NB decomposition by different metal oxide-PMS oxidant ($[PN] = 20 \mu M$, $[PMS] = 200 \mu M$, $[metal\ oxide] = 0.1\ g/L$, $[borate\ buffer\ solution] = 18.75\ mM$, $[pH] = 7.5\text{--}8.0$, $[TBA] = 100\ mM$, $[IPA] = 100\ mM$, $[NB]_0 = 20 \mu M$).

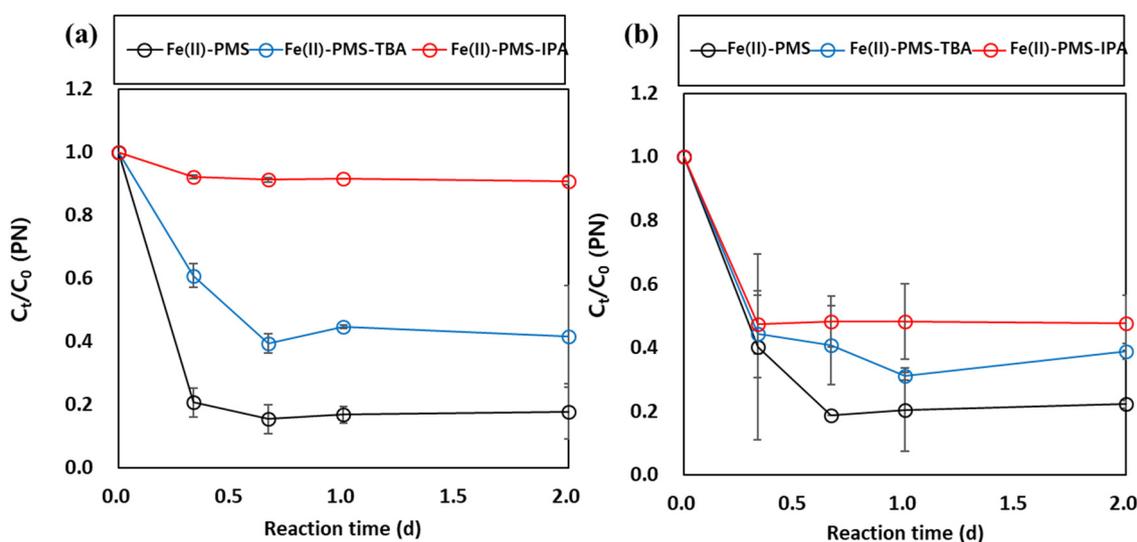


Figure 5. The quenching experiments in the absence/presence of borate buffer solution with $Fe(II)$ ions as a catalyst (a) the absence of borate buffer solution and (b) the presence of borate buffer solution ($[PN] = 20 \mu M$, $[PMS] = 200 \mu M$, $[borate\ buffer\ solution] = 18.75\ mM$, $[pH] = 7.5\text{--}8.0$, $[TBA] = 100\ mM$, $[IPA] = 100\ mM$, $[Fe(II)SO_4] = 0.1\ mM$).

3.3. Optimization of Borate Buffer Concentration

The optimal concentration of borate ions for enabling their use as a buffer solution and simultaneously not affecting PMS reactivity was determined by comparing the rates of PN degradation with respect to the presence and absence of metal oxides (Figure 6a–d) and

monitoring changes in pH in terms of the various concentrations of borate ions investigated (Figure 6e). Borate-ion concentrations of 2 mM and 5 mM result in systems with Fe_2O_3 exhibiting accelerated PN degradation or no differences compared to that in systems without it, respectively. However, an increase in the borate-ion concentration from 10 mM to 20 mM leads to the metal-oxide-deprived systems exhibiting accelerated degradation compared to that of systems with metal oxides. With respect to changes in pH during the reaction, the investigated borate-ion concentrations fail at maintaining the initial pH for 2 d, except for the borate concentration of 20 mM (Figure 6e). Therefore, while the catalytic activity of the metal oxides is not hindered at a borate-ion concentration of 2 mM, it cannot function as a buffer solution, which necessitates the use of an alternative buffer solution in PN-PMS degradation to avoid experimental artifacts. In addition, the ability of phosphate buffer solution (PBS), which is ubiquitously used to control pH in the range of 5.8–7.4, to maintain the target pH during the BZA decomposition reaction and permit PMS reactivity was investigated (Figure 7). Although the presence of phosphate ions appears to hinder BZA degradation at a PBS concentration of 0.02 mM, the degree of reduction is not as significant as that with the borate buffer solution (Figure 7a). PMS and phosphate anions are known to react with each other and produce $\bullet\text{OH}$ radicals as the predominant radicals, thereby allowing the generation of radicals, unlike the behavior of borate buffer [48]. With respect to the time-evolution of pH, a PBS concentration of 0.2–2.0 mM can maintain the target pH for 2 d (Figure 7b). Therefore, the impact of oxyanions, such as borate and phosphate ions, on PMS reactivity must be considered in their application as a buffer solution with the PMS oxidant and metal oxide catalysts.

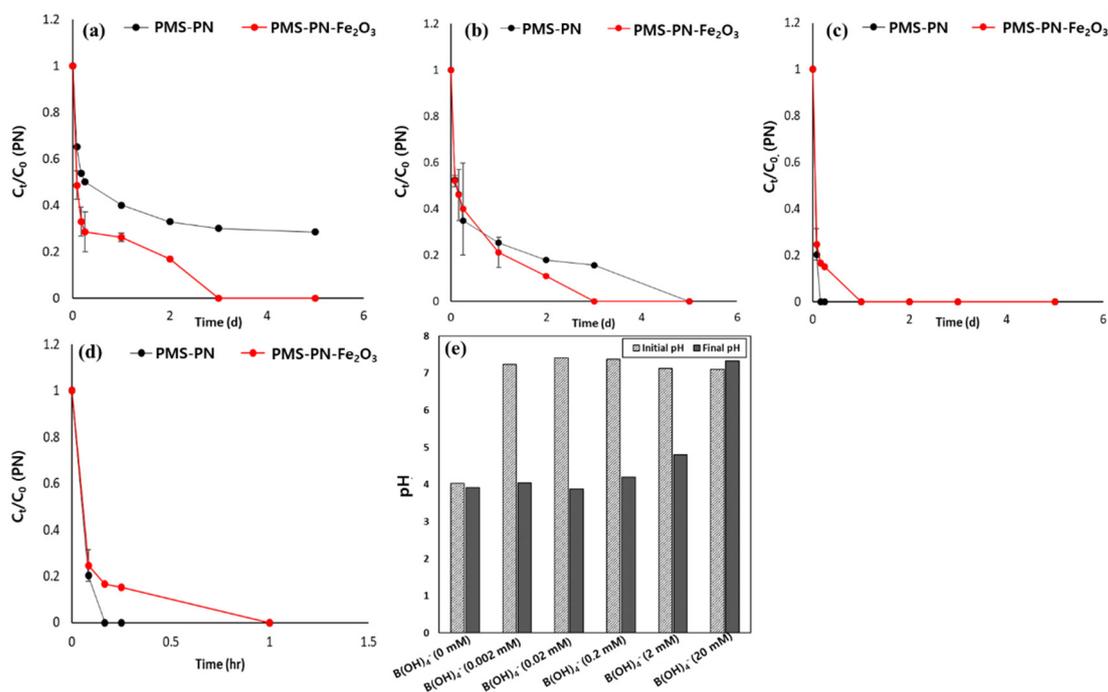


Figure 6. Comparison of PN degradation rates in the presence of Fe_2O_3 and in the absence systems in various ranges of borate ion concentration (a) 2 mM of borate ions, (b) 5 mM, (c) 10 mM, and (d) 20 mM, and (e) the pH change during the reaction time ([PN] = 20 μM , [PMS] = 200 μM , [Fe_2O_3] = 0.1 g/L, [pH] = 7.5–8.0).

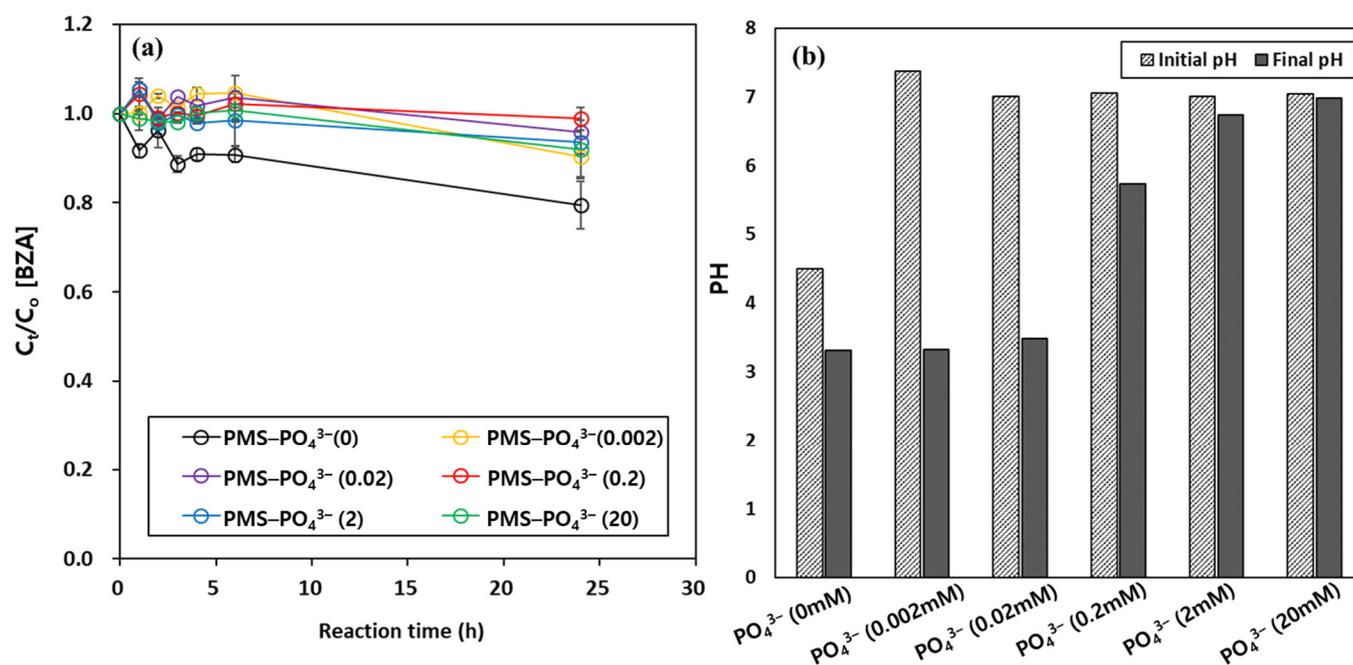


Figure 7. (a) Effect of phosphate ion concentrations on benzoic acid (BZA) decomposition by PMS oxidant, (b) the change of pH over the reaction ($[BZA] = 20 \mu\text{M}$, $[PMS] = 200 \mu\text{M}$, $[\text{phosphate ions}] = 0\text{--}20 \text{ mM}$).

4. Conclusions

This study investigated the effects of borate buffer on the degradation of organics (CBZ and PN) by the PMS oxidant in the presence of various metal-oxide catalysts. The metal oxides acted as catalysts of PMS in CBZ degradation; however, they failed to exhibit catalytic activity for PN degradation. Scavenging experiments revealed that neither $\bullet\text{OH}$ nor $\text{SO}_4^{\bullet-}$ radicals were generated in PN degradation by the PMS oxidant in the presence of the borate buffer and metal oxides. This observation meant that the borate buffer solution was hypothesized to hinder radical generation by the PMS oxidant in the presence of metal oxides, especially during the relatively faster/easier degradation of target compounds such as PN. It is likely that borate ions may react with Lewis acid of metal oxides, thus, both borate and metal oxides disable playing a role as an activator of PMS. The optimal concentration of borate ions for controlling the pH and simultaneously facilitating catalytic activity was determined. Starting at 2 mM, borate ion already showed hindering PN degradation in the presence of Fe_2O_3 and only 20 mM borate buffer solution was able to maintain the initial pH; thus, we failed to find the optimal borate concentration controlling pH simultaneously not affecting PMS reactivity. Phosphate ions were used as an alternative buffer, and exhibited a similar trend by affecting radical formation to an extent not as significant as that of the borate ions. Therefore, the use of an optimal concentration of oxyanion buffer (borate and phosphate ions) was found to be vital for maintaining a target pH and simultaneously permitting the catalytic activity of metal oxides in PMS oxidation, especially during the faster/easier degradation of target compounds.

Author Contributions: S.P. performed and designed most of experiments and wrote the manuscript. S.O. supported the experiments and conducted the literature review and provided the constructive discussion on this study. I.K. contributed to the concept of the study and writing-review, editing, supervision of this study. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Deng, Y.; Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Curr. Pollut. Rep.* **2015**, *1*, 167–176. [[CrossRef](#)]
2. Yang, T.; Yu, D.; Wang, D.; Yang, T.; Li, Z.; Wu, M.; Petru, M.; Crittenden, J. Accelerating Fe(III)/Fe(II) via Fe(II) substitution for enhancing Fenton-like performance of Fe-MOFs. *Appl. Catal B* **2021**, *286*, 119859. [[CrossRef](#)]
3. Mishra, N.; Reddy, R.; Kuila, A.; Rani, A.; Nawaz, A.; Pichiah, S. A Review on Advanced Oxidation Processes for Effective Water Treatment. *Curr. World Environ.* **2017**, *12*, 469–489. [[CrossRef](#)]
4. Ghanbari, F.; Moradi, M.; Gohari, F. Degradation of 2,4,6-trichlorophenol in aqueous solutions using peroxymonosulfate/activated carbon/UV process via sulfate and hydroxyl radicals. *J. Water Process. Eng.* **2016**, *9*, 22–28. [[CrossRef](#)]
5. Lee, J.; Von Gunten, U.; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* **2020**, *54*, 3064–3081. [[CrossRef](#)]
6. Song, W.; Li, J.; Wang, Z.; Zhang, X. A mini review of activated methods to persulfate-based advanced oxidation process. *Water Sci. Technol.* **2018**, *79*, 573–579. [[CrossRef](#)]
7. Brienza, M.; Katsoyiannis, I.A. Sulfate Radical Technologies as Tertiary Treatment for the Removal of Emerging Contaminants from Wastewater. *Sustainability* **2017**, *9*, 1604. [[CrossRef](#)]
8. Matta, R.; Tlili, S.; Chiron, S.; Barbati, S. Removal of carbamazepine from urban wastewater by sulfate radical oxidation. *Environ. Chem. Lett.* **2010**, *9*, 347–353. [[CrossRef](#)]
9. Ghanbari, F.; Moradi, M. Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review. *Chem. Eng. J.* **2017**, *310*, 41–62. [[CrossRef](#)]
10. Tsitonaki, A.; Smets, B.F.; Bjerg, P.L. Effects of heat-activated persulfate oxidation on soil microorganisms. *Water Res.* **2008**, *42*, 1013–1022. [[CrossRef](#)]
11. Kim, E.-J.; Park, S.; Adil, S.; Lee, S.; Cho, K. Biogeochemical Alteration of an Aquifer Soil during In Situ Chemical Oxidation by Hydrogen Peroxide and Peroxymonosulfate. *Environ. Sci. Technol.* **2021**, *55*, 5301–5311. [[CrossRef](#)]
12. Zeng, H.; Zhao, X.; Zhao, F.; Park, Y.; Repo, E.; Thangaraj, S.K.; Jänis, J.; Sillanpää, M. Oxidation of 2,4-dichlorophenol in saline water by unactivated peroxymonosulfate: Mechanism, kinetics and implication for in situ chemical oxidation. *Sci. Total. Environ.* **2020**, *728*, 138826. [[CrossRef](#)]
13. Oba, B.T.; Zheng, X.; Aborisade, M.A.; Liu, J.; Yohannes, A.; Kavwenje, S.; Sun, P.; Yang, Y.; Zhao, L. Remediation of trichloroethylene contaminated soil by unactivated peroxymonosulfate: Implication on selected soil characteristics. *J. Environ. Manag.* **2021**, *285*, 112063. [[CrossRef](#)] [[PubMed](#)]
14. Fang, G.; Gao, J.; Dionysiou, D.D.; 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. [[CrossRef](#)] [[PubMed](#)]
15. Zhou, Y.; Jiang, J.; Gao, Y.; Ma, J.; Pang, S.-Y.; Li, J.; Lu, X.-T.; Yuan, L.-P. Activation of Peroxymonosulfate by Benzoquinone: A Novel Nonradical Oxidation Process. *Environ. Sci. Technol.* **2015**, *49*, 12941–12950. [[CrossRef](#)]
16. Wen, G.; Qiang, C.; Feng, Y.; Huang, T.; Ma, J. Bromate formation during the oxidation of bromide-containing water by ozone/peroxymonosulfate process: Influencing factors and mechanisms. *Chem. Eng. J.* **2018**, *352*, 316–324. [[CrossRef](#)]
17. Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517. [[CrossRef](#)]
18. Oyekunle, D.T.; Zhou, X.; Shahzad, A.; Chen, Z. Review on carbonaceous materials as persulfate activators: Structure-performance relationship, mechanism and future perspectives on water treatment. *J. Mater. Chem. A* **2021**, *9*, 8012. [[CrossRef](#)]
19. Zhao, C.; Shao, B.; Yan, M.; Liu, Z.; Liang, Q.; He, Q.; Wu, T.; Liu, Y.; Pan, Y.; Huang, J.; et al. Activation of peroxymonosulfate by biochar-based catalysts and applications in the degradation of organic contaminants: A review. *Chem. Eng. J.* **2021**, *416*, 128829. [[CrossRef](#)]
20. Buxton, G.V.; Greenstock, C.L.; Helman, W.P.; Ross, A.B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886. [[CrossRef](#)]
21. Neta, P.; Huie, R.E.; Ross, A.B. Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027–1284. [[CrossRef](#)]
22. Munter, R. Advanced oxidation processes –Current status and prospects. *Proc. Est. Acad. Sci. Chem.* **2001**, *50*, 59–80.
23. Wang, L.; Jiang, J.; Pang, S.-Y.; Zhou, Y.; Li, J.; Sun, S.; Gao, Y.; Jiang, C. Oxidation of bisphenol A by nonradical activation of peroxymonosulfate in the presence of amorphous manganese dioxide. *Chem. Eng. J.* **2018**, *352*, 1004–1013. [[CrossRef](#)]
24. Yang, Y.; Banerjee, G.; Brudvig, G.W.; Kim, J.-H.; Pignatello, J.J. Oxidation of Organic Compounds in Water by Unactivated Peroxymonosulfate. *Environ. Sci. Technol.* **2018**, *52*, 5911–5919. [[CrossRef](#)]

25. Nihemaiti, M.; Permala, R.R.; Croué, J.-P. Reactivity of unactivated peroxymonosulfate with nitrogenous compounds. *Water Res.* **2019**, *169*, 115221. [[CrossRef](#)]
26. Park, S.; Angraini, T.M.; Chung, J.; Kang, P.K.; Lee, S. Microfluidic pore model study of precipitates induced by the pore-scale mixing of an iron sulfate solution with simulated groundwater. *Chemosphere* **2021**, *271*, 129857. [[CrossRef](#)] [[PubMed](#)]
27. DeSimone, L.A.; Pope, J.P.; Ransom, K.M. Machine-learning models to map pH and redox conditions in groundwater in a layered aquifer system, Northern Atlantic Coastal Plain, eastern USA. *J. Hydrol. Reg. Stud.* **2020**, *30*, 100697. [[CrossRef](#)]
28. Chen, Z.; Wan, Q.; Wen, G.; Luo, X.; Xu, X.; Wang, J.; Li, K.; Huang, T.; Ma, J. Effect of borate buffer on organics degradation with unactivated peroxymonosulfate: Influencing factors and mechanisms. *Sep. Purif. Technol.* **2020**, *256*, 117841. [[CrossRef](#)]
29. Xu, X.; Thomson, N.R. Hydrogen Peroxide Persistence in the Presence of Aquifer Materials. *Soil Sediment. Contam. Int. J.* **2010**, *19*, 602–616. [[CrossRef](#)]
30. Murad, E.; Fischer, W.R. The geochemical cycle of iron. In *Iron in Soils and Clay Minerals*; Stucki, J.W., Goodman, B.A., Schwertmann, U., Reidel, D., Eds.; Springer: Dordrecht, The Netherlands, 1988; pp. 1–18.
31. Fuller, W.W.; Warrick, A.W. *Soils in Waste Treatment and Utilization. Land Treatment I*; CR Press, Inc.: Boca Raton, FL, USA, 1985.
32. Yu, M.; Teel, A.L.; Watts, R.J. Activation of Peroxymonosulfate by Subsurface Minerals. *J. Contam. Hydrol.* **2016**, *191*, 33–43. [[CrossRef](#)]
33. Liu, H.; Bruton, T.A.; Li, W.; Buren, J.V.; Prasse, C.; Doyle, F.M.; Sedlak, D.L. Oxidation of benzene by persulfate in the presence of Fe(III)- and Mn(VI)-containing oxides: Stoichiometric efficiency and transformation products. *Environ. Sci. Technol.* **2016**, *50*, 890–898. [[CrossRef](#)] [[PubMed](#)]
34. Anipsitakis, G.P.; Dionysiou, D.D. Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environ. Sci. Technol.* **2004**, *38*, 3705–3712. [[CrossRef](#)]
35. Feng, J.; Aki, S.N.V.K.; Chateauneuf, J.E.; Brennecke, J.F. Hydroxyl Radical Reactivity with Nitrobenzene in Subcritical and Supercritical Water. *J. Am. Chem. Soc.* **2002**, *124*, 6304–6311. [[CrossRef](#)] [[PubMed](#)]
36. Sang, W.; Li, Z.; Huang, M.; Wu, X.; Li, D.; Mei, L.; Cui, J. Enhanced transition metal oxide based peroxymonosulfate activation by hydroxylamine for the degradation of sulfamethoxazole. *Chem. Eng. J.* **2019**, *383*, 123057. [[CrossRef](#)]
37. Li, W.; Orozco, R.; Camargos, N.; Liu, H. Mechanisms on the Impacts of Alkalinity, pH, and Chloride on Persulfate-Based Groundwater Remediation. *Environ. Sci. Technol.* **2017**, *51*, 3948–3959. [[CrossRef](#)] [[PubMed](#)]
38. Ding, M.; Chen, W.; Xu, H.; Shen, Z.; Lin, T.; Hu, K.; Lu, C.H.; Xie, Z. Novel α -Fe₂O₃/MXene nanocomposite as heterogeneous activator of peroxymonosulfate for the degradation of salicylic acid. *J. Haz. Mater.* **2020**, *382*, 121964. [[CrossRef](#)] [[PubMed](#)]
39. Oh, W.-D.; Dong, Z.; Hu, Z.-T.; Lim, T.-T. A novel quasi-cubic CuFe₂O₄-Fe₂O₃ catalyst prepared at low temperature for enhanced oxidation of bisphenol A via peroxymonosulfate activation. *J. Mater. Chem. A* **2015**, *3*, 22208–22217. [[CrossRef](#)]
40. Ji, F.; Li, C.; Wei, X.; Yu, J. Efficient performance of porous Fe₂O₃ in heterogeneous activation of peroxymonosulfate for decolorization of Rhodamine B. *Chem. Eng. J.* **2013**, *231*, 434–440. [[CrossRef](#)]
41. Gong, C.; Chen, F.; Yang, Q.; Luo, K.; Yao, F.; Wang, S.; Wang, X.; Wu, J.; Li, X.; Wang, D.; et al. Heterogeneous activation of peroxymonosulfate by Fe-Co layered double hydroxide for efficient catalytic degradation of Rhodamine B. *Chem. Eng. J.* **2017**, *321*, 222–232. [[CrossRef](#)]
42. Li, L.; Wu, H.; Chen, H.; Zhang, J.; Xu, X.; Wang, S.; Wang, S.; Sun, H. Heterogeneous activation of peroxymonosulfate by hierarchically porous cobalt/iron bimetallic oxide nanosheets for degradation of phenol solutions. *Chemosphere* **2020**, *256*, 127160. [[CrossRef](#)]
43. Fan, J.; Zhao, Z.; Ding, Z.; Liu, J. Synthesis of different crystallographic FeOOH catalysts for peroxymonosulfate activation towards organic matter degradation. *RSC Adv.* **2018**, *8*, 7269–7279. [[CrossRef](#)]
44. Othman, I.; Zain, J.H.; Abu Haija, M.; Banat, F. Catalytic activation of peroxymonosulfate using CeVO₄ for phenol degradation: An insight into the reaction pathway. *Appl. Catal. B Environ.* **2020**, *266*, 118601. [[CrossRef](#)]
45. Muhammad, S.; Saputra, E.; Sun, P.H.; Izidoro, J.D.C.; Fungaro, D.A.; Ang, H.M.; Tade, M.; Wang, S. Coal fly ash supported Co₃O₄ catalysts for phenol degradation using peroxymonosulfate. *RSC Adv.* **2012**, *2*, 5645–5650. [[CrossRef](#)]
46. Saputra, E.; Muhammad, S.; Sun, P.H.; Ang, H.-M.; Tade, M.; Wang, S. Manganese oxides at different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions. *Appl. Catal. B Environ.* **2013**, *142–143*, 729–735. [[CrossRef](#)]
47. Metiu, H.; Chrétien, S.; Hu, Z.; Li, B.; Sun, X.Y. Chemistry of Lewis Acid-Base pairs on oxide surfaces. *J. Phys. Chem. C* **2012**, *116*, 10439–10450. [[CrossRef](#)]
48. Lou, X.; Wu, L.; Guo, Y.; Chen, C.; Wang, Z.; Xiao, D.; Fang, C.; Liu, J.; Zhao, J.; Lu, S. Peroxymonosulfate activation by phosphate anion for organics degradation in water. *Chemosphere* **2014**, *117*, 582–585. [[CrossRef](#)] [[PubMed](#)]