

Persulfate activation on crystallographic manganese oxides: Mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants

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ABSTRACT

Minerals and transitional metal oxides of earth-abundant elements are desirable catalysts for *in situ* chemical oxidation in environmental remediation. However, catalytic activation of peroxydisulfate (PDS) by manganese oxides was barely investigated. In this study, one-dimension manganese dioxides (α - and β -MnO₂) were discovered as effective PDS activators among the diverse manganese oxides for selective degradation of organic contaminants. Compared with other chemical states and crystallographic structures of manganese oxide, β -MnO₂ nanorods exhibited the highest phenol degradation rate (0.044 min⁻¹, 180 min) by activating PDS. A comprehensive study was conducted utilizing electron paramagnetic resonance, chemical probes, radical scavengers, and different solvents to identity the reactive oxygen species (ROS). Singlet oxygen (¹O₂) was unveiled to be the primary ROS, which was generated by direct oxidation or recombination of superoxide ions and radicals from a metastable manganese intermediate at neutral pH. The study dedicates to the first mechanistic study into PDS activation over manganese oxides and provides a novel catalytic system for selective removal of organic contaminants in wastewater.

INTRODUCTION

In situ chemical oxidation (ISCO) has been extensively applied for remediation of organic contaminants in soil and groundwater, taking leverage of highly reactive oxygen species (ROS) released from diverse peroxides. Persulfate (also known as peroxydisulfate, PDS) is more favorable in ISCO compared to hydrogen peroxide (H_2O_2), ozone (O_3), and peroxymonosulfate (PMS) due to better chemical stability in transport and storage, lower cost and longer half-life for a profound efficiency.¹ However, PDS activation usually requires an intensive energy input via physical approaches (UV, heat, and sonication), which elevates the operational cost in actual remediation of contaminated water matrix. Dionysiou and co-workers discovered that transition metal ions can promote homogeneous PDS dissociation to evolve sulfate radicals ($\text{SO}_4^{\bullet-}$) for organic mineralization.^{2, 3} Furthermore, the ubiquitous presence of minerals at the subsurface environment inspired the investigations into the reactions between PDS and transition metal oxides. Copper oxide was reported to activate PDS to form a surface metastable complex, which can oxidize chlorophenols via a nonradical pathway.⁴ Fang and co-workers illustrated that iron oxides (Fe_3O_4) can catalyze PDS to produce sulfate radicals derived from generated superoxide ion radicals ($\text{O}_2^{\bullet-}$).⁵ The vanadium oxides also exhibited a high activity for sulfate radical production via electron transfer between PDS and redox centers of V(III)/V(IV).⁶

Manganese oxides are low in biotoxicity and rich in natural stock. As a dominated component of minerals in soils or aquifer materials, manganese dioxide (MnO_2) with multivalent nature can either directly oxidize contaminants^{7, 8} or catalyze hydrogen peroxide based ISCO.⁹ Chemical probes and electron paramagnetic resonance (EPR) methods have confirmed that both $\text{O}_2^{\bullet-}$ and hydroperoxide (HO_2^-) were the dominated ROS in $\text{H}_2\text{O}_2/\text{MnO}_2$ at neutral pH.^{9, 10} Our previous studies have illustrated

64 that crystalline MnO_2 can effectively activate PMS to generate $\text{SO}_4^{\bullet-}$ for phenol oxidation, and that the
65 catalytic activity was intrinsically determined by the crystallographic structure, orientations,
66 dimensions and nanostructures of manganese oxides.^{11, 12} Nevertheless, PDS activation by manganese
67 containing minerals was reported in early investigations,^{13, 14} and the underlining mechanism has not
68 yet been elucidated. Recently, the reactive complexes were discovered to be produced between PMS
69 and amorphous MnO_2 interfaces as nonradical reactive species that can directly oxidize bisphenol-A.
70 ¹⁵ Moreover, biogenic MnO_2 could activate PMS to produce singlet oxygen ($^1\text{O}_2$) via a self-
71 decomposition and energy quenching mechanism.¹⁶

72 In this study, we performed a systematic investigation of PDS activation over a wide array of
73 manganese oxides with different crystal structures and valence states. Intriguingly, one-dimensional
74 MnO_2 was discovered to be most catalytically reactive to drive PDS decomposition to evolve singlet
75 oxygen, rather than the aforementioned sulfate radical and nonradical pathways. Compared to free
76 radicals ($\text{SO}_4^{\bullet-}$ 2.5–3.1 V vs. $^{\bullet}\text{OH}$ 2.7 V), the $^1\text{O}_2$ -based system typically manifested a mild redox
77 capacity (2.2 V) with a high selectivity to attack organic substrates. Since there are still debates on
78 identification of $^1\text{O}_2$ in recent metal/metal-free advanced oxidation processes (AOPs),¹⁷ we integrated
79 several strategies to identify the ROS. Both chemical probes and *in situ* ROS capture by EPR suggested
80 that $^1\text{O}_2$ was generated and accounted for the oxidation. The pH and solvent dependence further
81 certified the dominated role of $^1\text{O}_2$, especially in neutral pH solution. A detailed mechanism was first
82 proposed for PDS activation over manganese oxides to generate $^1\text{O}_2$. Therefore, this study may provide
83 a new system for selective removal of targeted organic contaminants in water and boost the mechanistic
84 innovations in PDS-based ISCO.

MATERIALS AND METHODS

Materials preparation and characterization. Firstly, different manganese dioxides (α -, β -, and γ - MnO_2) were synthesized from the previous studies.^{11, 18, 19} Briefly, a certain amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was employed to react with MnSO_4 in a hydrothermal process. The different crystal structures of manganese dioxides were achieved by controlling the concentration of inorganic cations and reaction temperatures. Moreover, we prepared Mn_2O_3 and Mn_3O_4 under oxidation conditions.²⁰ The details of the preparation are provided in Supporting Information (SI, Text 1). The information of characterization instruments and their operation is also provided in SI, Text S2 and S6.

Catalytic performance evaluation. The degradation performance was evaluated in a batch reactor with organic compounds in a buffered solution. The oxidation was initiated by adding fixed amounts of catalyst and PDS at a rotation speed of 300 rpm. In evaluation of solution pH impacts, different buffers were adopted with 1 mM acetate for pH 5, 1 mM borate for pH 6.5 or 8.5, and 1 mM bicarbonate for pH 10. At certain time intervals, the solution was filtered through a 0.45 μm filter into a HPLC vial and mixed with methanol to terminate the oxidation. Benzoic acid (BA), nitrobenzene (NB), hydrobenzoic acid (HBA), bisphenol A (BPA), rhodamine B (RB), and phenol (PN) were chosen as probe contaminants to evaluate the oxidation capacity of PDS/manganese-oxide systems. The concentrations of the organic compounds were analyzed by an ultra-high performance liquid chromatography (UHPLC, Thermo Fisher, USA) with a C18 column. An UV-vis spectrophotometer (Spectronic 20 Genesys, Thermo Fisher, USA) was also used to determine Rhodamine B (RhB) concentration at the wavelength of 554 nm. The detailed analysis of organic compounds is provided in SI, Text 3. The PDS concentration was determined by a spectrophotometric method.²¹ All the key

106 experiments were conducted in triplicates and presented with mean values and standard derivations in
107 Figures.

108 **Detection of ROS** The radical scavengers of methanol (MeOH, 200-1000 mM), tert-butyl alcohol
109 (TBA, 200 mM), sodium azide (NaN₃, 1 mM) and furfuryl alcohol (FFA, 0.1 - 1 mM) were added into
110 β-MnO₂/PDS system to probe the generated ROS such as free radicals and singlet oxygen.
111 Benzoquinone (BQ, 1 mM) and carbonate ion (CO₃²⁻, 1 - 50 mM) were used to probe the superoxide
112 intermediates. The solutions for radical quenching tests were buffered at pH of 6.5. The solvent effect
113 of deuterated water (D₂O) and H₂O was investigated at constant buffered pH. An electron paramagnetic
114 resonance (EPR) spectrometer (EMX 10/12, Bruker, Germany) was employed to detect the ROS by
115 reacting with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol
116 (TEMP). The details of the methods and instrument parameters are listed in SI, Text S4 and S5. The
117 photosensitized singlet oxygenation was adopted as a reference system to analyze the intermediate
118 distribution and the details are provided in SI, Text S8.

119 **RESULTS AND DISCUSSION**

120 **Persulfate activation on manganese oxides for catalytic degradation.** Manganese oxides with
121 different crystal structures and valence states were evaluated for PDS activation as shown in Figure 1.
122 At neutrally buffered pH (6.5 ± 0.3), PDS alone cannot degrade PN (Figure S1) and adsorptive removal
123 of PN on manganese oxides was very limited (Figure S2, < 12%). Over 99% PN removals were
124 achieved in the presence of α-MnO₂ and β-MnO₂, which were apparently more reactive than other
125 manganese oxides (γ-MnO₂, Mn₂O₃ and Mn₃O₄) with less than 30% PN degradation. Considering the
126 moderate substrate concentration, the pseudo first-order kinetics was adopted. The corresponding rate

127 constants of manganese oxides were exhibited in Figure S1. The rate constants, $k_1(\text{PN})$, for $\beta\text{-MnO}_2$
128 and $\alpha\text{-MnO}_2$ were 0.0441 min^{-1} and 0.0264 min^{-1} , respectively, which were higher than 0.0018 min^{-1}
129 of $\gamma\text{-MnO}_2$. Manganese species in higher valence states were also evaluated showing lower values of
130 $k_1(\text{PN})$ for Mn_2O_3 (0.0007 min^{-1}) and Mn_3O_4 (0.0001 min^{-1}).

131 Since Mn^{2+} ions are not reactive for catalytic PDS activation,² the impacts of Mn leaching can be
132 ruled out. Thus, the discrepant catalytic performances of manganese oxides originate from the intrinsic
133 properties of the chemical states and crystal orientations of manganese species.¹¹ The crystal structures
134 of manganese oxides were identified by XRD patterns (Figure S3, Text S6). As illustrated in Figure
135 S4, the crystallographic structures of α , β , and $\gamma\text{-MnO}_2$ were all built with edge-sharing
136 MnO_6 octahedra. Distinctively, $\alpha\text{-MnO}_2$ was composed of (2×2) and (1×1) tunnels. $\beta\text{-MnO}_2$ was
137 provided with (1×1) tunnels while $\gamma\text{-MnO}_2$ was constructed with (2×2) and (1×2) tunnels. The $(1$
138 $\times 1)$ tunnel of MnO_2 has been reported to be beneficial for cleavage of peroxide bond whereas larger
139 tunnels may restrain the catalytic potential.²² This may explain the best PDS activation by α - and β -
140 MnO_2 . Moreover, manganese oxides with different oxidation states manifested different catalytic
141 activities. Interestingly, Mn_2O_3 and Mn_3O_4 (Figures S1 and S2) with lower valence states ($\text{Mn}^{2+}/\text{Mn}^{3+}$)
142 are not active, suggesting that the manganese species in PDS activation may not simply work as the
143 electron donor as in Ag^+ ² and zero-valent iron²³ based systems to evolve sulfate radicals. Then, β -
144 MnO_2 was further investigated for the subsequent mechanistic and kinetic studies. The nanostructure
145 of $\beta\text{-MnO}_2$ was spotted as nanorods with a width of 20 nm (Figures S5a, b and c) and specific surface
146 area of $11.9 \text{ m}^2/\text{g}$ (Figure S6). Uniform lattice fringes of 0.31 nm was identified in the HRTEM images
147 (Figures S5d and e) representing for the $[110]$ facet of $\beta\text{-MnO}_2$.

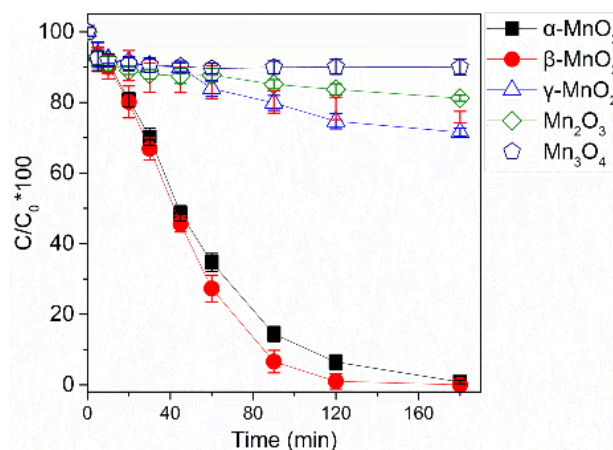


Figure 1. A comparison of PDS activation performances for phenol oxidative degradation by different manganese oxides. [Manganese oxide]₀ = 400 mg/L, [PDS]₀ = 4 mM, [organics] = 100 μM, pH buffered around 6.5.

The reactivity of β-MnO₂/PDS system toward different organic contaminants was also investigated. BA was the chemical probe for SO₄^{•-} and [•]OH ($k_2(\text{BA}, \text{SO}_4^{\bullet-}) = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2(\text{BA}, ^\bullet\text{OH}) = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)²⁴, while NB was the chemical probe for [•]OH ($k_2(\text{NB}, ^\bullet\text{OH}) = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) accordingly.²⁵ In Figure 2a, BA and NB were barely oxidized (< 8%) in 180 min, indicating that both SO₄^{•-} and [•]OH were not generated in β-MnO₂/PDS. The complete oxidations of BPA, PN and RB and a moderate removal efficiency of HBA (53.7%) were observed in Figure 2a. Similar selective oxidation of organics was also observed in the nonradical pathways in previous studies.²⁶⁻²⁸

The ionization potential (IP) of the organic compounds has been utilized as an indicator to estimate the redox capacity of an oxidative system.²⁹ In the electron mediation mechanism, an organic compound with an IP beyond 9.0 eV (the threshold) cannot be oxidized in N-graphene/PMS system due to the relatively mild redox potential of the surface confined metastable nonradical ROS. In this work, BA and NB with IP values above the threshold were hardly decomposed (Figure 2b), whereas the organics (PN, BPA, and HBA with lower IP values were vulnerable to be degraded with high

165 reaction rates (Table S1, Figures 2b and S7). This suggests that the oxidative system may not rely on
166 free radicals but nonradical species. Some recent studies discovered that singlet oxygen ($^1\text{O}_2$) could be
167 generated in non-photocatalytic AOPs, which also exhibited a high selectivity towards electron-rich
168 phenolic compounds as the nonradical pathway.^{30, 31} Therefore, the existence of $^1\text{O}_2$ in $\beta\text{-MnO}_2/\text{PDS}$
169 system may need to be considered.

170 **Probing the singlet oxygen generation in nonradical process.** In order to confirm the contributions
171 from free radicals during the oxidation, TBA and MeOH were employed to act as selective radical
172 scavengers because of their distinct second-order rate constants with sulfate radicals ($k_2(\text{TBA}, \text{SO}_4^{\bullet-})$
173 $= 4 - 9.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_2(\text{MeOH}, \text{SO}_4^{\bullet-}) = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and hydroxyl radicals ($k_2(\text{TBA}, \bullet\text{OH}) =$
174 $3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_2(\text{MeOH}, \bullet\text{OH}) = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).^{25, 32} The addition of 200 mM TBA or
175 MeOH showed a negligible impact on phenol oxidation (Figure 3a), suggesting that both $\bullet\text{OH}$ and
176 $\text{SO}_4^{\bullet-}$ were not produced. This can be confirmed by further increasing MeOH to 1000 mM which still
177 cannot induce any adverse effect on phenol degradation (Figures 3a and S8).

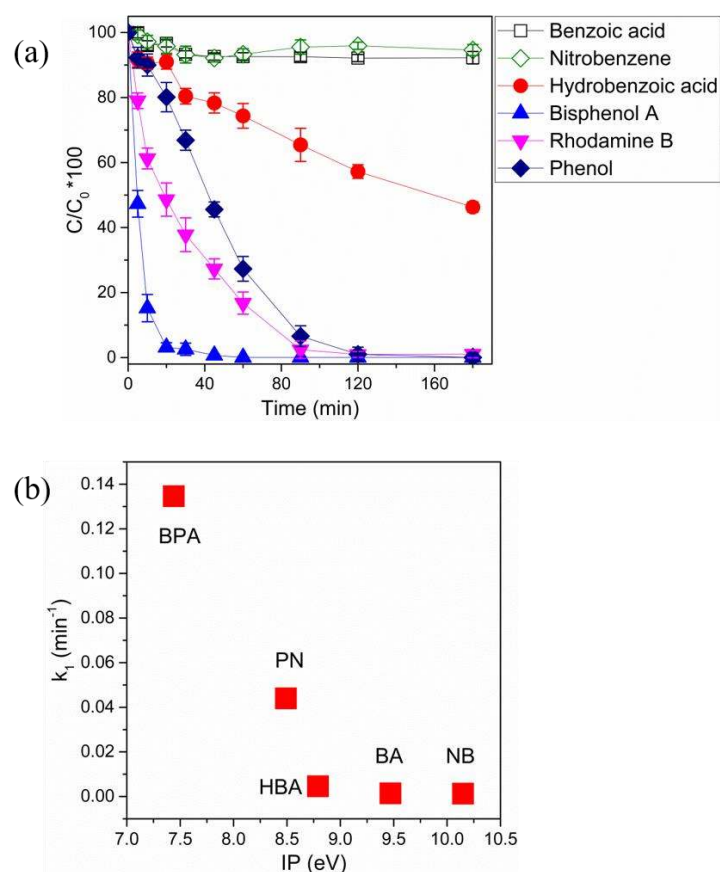


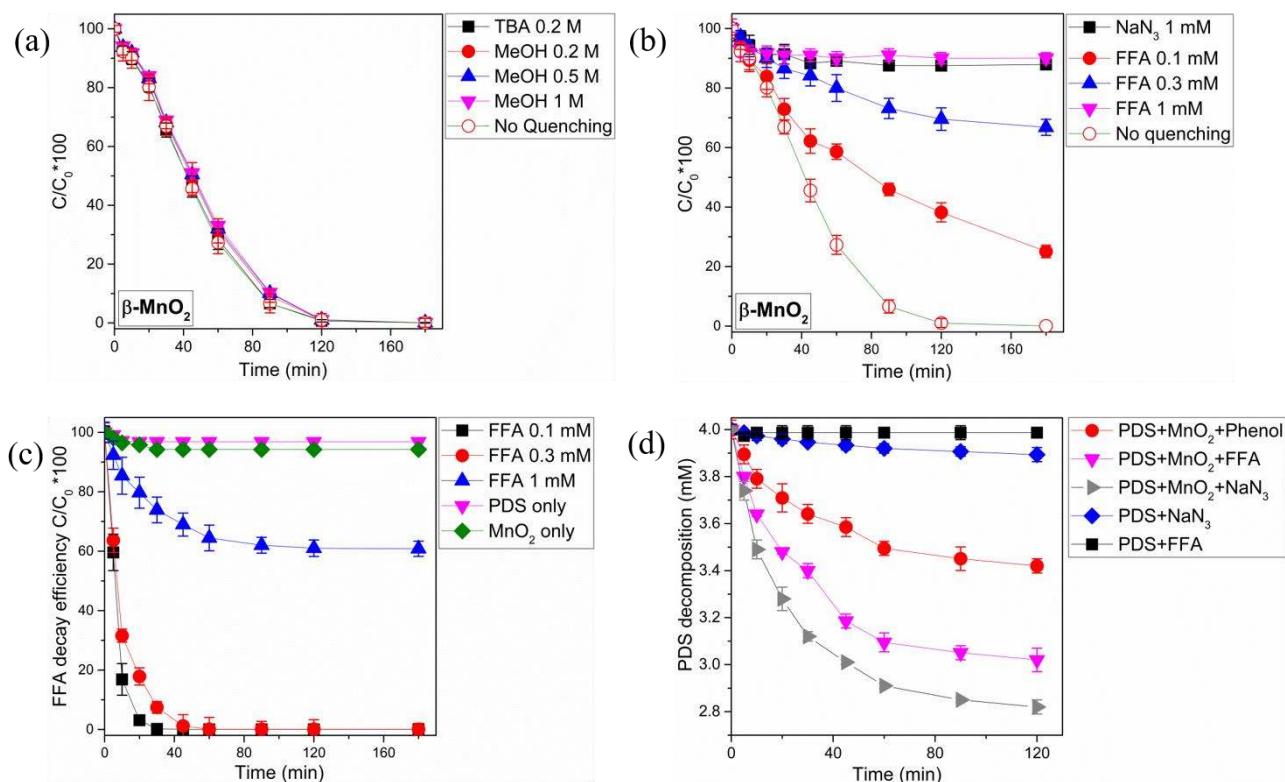
Figure 2. (a) Selective oxidation in β -MnO₂/PDS activation. [Manganese oxide]₀ = 400 mg/L, [PDS]₀ = 4 mM, [organics] = 100 μ M, pH buffered around 6.5. (b) The relationship between organics degradation rates and their ionization potentials (IP).

Moreover, we employed azide with a moderate concentration (1 mM) to quench the oxidation by ¹O₂ (k_2 (NaN₃, ¹O₂) = 1×10^9 M⁻¹ s⁻¹).³³ In the presence of azide ions, phenol degradation by β -MnO₂/PDS was almost suspended (Figures 3b and S8) with only 12% removal in 180 min (mostly by adsorption, Figure S2). FFA was further used as a chemical probe for ¹O₂ generation, which manifested a higher second order rate of 1.2×10^8 M⁻¹ s⁻¹^{34, 35} than the targeted phenolic compound (2.0 - 3.0×10^6 M⁻¹ s⁻¹)^{31, 36} with ¹O₂. A minor amount of FFA (0.1 mM, equal to phenol concentration), caused a noticeable decline in phenol removal rate from 0.0441 to 0.0093 min⁻¹ (Figures 3b and S8). When FFA was increased to 0.3 mM, the reaction rate further decreased to 0.0036 min⁻¹ and phenol oxidation was

196 terminated with 1.0 mM FFA. Herein, both the selective radical quenching and chemical probing
 197 indicated that $^1\text{O}_2$ was generated and accounted for the organic degradation in $\beta\text{-MnO}_2/\text{PDS}$ system.
 198 Notably, although azide and FFA also exhibited a high reactivity with free radicals (i.e. $k_2(\text{NaN}_3, \text{SO}_4^{\bullet-})$
 199 $= 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2(\text{FFA}, ^\bullet\text{OH}) = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),^{37, 38} the overabundant loading of MeOH
 200 exhibited higher rates at 1 or 2 orders of magnitude towards the radicals. Since the inhibition effect of
 201 MeOH was trivial, the sulfate and hydroxyl radicals were not produced and the reaction of azide or
 202 FFA with the radicals could be neglected. Thus, azide and FFA could be regarded as the exclusive $^1\text{O}_2$
 203 scavengers in the study. The quenching effects of TBA, MeOH, and FFA on phenol oxidation by $\alpha\text{-}$
 204 MnO_2/PDS (Figure S9) exhibited the similar characteristics to $\beta\text{-MnO}_2$, which implied the same
 205 catalytic pathway involving $^1\text{O}_2$.

206 FFA decay was recorded to quantify the $^1\text{O}_2$ production in $\beta\text{-MnO}_2/\text{PDS}$ system. In Figure 3c, PDS
 207 alone cannot degrade FFA and FFA adsorption on $\beta\text{-MnO}_2$ was marginal. However, FFA began to
 208 decompose once PDS and MnO_2 co-existed. At a low initial FFA concentration (0.1 mM), the
 209 completed FFA oxidation was obtained within 60 min with a rate constant of 0.162 min^{-1} , which is
 210 far higher than that of phenol (0.0441 min^{-1}). When the initial FFA concentration was increased to 0.3
 211 mM and 1 mM, 99.5% and 39.2% of FFA degradations were observed, respectively. Assuming that
 212 FFA decay follows a first order kinetics, then the values of $\ln([\text{FFA}]_t/[\text{FFA}]_0) = -k_{\text{obs}} t$, k_{obs} may be
 213 relevant to $[\text{MnO}_2]$, $[\text{PDS}]$, and pH values. The correlation of $[\text{FFA}]_0$ and k_{obs} was fitted in Figure S10
 214 and the good linear relationship ($R^2 = 0.986$) verified the first order kinetics of FFA degradation. The
 215 first order rather than zero order kinetics indicated that the $^1\text{O}_2$ oxidation participated in the bulk
 216 solution rather than on the catalyst surface region via electron transfer, which was also discovered in

217 previous $^1\text{O}_2$ based systems.^{30, 39}



218

219 **Figure 3.** The determination of ROS species for oxidation in $\beta\text{-MnO}_2/\text{PDS}$. (a) the quenching effect
 220 of free radicals on phenol oxidation degradation (TBA 200 mM, MeOH 200-1000 mM), (b) the
 221 quenching effect of singlet oxygen on phenol oxidative degradation (NaN_3 1 mM, FFA 100-1000 μM),
 222 (c) FFA decay in $\beta\text{-MnO}_2$ /PDS (FFA conc. 100-1000 μM), (d) PDS decomposition under different
 223 experimental conditions (phenol or FFA conc. 100 μM). [$\beta\text{-MnO}_2$]₀ = 400 mg/L, [PDS]₀ = 4 mM, pH
 224 buffered around 6.5.

225 PDS concentration was monitored to affirm persulfate decomposition in different situations. PDS
 226 alone could not be consumed by phenol at neutral pH, whereas the presence of $\beta\text{-MnO}_2$ can
 227 decompose PDS to a certain extent without the presence of organics (Figure S11). The rapid PDS
 228 decomposition was not experienced in the study, which was different from the Ag^+/PDS system in
 229 continuously producing free radicals.⁴⁰ Moreover, the introduced PN led to a higher PDS depletion

(Figure 3d), suggesting that the organic pollutants can rapidly scavenge the generated $^1\text{O}_2$ and accelerate PDS decomposition. This is also different from the surface radical-based oxidation where the persulfate depletion would be restrained with more participation of organics and the competitive reaction with the surface active sites between organics and oxyanion.⁴¹ Figure 3d depicts that azide and FFA yielded a higher efficiency than phenol for catalytic PDS decomposition with $\beta\text{-MnO}_2$, possibly due to their higher reaction rates towards $^1\text{O}_2$. A previous study indicated that azide or FFA is a reducing agent which may react with PMS and cannot verify the quenching effect toward $^1\text{O}_2$.⁴² Figure 3d shows that PDS cannot be directly decomposed by azide or FFA (1 mM), suggesting that the reactivity of PDS towards the quenching agents was low. Thus, the inhibition of phenol degradation originated from $^1\text{O}_2$ quenching by azide or FFA.

EPR technique was applied to *in situ* capture the ROS generated from $\beta\text{-MnO}_2$ /PDS system using DMPO as a spin trapping agent. Not surprisingly, neither DMPO-OH nor DMPO-SO₄ was discovered. Instead, the characteristic peaks (Figure S12) with the hyperfine splittings of 1:2:1:2:1:2:1, were assigned to 5,5-dimethyl-1-pyrrolidone-2-oxyl (DMPOX, $\alpha_{\text{N}} = 7.3$ G, $\alpha_{\text{H}} = 3.9$ G), as a resulting product from DMPO direct oxidation by $^1\text{O}_2$.^{44,45} Besides, TEMP was a specific spin trapping agent for identification of $^1\text{O}_2$. The intense three-line signals (1:1:1) of TEMPN adducts (Figure 4, $\alpha = 16.9$ G) by $^1\text{O}_2$ oxidation was observed, which was another solid evidence of $^1\text{O}_2$ generation. The addition of FFA (1 mM) would decrease the intensity of TEMPN signals (Figure 4) due to the consumption of $^1\text{O}_2$. Moreover, a methylene blue (MB)/irradiation system was employed as a reference to identify the $^1\text{O}_2$ generation. The intermediate distributions during BPA oxidation was analyzed for both MnO_2 /PDS and MB/irradiation. The LC-MS results in Figure S13 demonstrated that the intermediate

products in the MnO_2/PDS system were almost the same as the singlet oxygen based system (MB/irradiation), indicating that the $^1\text{O}_2$ was produced and serves as the primary ROS in MnO_2/PDS system. The details of intermediate products are listed in Table S2.

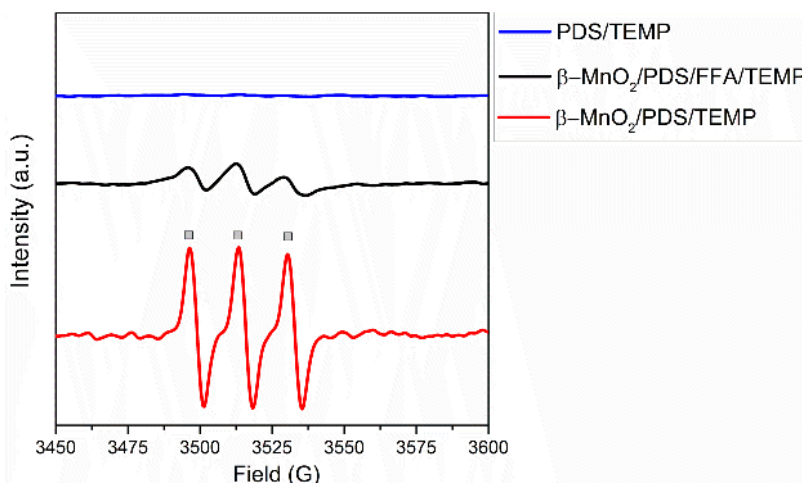


Figure 4. EPR spectra of singlet oxygen detection in the presence of TEMP. $[\beta\text{-MnO}_2]_0 = 400 \text{ mg/L}$, $[\text{PDS}]_0 = 4 \text{ mM}$, $[\text{FFA}]_0 = 100 \text{ }\mu\text{M}$, $[\text{TEMP}]_0 = 25 \text{ mM}$, pH buffered around 6.5, gray square: TMPO adducts.

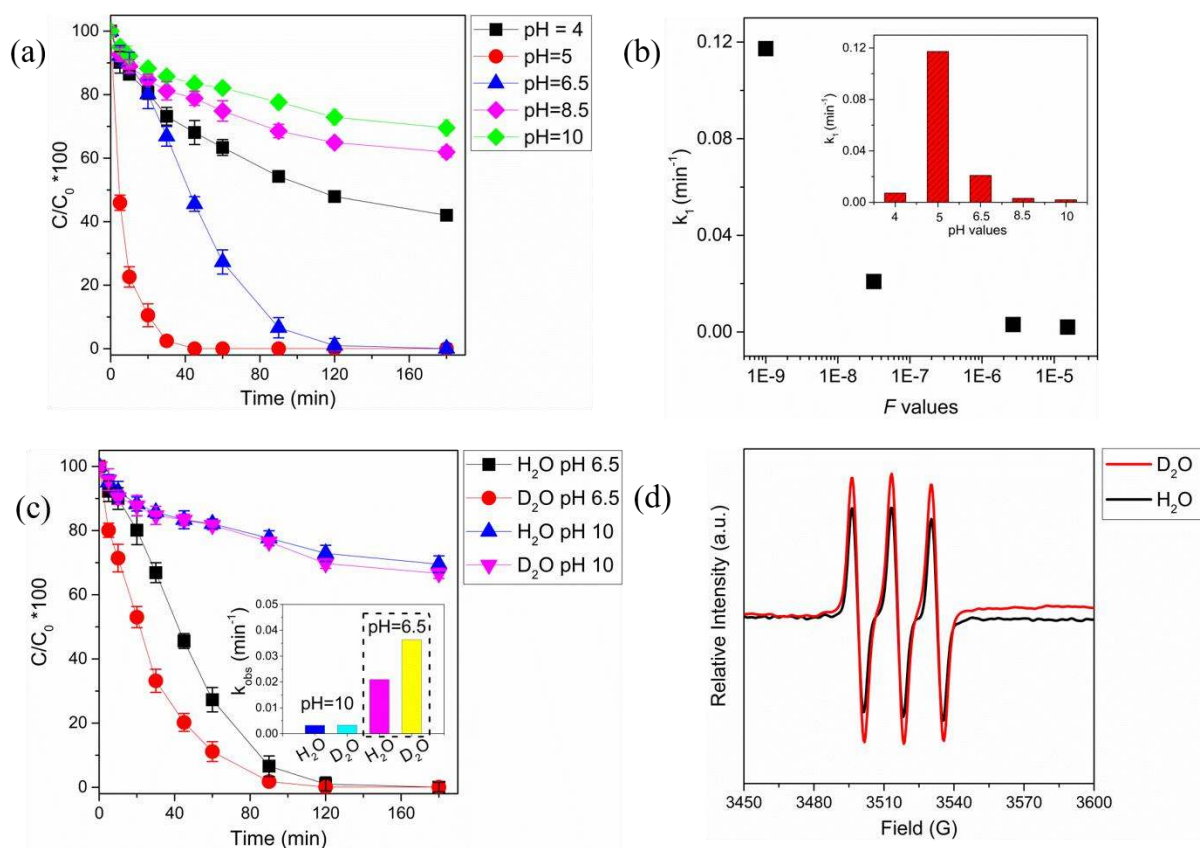
Mechanism of singlet oxygen evolution. The impacts of solution pH and reaction substrates were investigated on $^1\text{O}_2$ generation from $\beta\text{-MnO}_2/\text{PDS}$. In Figure 5a, phenol degradation rates were significantly improved by decreasing the buffered pH from 10 to 5. At pHs 5 and 6.5, complete phenol oxidation can be achieved in 45 and 120 min, respectively, whereas only 38.1% and 31.5% of organic removals were yielded at pHs 8.5 and 10 in 180 min, respectively. Intriguingly, only 57.9% of phenol was oxidized at a lower pH of 4. At the extreme low pH region (≤ 4), significant Mn dissolution (Figure S2) was experienced and the leached Mn^{2+} is inactive for PDS activation. Moreover, surface structure of MnO_2 was destroyed, which would decrease the catalytic performance. Since the zero potential point of crystal MnO_2 was around 3.5,^{46, 47} a higher pH (8.5 - 10) would cause phenomenal

electrostatic repulsions between the MnO₂ surface and persulfate anions, herein slowing down the reaction rates (Figure S14). Nevertheless, though ¹O₂ favored to react with phenolic anions at the alkaline condition,⁴⁸ the immense repulsive forces hindered the interactions between MnO₂ and PDS and significantly prohibited the ¹O₂ generation. Moreover, the pH effects in MnO₂/PDS manifested a completely different trend from MB/irradiation system (Figure S15), suggesting that the ¹O₂ generation rate exerted a more significant contribution to the phenol oxidation in MnO₂/PDS, regardless of the existent forms of phenolics in the near-neutral conditions. Therefore, a neutral pH solution was more favorable.

We employed an F factor ($F = K_w/[H]^+ + K_a$, where K_a is the ionization constant of PDS at 5.5×10^{-10}) to estimate the impact of solution pH. A positive linearity between the F values and peroxide activation indicates that the reaction is pH-dependent and dominated by the persulfate ionization or base activation.³⁰ In this study, the nonlinear correlation between phenol degradation rate and F (Figure 5b) suggested that the reaction under neutral condition followed a heterogeneously catalytic process, whereas surface electrostatic charge may gradually impede the reaction under extreme pH conditions.⁴⁹ Nevertheless, base activation of PDS (Figure S16) may take place at high pH to generate a minor amount of hydroxyl radicals. However, the radical was less effective than the ¹O₂-based oxidation because the electron-rich phenolic compounds were more susceptible to ¹O₂.^{31, 50}

Additionally, different solvents were applied to confirm the existence of ¹O₂. The lifetime of ¹O₂ in D₂O (20 - 32 μs) was more than 10-fold longer than in H₂O (2 μs),⁵¹ which can kinetically accelerate the oxidation in ¹O₂ based systems.^{34, 42} In this study, when the solvent H₂O was completely replaced with D₂O, the phenol degradation by β-MnO₂/PDS was barely impacted at pH 10 (Figure 5c),

288 indicating that $^1\text{O}_2$ was not the dominant ROS under alkaline condition. However, 50% enhancement
 289 of the first order rate in phenol removal was observed at pH 6.5 in D_2O (Figure 5c, inset) compared
 290 with that in H_2O . This suggested that singlet oxygen was generated and accounted for organic
 291 degradation at the neutral pH. This is further confirmed by the EPR spectra that the intensity of
 292 TEMPN adducts in $\beta\text{-MnO}_2/\text{PDS}/\text{D}_2\text{O}$ was increased obviously by 30% compared with that in $\beta\text{-}$
 293 $\text{MnO}_2/\text{PDS}/\text{H}_2\text{O}$ at pH 6.5 as shown in Figure 5d.

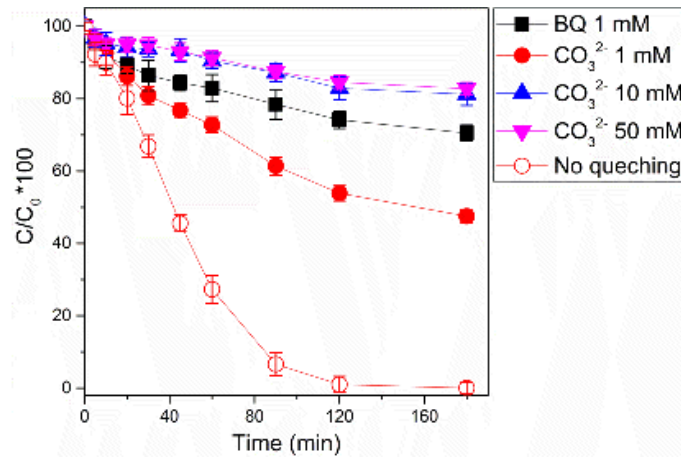


305 **Figure 5.** The insightful identification of singlet oxygen generation in $\beta\text{-MnO}_2/\text{PDS}$. (a) Phenol
 306 oxidation degradation in $\beta\text{-MnO}_2/\text{PDS}$ under different buffered pH conditions, (b) the relation of F
 307 values and degradation rates at different pH values, (c) the effect of reaction solvents (H_2O and D_2O)
 308 upon degradation, (d) EPR spectra of $\beta\text{-MnO}_2/\text{PDS}$ in the H_2O and D_2O solvents ($[\text{TEMP}]_0 = 25$ mM).

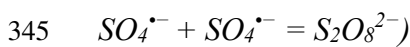
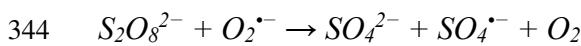
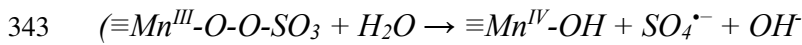
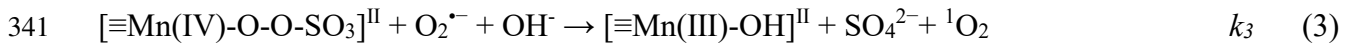
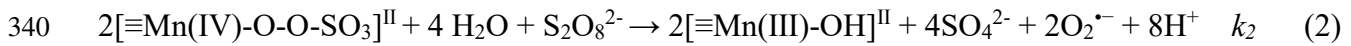
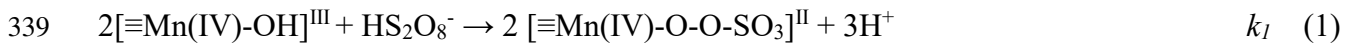
309 $[\beta\text{-MnO}_2]_0 = 400 \text{ mg/L}$, $[\text{PDS}]_0 = 4 \text{ mM}$, $[\text{phenol}]_0 = 100 \text{ }\mu\text{M}$. 1 mM acetate buffered for pH 5, 1 mM
310 borate buffered for pH 6.5 or 8.5, and 1 mM bicarbonate buffered for pH 10.

311
312 Typically, singlet oxygen can be generated from several pathways such as the reaction between
313 persulfate (PMS/PDS) and ketonic groups on carbonaceous materials,⁵² photo-excitation of oxygen
314 molecules (in a triplet ground state) via an energy-transfer process.²⁸ In this study, the $^1\text{O}_2$ generation
315 may be resulted from the direct oxidation or recombination of superoxide intermediates ($\text{O}_2^{\bullet-}$), which
316 could be generated over manganese dioxide.^{5, 7, 9, 10} The production and role of $\text{O}_2^{\bullet-}$ can be confirmed
317 by selective scavengers of carbonate (CO_3^{2-} , $k_2 = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).⁵³ Due to the fact that
318 hydroxyl radical was not produced in this system, a high reaction rate of carbonate towards
319 hydroxyl radical ($k_2 = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) would not influence the inhibitory effect of $\text{O}_2^{\bullet-}$. In Figure 6,
320 addition of 1 mM carbonate decreased the phenol degradation from 100% (control experiment) to 52.5%
321 in $\beta\text{-MnO}_2/\text{PDS}$ system. Only 18.8% and 17.6% phenol removals were observed when 10 and 50 mM
322 of carbonate were introduced, respectively. Besides, addition of 1 mM BQ, another more selective
323 radical scavenger for $\text{O}_2^{\bullet-}$ (BQ, $k_2 = 2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁵⁴ also impressively inhibited the phenol
324 degradation with only 29.5% organic removal. The radical quenching tests affirmed that $\text{O}_2^{\bullet-}$ was
325 involved in $^1\text{O}_2$ generation and catalytic degradation. Therefore, a superoxide-based reaction pathway
326 toward $^1\text{O}_2$ evolution on MnO_2 was proposed as displayed in Eqs 1-5. A metastable manganese
327 intermediate ($\text{Mn}^{\text{IV}}\text{-O-O-SO}_3$) was first formed at the surface of MnO_2 , and then $\text{O}_2^{\bullet-}$ was generated
328 by reacting with another $\text{S}_2\text{O}_8^{2-}$ along with the breakage of $\text{Mn}^{\text{IV}}\text{-O}$.^{45, 55} Afterwards, $^1\text{O}_2$ was generated
329 from a direct oxidation of $\text{O}_2^{\bullet-}$ by Mn^{IV} , which is thermodynamically favored ($E_0(\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}) = 0.95$

330 V_{NHE} and $E_0(\text{O}_2^{\bullet-}/^1\text{O}_2) = -0.34 V_{\text{NHE}}$) or a recombination of two superoxide radicals. The details were
 331 shown in SI (Text S7). The similar processes were also reported in a periodate oxide/base system.²⁷
 332 Moreover, the specific pathway of $^1\text{O}_2$ generation by surface reactions may lead to different $^1\text{O}_2$
 333 generation rates. On one hand, the competitive adsorption of different organics may result in the
 334 different $^1\text{O}_2$ generation rates. On the other hand, the degradation rate can be also impacted by the
 335 migration distance of $^1\text{O}_2$ as well as the ionized potential of the organics (the reactivity toward $^1\text{O}_2$).⁵⁶



336
 337 **Figure 6.** The determination of superoxide radicals by efficient scavengers. $[\beta\text{-MnO}_2]_0 = 400 \text{ mg/L}$,
 338 $[\text{PDS}]_0 = 4 \text{ mM}$, $[\text{phenol}]_0 = 100 \mu\text{M}$, $[\text{BQ}] = 1 \text{ mM}$, $[\text{CO}_3^{2-}] = 1 - 50 \text{ mM}$, pH buffered around 6.5.



347 The surface properties of β -MnO₂ were analyzed before and after the catalytic reaction. From the
348 deconvolution peaks of Mn 2p_{3/2} in XPS spectrum (Figure S17a), the peaks of binding energies at
349 643.2 and 642.4 eV were assigned to Mn^{IV} and the peak at 641.3 eV corresponds to Mn^{III} species.⁵⁷
350 Compared to fresh MnO₂, the peak of Mn^{III} species was enhanced obviously after the reaction. The
351 two fitted peaks of O 1s at 530.3 and 532.0 eV (Figure S17b) can be assigned to the classical Mn-O-
352 Mn bonds and Mn-O-X bond, respectively. The intensity of Mn-O-X bond was also enhanced in the
353 used catalyst due to the formation of metastable oxygen-containing bonds. Therefore, the alteration of
354 surface redox states of manganese supported the proposed mechanism with the involvement of Mn^{III}
355 intermediates, which was in agreement with FTIR and Raman analyses in Figures S18 and S19.

356 The corresponding kinetics (Eqs. 6-8) was established for the proposed mechanism and pseudo first-
357 order model was calculated. The influences of single variable such as PDS and β -MnO₂ concentrations
358 on phenol degradation at pH 6.5 (Figure S20) displayed that a higher loading of PDS or catalyst would
359 enhance the phenol oxidation. Then, the curves between the $\ln(K_{l,obs})$ and initial PDS and MnO₂
360 concentrations were plotted and fitted. The good linear correlations between $\ln(K_{l,obs})$ and $\ln([MnO_2])$
361 ($R^2 = 0.964$) or $\ln([PDS])$ ($R^2 = 0.939$) were observed in the insets of Figure S21. The slopes of \ln
362 ($K_{l,obs}$) with $\ln([MnO_2])$ and $\ln([PDS])$ were estimated to be 0.989 and 1.001 accordingly, suggesting
363 that the kinetic orders were both equal to 1. The first order of $[MnO_2]$ and $[PDS]$ could be assigned to
364 the reactions, Eq1 and Eq2, respectively. Due to the initial amount of persulfate at an excessive level
365 and the effect of $[PDS]$ is neglecting, reaction rate in reaction 1 only depended on the $[MnO_2]$, which
366 could be considered as a pseudo first-order reaction. Thus, reaction 2 was entirely related to $[PDS]$
367 irrespective of $[MnO_2]$. The kinetic studies suggested that the formation of metastable manganese

intermediates (reaction 1) was a catalytic process, primarily relying on MnO₂, while the final step in evolution of ¹O₂ may be determined by the existence form of persulfate anions. Based on PDS decomposition with manganese dioxide surface with/without phenol, the reaction rates of Eqs 1 and 2 were confirmed in Text S7. We used the Langmuir–Hinshelwood model (Text S9) to identify the role of the metastable manganese intermediates. The well fitted Langmuir–Hinshelwood model curve of PDS ($R^2 = 0.942$, Figure S22) indicated that the surface-mediated reaction of PDS on the MnO₂ was enhanced by increasing the PDS concentration. The enhanced surface-mediated reaction by PDS was resulted from the formation of metastable manganese-PDS intermediates, which further led to ¹O₂ generation. Furthermore, the reaction rate from O₂^{•-} to ¹O₂ in Eq 3 was calculated as $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (K_3), which is three-magnitude higher than the reaction rate between superoxide and phenol ($5.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$).⁵⁸ This suggested that generated O₂^{•-} in this system was primarily consumed for ¹O₂ generation rather than direct contributing to phenol degradation. Moreover, based the singlet oxygen-mediated degradation of FFA, we can calculate the amount of generated ¹O₂ by the equation of $[^1\text{O}_2] = k_{obs} / k_{FFA}$. The calculated amount of ¹O₂ in MnO₂/PDS was $1.65 \times 10^{-11} \text{ M}$ (FFA 0.3 mM), which is much higher than the amount in the typical ¹O₂-based system of Rose Bengal/irradiation (FFA 0.27 mM, $0.05 \times 10^{-11} \text{ M}$).⁵⁹

The simplified kinetic models were proposed as follows:

$$-\frac{d[\text{organic}]}{dt} = k [\text{organic}]_0 \quad (6)$$

$$\ln \left(\frac{[\text{organics}]_t}{[\text{organics}]_0} \right) = -K_{1,obs} t = -Ck_1K_2K_3(\text{or } K_4)K_5 [\text{MnO}_2]^{n1} [\text{PDS}]^{n2} t \quad (7)$$

For apparent first-order rate constant,

$$K_{obs} = C K_1K_2K_3(\text{or } K_4)K_5 [\text{MnO}_2]^{n1} [\text{PDS}]^{n2} \quad (8)$$

389 where $[\text{organics}]_0$ is the initial concentration of the organic substrate, $[\text{MnO}_2]$ is the MnO_2
390 concentration, $[\text{PDS}]$ is the total persulfate anions ($[\text{HS}_2\text{O}_8^-] + [\text{S}_2\text{O}_8^{2-}]$), C is the reaction constant, k_1
391 represents the rate of forming metastable manganese intermediate, K_2 represents the rate of forming
392 superoxide, K_3 represents the rate of direct oxidation of superoxide for $^1\text{O}_2$ generation, K_4 represents
393 the rate of recombination of superoxide for $^1\text{O}_2$ generation, and K_5 represents the rate of organics
394 degradation by $^1\text{O}_2$.

395 **Environmental Implication**

396 In summary, we performed a comprehensive study to investigate PDS activation on manganese
397 oxide families. Among the Mn_xO_y with distinct crystal orientations and redox states, α - and β - MnO_2
398 exhibited the best catalytic performance for PDS decomposition and organic degradation. Singlet
399 oxygen was unveiled be to the primary reactive oxygen species, which exhibited a specific selectivity
400 to the organic substances due to the mild redox potential and unique oxidation pathway. The evolution
401 of $^1\text{O}_2$ at neutral pH was evidenced by multiple approaches such as chemical probes, quenching agents,
402 EPR capture, and solvent exchange. In the proposed mechanism, $^1\text{O}_2$ was generated from a direct
403 oxidation or recombination of superoxide ion radicals, and the formation of metastable manganese
404 intermediates was identified as the key step. The hypothesis was supported by the altered manganese
405 states after reaction and the kinetic analysis. The understanding of PDS activation by manganese
406 oxides will be of scientific significance in manganese based ISCO and practical wastewater
407 remediation. Firstly, the study enables the first mechanistic insights into PDS activation on manganese
408 oxides. The catalytically active phases of MnO_2 were identified, which may contribute to the
409 understanding of ISCO by manganese based minerals or sediment with the low-cost and chemically

stable PDS for practical remediation of contaminated soils and underground water. Secondly, apart from the classic sulfate radical based AOPs (SR-AOPs), a novel oxidative system of $^1\text{O}_2$ was identified in MnO_2 /PDS system, which can be utilized for selective removal of trace organic contaminants in complicated wastewater matrix.

ASSOCIATED CONTENT

Supporting Information

The details of preparation and characterization of manganese oxides. The methods of HPLC, EPR detection, and determination of PDS concentration. Analysis of XRD patterns. The methods of LC-MS. Results of phenol removal by manganese oxides alone and Mn leaching. The phenol degradation rates by different manganese oxides. Crystal structures of Mn_2O_3 and Mn_3O_4 . TEM and N_2 adsorption/desorption results. The degradation rates of different organics. Results of quenching effect. The first order kinetic of FFA decay. PDS decomposition by $\beta\text{-MnO}_2$, phenol, and $\beta\text{-MnO}_2$ /phenol. EPR results by DMPO. The phenol removal by PDS alone upon different pH values. XPS spectrum results. FTIR and Raman results. The kinetic model of overall reactions.

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Notes

The authors declare no competing financial interest.

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References

1. Anipsitakis, G. P.; Dionysiou, D. D.; Gonzalez, M. A. Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions. *Environ. Sci. Technol.* **2006**, *40*, 1000-1007.
2. Anipsitakis, G. P.; Dionysiou, D. D. Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol.* **2004**, *38*, 3705-3712.
3. Anipsitakis, G. P.; Dionysiou, D. D. Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. *Environ. Sci. Technol.* **2003**, *37*, 4790-4797.
4. Zhang, T.; Chen, Y.; Wang, Y.; Le Roux, J.; Yang, Y.; Croué, J.-P. Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation. *Environ. Sci. Technol.* **2014**, *48*, 5868-5875.
5. Fang, G. D.; Dionysiou, D. D.; Al-Abed, S. R.; Zhou, D.-M. Superoxide radical driving the activation of persulfate by magnetite nanoparticles: implications for the degradation of PCBs. *Appl. Catal., B* **2013**, *129*, 325-332.

- 452 6. Fang, G.; Wu, W.; Liu, C.; Dionysiou, D. D.; Deng, Y.; Zhou, D. Activation of persulfate with
453 vanadium species for PCBs degradation: A mechanistic study. *Appl. Catal., B* **2017**, *202*, 1-11.
- 454 7. Lin, K.; Liu, W.; Gan, J. Oxidative removal of bisphenol A by manganese dioxide: efficacy,
455 products, and pathways. *Environ. Sci. Technol.* **2009**, *43*, 3860-3864.
- 456 8. Chen, W. R.; Ding, Y.; Johnston, C. T.; Teppen, B. J.; Boyd, S. A.; Li, H. Reaction of lincosamide
457 antibiotics with manganese oxide in aqueous solution. *Environ. Sci. Technol.* **2010**, *44*, 4486-4492.
- 458 9. Furman, O.; Laine, D. F.; Blumenfeld, A.; Teel, A. L.; Shimizu, K.; Cheng, I. F.; Watts, R. J.
459 Enhanced reactivity of superoxide in water – solid matrices. *Environ. Sci. Technol.* **2009**, *43*, 1528-
460 1533.
- 461 10. Watts, R. J.; Sarasa, J.; Loge, F. J.; Teel, A. L. Oxidative and reductive pathways in manganese-
462 catalyzed Fenton's reactions. *J. Environ. Eng.* **2005**, *131*, 158-164.
- 463 11. Saputra, E.; Muhammad, S.; Sun, H.; Ang, H. M.; Tade, M.; Wang, S. Different crystallographic
464 one-dimensional MnO₂ nanomaterials and their superior performance in catalytic phenol degradation.
465 *Environ. Sci. Technol.* **2013**, *47*, 5882-5887.
- 466 12. Wang, Y.; Indrawirawan, S.; Duan, X.; Sun, H.; Ang, H. M.; Tade, M. O.; Wang, S. New insights
467 into heterogeneous generation and evolution processes of sulfate radicals for phenol degradation over
468 one-dimensional α -MnO₂ nanostructures. *Chem. Eng. J.* **2015**, *266*, 12-20.
- 469 13. Liu, H.; Bruton, T. A.; Li, W.; Buren, J. V.; Prasse, C.; Doyle, F. M.; Sedlak, D. L. Oxidation of
470 benzene by persulfate in the presence of Fe (III) - and Mn (IV) - containing oxides: stoichiometric
471 efficiency and transformation products. *Environ. Sci. Technol.* **2016**, *50*, 890-898.
- 472 14. Liu, H.; Bruton, T. A.; Doyle, F. M.; Sedlak, D. L. In situ chemical oxidation of contaminated

473 groundwater by persulfate: decomposition by Fe (III) - and Mn (IV) - containing oxides and aquifer
 474 materials. *Environ. Sci. Technol.* **2014**, 48, 10330-10336.

475 15. Wang, L.; Jiang, J.; Pang, S.-Y.; Zhou, Y.; Li, J.; Sun, S.; Gao, Y.; Jiang, C. Oxidation of bisphenol
 476 A by nonradical activation of peroxymonosulfate in the presence of amorphous manganese dioxide.
 477 *Chem. Eng. J.* **2018**, 352, 1004-1013.

478 16. Tian, N.; Tian, X.; Nie, Y.; Yang, C.; Zhou, Z.; Li, Y. Biogenic manganese oxide: an efficient
 479 peroxymonosulfate activation catalyst for tetracycline and phenol degradation in water. *Chem. Eng. J.*
 480 **2018**, 352, 469-476.

481 17. Duan, X.; Sun, H.; Shao, Z.; Wang, S. Nonradical reactions in environmental remediation
 482 processes: uncertainty and challenges. *Appl. Catal., B* **2017**, 224, 973-982.

483 18. Wang, X.; Li, Y. Selected-control hydrothermal synthesis of α - and β -MnO₂ single crystal
 484 nanowires. *J. Am. Chem. Soc.* **2002**, 124, 2880-2881.

485 19. Wang, X.; Li, Y. Synthesis and formation mechanism of manganese dioxide nanowires/nanorods.
 486 *Chem.-Eur. J.* **2003**, 9 (1), 300-306.

487 20. Saputra, E.; Muhammad, S.; Sun, H.; Ang, H.-M.; Tadé, M. O.; Wang, S. Manganese oxides at
 488 different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation
 489 in aqueous solutions. *Appl. Catal., B* **2013**, 142, 729-735.

490 21. Lee, H.; Lee, H.-J.; Jeong, J.; Lee, J.; Park, N.-B.; Lee, C. Activation of persulfates by carbon
 491 nanotubes: Oxidation of organic compounds by nonradical mechanism. *Chem. Eng. J.* **2015**, 266, 28-
 492 33.

493 22. Han, X.; Zhang, T.; Du, J.; Cheng, F.; Chen, J. Porous calcium–manganese oxide microspheres

- 494 for electrocatalytic oxygen reduction with high activity. *Chem. Sci.* **2013**, *4*, 368-376.
- 495 23. Kim, C.; Ahn, J.-Y.; Kim, T. Y.; Shin, W. S.; Hwang, I. Activation of persulfate by nanosized zero-
496 valent iron (NZVI): Mechanisms and transformation products of NZVI. *Environ. Sci. Technol.* **2018**,
497 *52*, 3625-3633.
- 498 24. Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. Rate constants and mechanism of reaction
499 of sulfate radical anion with aromatic compounds. *J. Am. Chem. Soc.* **1977**, *99*, 163-164.
- 500 25. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for
501 reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^-$ in aqueous solution.
502 *J. Phys. Chem. Ref. Data* **1988**, *17*, 513-886.
- 503 26. Yun, E. T.; Moon, G. H.; Lee, H.; Jeon, T. H.; Lee, C.; Choi, W.; Lee, J. Oxidation of organic
504 pollutants by peroxymonosulfate activated with low-temperature-modified nanodiamonds:
505 Understanding the reaction kinetics and mechanism. *Appl. Catal., B* **2018**, *237*, 432-441.
- 506 27. Bokare, A. D.; Choi, W. Singlet-oxygen generation in alkaline periodate solution. *Environ. Sci.*
507 *Technol.* **2015**, *49*, 14392-14400.
- 508 28. Lee, J.; Hong, S.; Mackeyev, Y.; Lee, C.; Chung, E.; Wilson, L. J.; Kim, J. H.; Alvarez, P. J.
509 Photosensitized oxidation of emerging organic pollutants by tetrakis C_{60} aminofullerene-derivatized
510 silica under visible light irradiation. *Environ. Sci. Technol.* **2011**, *45*, 10598-10604.
- 511 29. Hu, P.; Su, H.; Chen, Z.; Yu, C.; Li, Q.; Zhou, B.; Alvarez, P. J.; Long, M. Selective degradation
512 of organic pollutants using an efficient metal-free catalyst derived from carbonized polypyrrole via
513 peroxymonosulfate activation. *Environ. Sci. Technol.* **2017**, *51*, 11288-11296.
- 514 30. Zhou, Y.; Jiang, J.; Gao, Y.; Ma, J.; Pang, S. Y.; Li, J.; Lu, X. T.; Yuan, L. P. Activation of

515 peroxymonosulfate by benzoquinone: a novel nonradical oxidation process. *Environ. Sci. Technol.*
 516 **2015**, *49*, 12941-12950.

517 31. Tratnyek, P. G.; Hoigne, J. Oxidation of substituted phenols in the environment: a QSAR analysis
 518 of rate constants for reaction with singlet oxygen. *Environ. Sci. Technol.* **1991**, *25*, 1596-1604.

519 32. Neta, P.; Huie, R. E.; Ross, A. B. Rate constants for reactions of inorganic radicals in aqueous
 520 solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027-1284.

521 33. Gsponer, H. E.; Previtali, C. M.; García, N. A. Kinetics of the photosensitized oxidation of
 522 polychlorophenols in alkaline aqueous solution. *Toxicol Environ. Chem.* **1987**, *16*, 23-37.

523 34. Haag, W. R.; Hoigne, J. Singlet oxygen in surface waters. 3. Photochemical formation and steady-
 524 state concentrations in various types of waters. *Environ. Sci. Technol.* **1986**, *20*, 341-348.

525 35. Mostafa, S. N.; Rosario-Ortiz, F. L. Singlet oxygen formation from wastewater organic matter.
 526 *Environ. Sci. Technol.* **2013**, *47*, 8179-8186.

527 36. Scully Jr, F. E.; Hoigné, J. Rate constants for reactions of singlet oxygen with phenols and other
 528 compounds in water. *Chemosphere*, **1987**, *16*, 681-694.

529 37. Huie, R. E.; Clifton, C. L. Temperature dependence of the rate constants for reactions of the sulfate
 530 radical, SO_4^- , with anions. *J. Phys. Chem.* **1990**, *94*, 8561-8567.

531 38. Minero, C.; Mariella, G.; Maurino, V.; Vione, D.; Pelizzetti, E. Photocatalytic transformation of
 532 organic compounds in the presence of inorganic ions. 2. competitive reactions of phenol and alcohols
 533 on a titanium dioxide– fluoride system. *Langmuir* **2000**, *16*, 8964-8972.

534 39. Kim, H.; Kim, W.; Mackeyev, Y.; Lee, G. S.; Kim, H. J.; Tachikawa, T.; Hong, S.; Lee, S.; Kim,
 535 J.; Wilson, L. J. Selective oxidative degradation of organic pollutants by singlet oxygen-mediated

536 photosensitization: tin porphyrin versus C₆₀ aminofullerene systems. *Environ. Sci. Technol.* **2012**, *46*,
537 9606-9613.

538 40. Thompson, R. C. Catalytic decomposition of peroxymonosulfate in aqueous perchloric acid by
539 the dual catalysts silver (1⁺) and peroxydisulfate (2⁻) and by cobalt (2⁺). *Inorg. Chem.* **1981**, *20*, 1005-
540 1010.

541 41. Feng, Y.; Lee, P.-H.; Wu, D.; Shih, K. Surface-bound sulfate radical-dominated degradation of 1,
542 4-dioxane by alumina-supported palladium (Pd/Al₂O₃) catalyzed peroxymonosulfate. *Water Res.* **2017**,
543 *120*, 12-21.

544 42. Yang, Y.; Banerjee, G.; Brudvig, G. W.; Kim, J.-H.; Pignatello, J. J. Oxidation of organic
545 compounds in water by unactivated peroxymonosulfate. *Environ. Sci. Technol.* **2018**, *52*, 5911-5919.

546 43. Yun, E. T.; Lee, J. H.; Kim, J.; Park, H. D.; Lee, J. Identifying the nonradical mechanism in the
547 peroxymonosulfate activation process: Singlet oxygenation versus mediated electron transfer. *Environ.*
548 *Sci. Technol.* **2018**, *52*, 7032-7042.

549 44. Bilski, P.; Reszka, K.; Bilska, M.; Chignell, C. Oxidation of the spin trap 5, 5-dimethyl-1-pyrroline
550 N-oxide by singlet oxygen in aqueous solution. *J. Am. Chem. Soc.* **1996**, *118*, 1330-1338.

551 45. Pan, X.; Chen, J.; Wu, N.; Qi, Y.; Xu, X.; Ge, J.; Wang, X.; Li, C.; Qu, R.; Sharma, V. K.
552 Degradation of aqueous 2, 4, 4'-Trihydroxybenzophenone by persulfate activated with nitrogen doped
553 carbonaceous materials and the formation of dimer products. *Water Res.* **2018**, *143*, 176-187.

554 46. Zhao, Z.; Zhao, J.; Yang, C. Efficient removal of ciprofloxacin by peroxymonosulfate/Mn₃O₄ -
555 MnO₂ catalytic oxidation system. *Chem. Eng. J.* **2017**, *327*, 481-489.

556 47. Zhang, S.; Gutierrez, L.; Niu, X. Z.; Qi, F.; Croue, J. P. The characteristics of organic matter

influence its interfacial interactions with MnO₂ and catalytic oxidation processes. *Chemosphere* **2018**, 209, 950-959.

48. Miller, J. S. Rose bengal-sensitized photooxidation of 2-chlorophenol in water using solar simulated light. *Water Res.* **2005**, 39, 412-422.

49. Kolthoff, I.; Miller, I. The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium¹. *J. Am. Chem. Soc.* **1951**, 73, 3055-3059.

50. Furman, O. S.; Teel, A. L.; Watts, R. J. Mechanism of base activation of persulfate. *Environ. Sci. Technol.* **2010**, 44, 6423-6428.

51. Gorman, A.; Rodgers, M. Singlet molecular oxygen. *Chem. Soc. Rev.* **1981**, 10, 205-231.

52. Cheng, X.; Guo, H.; Zhang, Y.; Wu, X.; Liu, Y. Non-photochemical production of singlet oxygen via activation of persulfate by carbon nanotubes. *Water Res.* **2017**, 113, 80-88.

53. Lin, J. M.; Arakawa, H.; Yamada, M. Flow injection chemiluminescent determination of trace amounts of hydrogen peroxide in snow-water using KIO₄-K₂CO₃ system. *Anal. Chim. Acta* **1998**, 371, 171-176.

54. Eyer, P. Effects of superoxide dismutase on the autoxidation of 1, 4-hydroquinone. *Chem.-Biol. Interact.* **1991**, 80, 159-176.

55. Chan, Z. M.; Kitchaev, D. A.; Weker, J. N.; Schnedermann, C.; Lim, K.; Ceder, G.; Tumas, W.; Toney, M. F.; Nocera, D. G. Electrochemical trapping of metastable Mn³⁺ ions for activation of MnO₂ oxygen evolution catalysts. *Proc. Natl. Acad. Sci.* **2018**, 115, E5261-E5268.

56. Li, X.; Huang, X.; Xi, S.; Miao, S.; Ding, J.; Cai, W.; Liu, S.; Yang, X.; Yang, H.; Gao, J.; Wang, J.; Huang, Y.; Zhang, T.; Liu, B. Single cobalt atoms anchored on porous n-doped graphene with dual

578 reaction sites for efficient Fenton-like catalysis. *J. Am. Chem. Soc.* **2018**, *140*, 12469-12475.

579 57. Peng, X.; Guo, Y.; Yin, Q.; Wu, J.; Zhao, J.; Wang, C.; Tao, S.; Chu, W.; Wu, C.; Xie, Y. Double-
580 exchange effect in two-dimensional MnO₂ nanomaterials. *J. Am. Chem. Soc.* **2017**, *139*, 5242-5248.

581 58. Tsujimoto, Y.; Hashizume, H.; Yamazaki, M. Superoxide radical scavenging activity of phenolic
582 compounds. *Int. J. Biochem.* **1993**, *25*, 491-494.

583 59. Brame, J.; Long, M.; Li, Q.; Alvarez, P. Trading oxidation power for efficiency: differential
584 inhibition of photo-generated hydroxyl radicals versus singlet oxygen. *Water Res.* **2014**, *60*, 259-266.

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