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

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22 **ABSTRACT**

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

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43 INTRODUCTION

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

59 Manganese oxides are low in biotoxicity and rich in natural stock. As a dominated component of
60 minerals in soils or aquifer materials, manganese dioxide (MnO_2) with multivalent nature can either
61 directly oxidize contaminants^{7, 8} or catalyze hydrogen peroxide based ISCO.⁹ Chemical probes and
62 electron paramagnetic resonance (EPR) methods have confirmed that both $\text{O}_2^{\bullet-}$ and hydroperoxide
63 (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 MnO₂ can effectively activate PMS to generate SO₄^{•-} 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 MnO₂ interfaces as nonradical reactive species that can directly oxidize bisphenol-A.
70 ¹⁵ Moreover, biogenic MnO₂ could activate PMS to produce singlet oxygen (¹O₂) 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 MnO₂ 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 (SO₄^{•-} 2.5–3.1 V vs. [•]OH 2.7 V), the ¹O₂-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 ¹O₂ 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 ¹O₂ was generated and accounted for the oxidation. The pH and solvent dependence further
81 certified the dominated role of ¹O₂, especially in neutral pH solution. A detailed mechanism was first
82 proposed for PDS activation over manganese oxides to generate ¹O₂. 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.

85 MATERIALS AND METHODS

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

93 **Catalytic performance evaluation.** The degradation performance was evaluated in a batch reactor
94 with organic compounds in a buffered solution. The oxidation was initiated by adding fixed amounts
95 of catalyst and PDS at a rotation speed of 300 rpm. In evaluation of solution pH impacts, different
96 buffers were adopted with 1 mM acetate for pH 5, 1 mM borate for pH 6.5 or 8.5, and 1 mM
97 bicarbonate for pH 10. At certain time intervals, the solution was filtered through a 0.45 μm filter into
98 a HPLC vial and mixed with methanol to terminate the oxidation. Benzoic acid (BA), nitrobenzene
99 (NB), hydrobenzoic acid (HBA), bisphenol A (BPA), rhodamine B (RB), and phenol (PN) were chosen
100 as probe contaminants to evaluate the oxidation capacity of PDS/manganese-oxide systems. The
101 concentrations of the organic compounds were analyzed by an ultra-high performance liquid
102 chromatography (UHPLC, Thermo Fisher, USA) with a C18 column. An UV-vis spectrophotometer
103 (Spectronic 20 Genesys, Thermo Fisher, USA) was also used to determine Rhodamine B (RhB)
104 concentration at the wavelength of 554 nm. The detailed analysis of organic compounds is provided in
105 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.

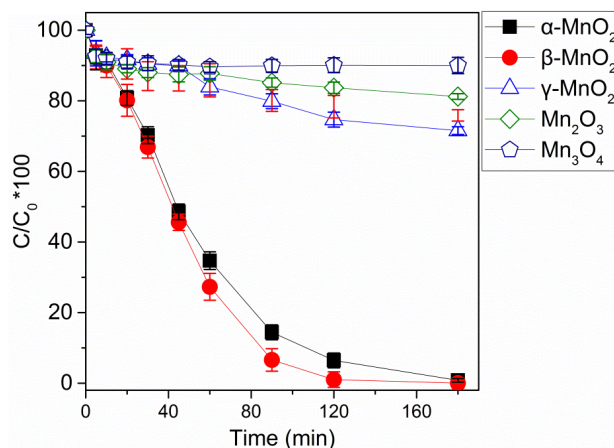
108 **Detection of ROS** The radical scavengers of methanol (MeOH, 200-1000 mM), tert-butyl alcohol
109 (TBA, 200 mM), sodium azide (NaN₃, 1 mM) and furfuryl alcohol (FFA, 0.1 - 1 mM) were added into
110 β-MnO₂/PDS system to probe the generated ROS such as free radicals and singlet oxygen.
111 Benzoquinone (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 $\beta\text{-MnO}_2$.



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

152 The reactivity of β-MnO₂/PDS system toward different organic contaminants was also investigated.
 153 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 $k_2(\text{BA}, ^\bullet\text{OH}) =$
 154 $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)²⁴, while NB was the chemical probe for [•]OH ($k_2(\text{NB}, ^\bullet\text{OH}) = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)
 155 accordingly.²⁵ In Figure 2a, BA and NB were barely oxidized (< 8%) in 180 min, indicating that both
 156 SO₄^{•-} and [•]OH were not generated in β-MnO₂/PDS. The complete oxidations of BPA, PN and RB and
 157 a moderate removal efficiency of HBA (53.7%) were observed in Figure 2a. Similar selective oxidation
 158 of organics was also observed in the nonradical pathways in previous studies.²⁶⁻²⁸

159 The ionization potential (IP) of the organic compounds has been utilized as an indicator to estimate
 160 the redox capacity of an oxidative system.²⁹ In the electron mediation mechanism, an organic
 161 compound with an IP beyond 9.0 eV (the threshold) cannot be oxidized in N-graphene/PMS system
 162 due to the relatively mild redox potential of the surface confined metastable nonradical ROS. In this
 163 work, BA and NB with IP values above the threshold were hardly decomposed (Figure 2b), whereas
 164 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).

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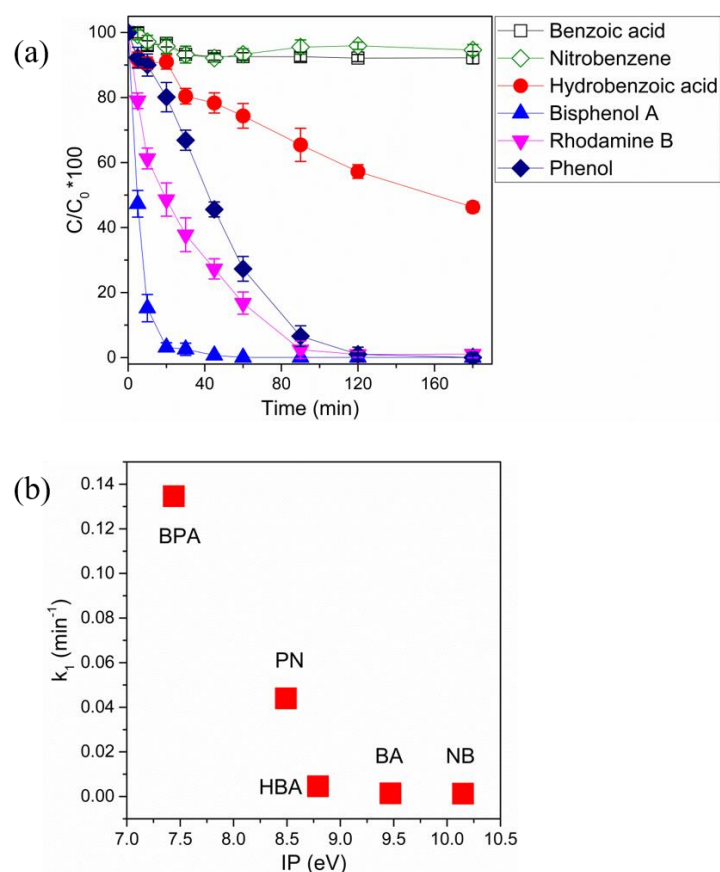
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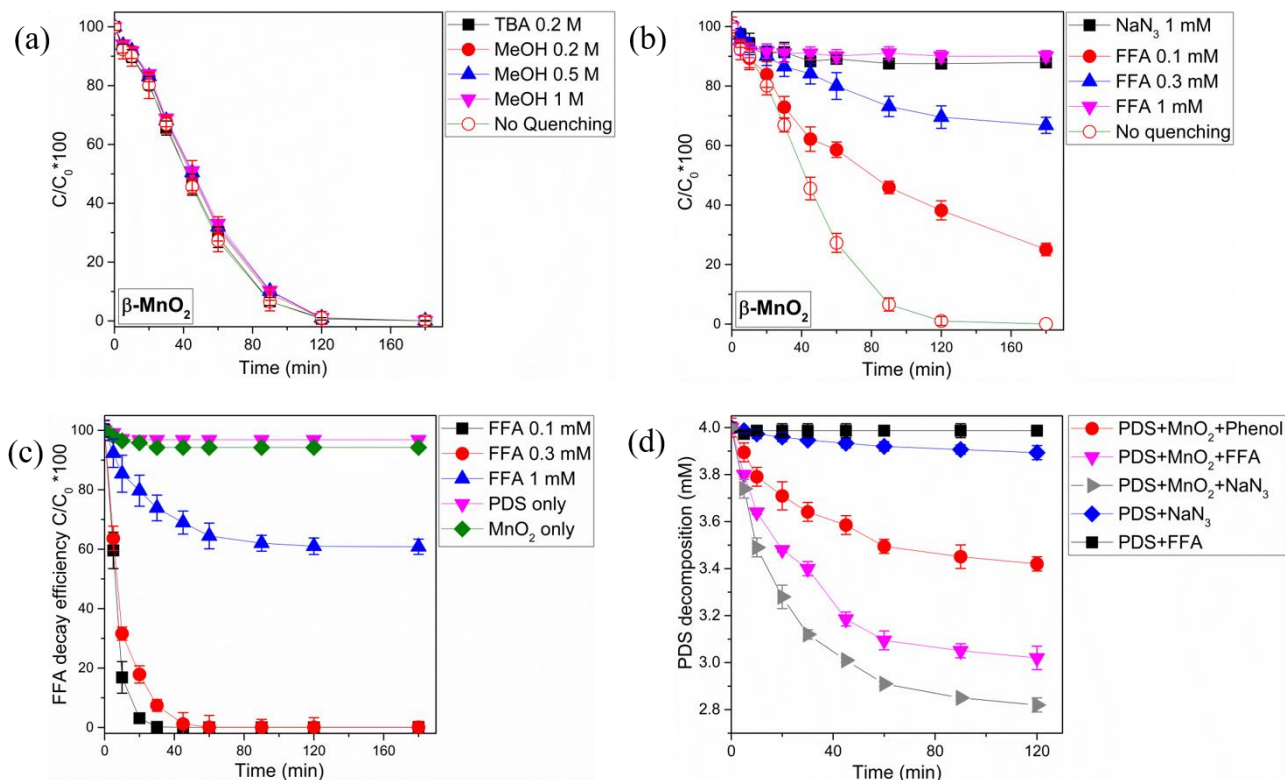
185 **Figure 2.** (a) Selective oxidation in β -MnO₂/PDS activation. [Manganese oxide]₀ = 400 mg/L, [PDS]₀
 186 = 4 mM, [organics] = 100 μ M, pH buffered around 6.5. (b) The relationship between organics
 187 degradation rates and their ionization potentials (IP).

188 Moreover, we employed azide with a moderate concentration (1 mM) to quench the oxidation by
 189 ¹O₂ ($k_2(\text{NaN}_3, ^1\text{O}_2) = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).³³ In the presence of azide ions, phenol degradation by β -
 190 MnO₂/PDS was almost suspended (Figures 3b and S8) with only 12% removal in 180 min (mostly by
 191 adsorption, Figure S2). FFA was further used as a chemical probe for ¹O₂ generation, which manifested
 192 a higher second order rate of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ^{34, 35} than the targeted phenolic compound ($2.0\text{-}3.0 \times$
 193 $10^6 \text{ M}^{-1} \text{ s}^{-1}$)^{31, 36} with ¹O₂. A minor amount of FFA (0.1 mM, equal to phenol concentration), caused a
 194 noticeable decline in phenol removal rate from 0.0441 to 0.0093 min⁻¹ (Figures 3b and S8). When FFA
 195 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. $k_2(\text{NaN}_3, \text{SO}_4^{\cdot-})$
199 $= 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2(\text{FFA}, \cdot\text{OH}) = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),^{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 α -
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 $\ln([\text{FFA}]_t/[\text{FFA}]_0) = -k_{obs} t$, 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}



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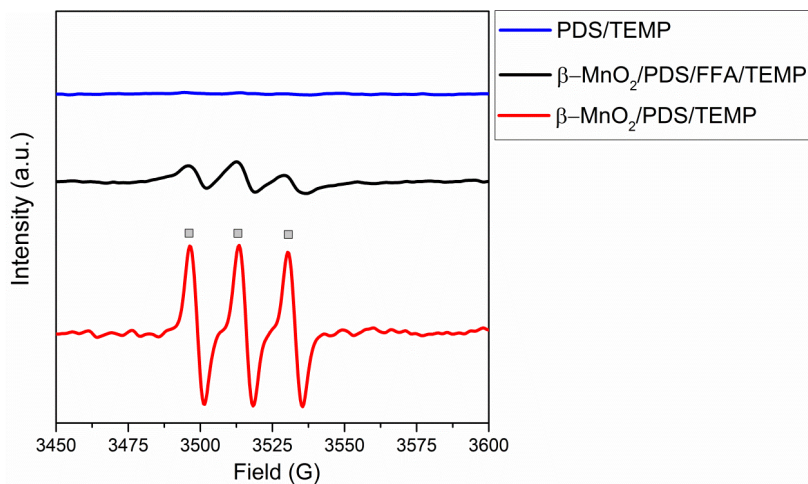
219 **Figure 3.** The determination of ROS species for oxidation in $\beta\text{-MnO}_2$ /PDS. (a) the quenching effect
220 of free radicals on phenol oxidation degradation (TBA 200 mM, MeOH 200-1000 mM), (b) the
221 quenching effect of singlet oxygen on phenol oxidative degradation (NaN_3 1 mM, FFA 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

230 (Figure 3d), suggesting that the organic pollutants can rapidly scavenge the generated $^1\text{O}_2$ and
231 accelerate PDS decomposition. This is also different from the surface radical-based oxidation where
232 the persulfate depletion would be restrained with more participation of organics and the competitive
233 reaction with the surface active sites between organics and oxyanion.⁴¹ Figure 3d depicts that azide
234 and FFA yielded a higher efficiency than phenol for catalytic PDS decomposition with $\beta\text{-MnO}_2$,
235 possibly due to their higher reaction rates towards $^1\text{O}_2$. A previous study indicated that azide or FFA
236 is a reducing agent which may react with PMS and cannot verify the quenching effect toward $^1\text{O}_2$.⁴²
237 ⁴³ Figure 3d shows that PDS cannot be directly decomposed by azide or FFA (1 mM), suggesting that
238 the reactivity of PDS towards the quenching agents was low. Thus, the inhibition of phenol
239 degradation originated from $^1\text{O}_2$ quenching by azide or FFA.

240 EPR technique was applied to *in situ* capture the ROS generated from $\beta\text{-MnO}_2$ /PDS system using
241 DMPO as a spin trapping agent. Not surprisingly, neither DMPO-OH nor DMPO-SO₄ was discovered.
242 Instead, the characteristic peaks (Figure S12) with the hyperfine splittings of 1:2:1:2:1:2:1, were
243 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
244 product from DMPO direct oxidation by $^1\text{O}_2$.^{44,45} Besides, TEMP was a specific spin trapping agent
245 for identification of $^1\text{O}_2$. The intense three-line signals (1:1:1) of TEMPN adducts (Figure 4, $\alpha = 16.9$
246 G) by $^1\text{O}_2$ oxidation was observed, which was another solid evidence of $^1\text{O}_2$ generation. The addition
247 of FFA (1 mM) would decrease the intensity of TEMPN signals (Figure 4) due to the consumption of
248 $^1\text{O}_2$. Moreover, a methylene blue (MB)/irradiation system was employed as a reference to identify the
249 $^1\text{O}_2$ generation. The intermediate distributions during BPA oxidation was analyzed for both
250 MnO_2 /PDS and MB/irradiation. The LC-MS results in Figure S13 demonstrated that the intermediate

251 products in the MnO₂/PDS system were almost the same as the singlet oxygen based system
252 (MB/irradiation), indicating that the ¹O₂ was produced and serves as the primary ROS in MnO₂/PDS
253 system. The details of intermediate products are listed in Table S2.



254
255 **Figure 4.** EPR spectra of singlet oxygen detection in the presence of TEMP. [β -MnO₂]₀ = 400 mg/L,
256 [PDS]₀ = 4 mM, [FFA]₀ = 100 μ M, [TEMP]₀ = 25 mM, pH buffered around 6.5, gray square: TMPO
257 adducts.

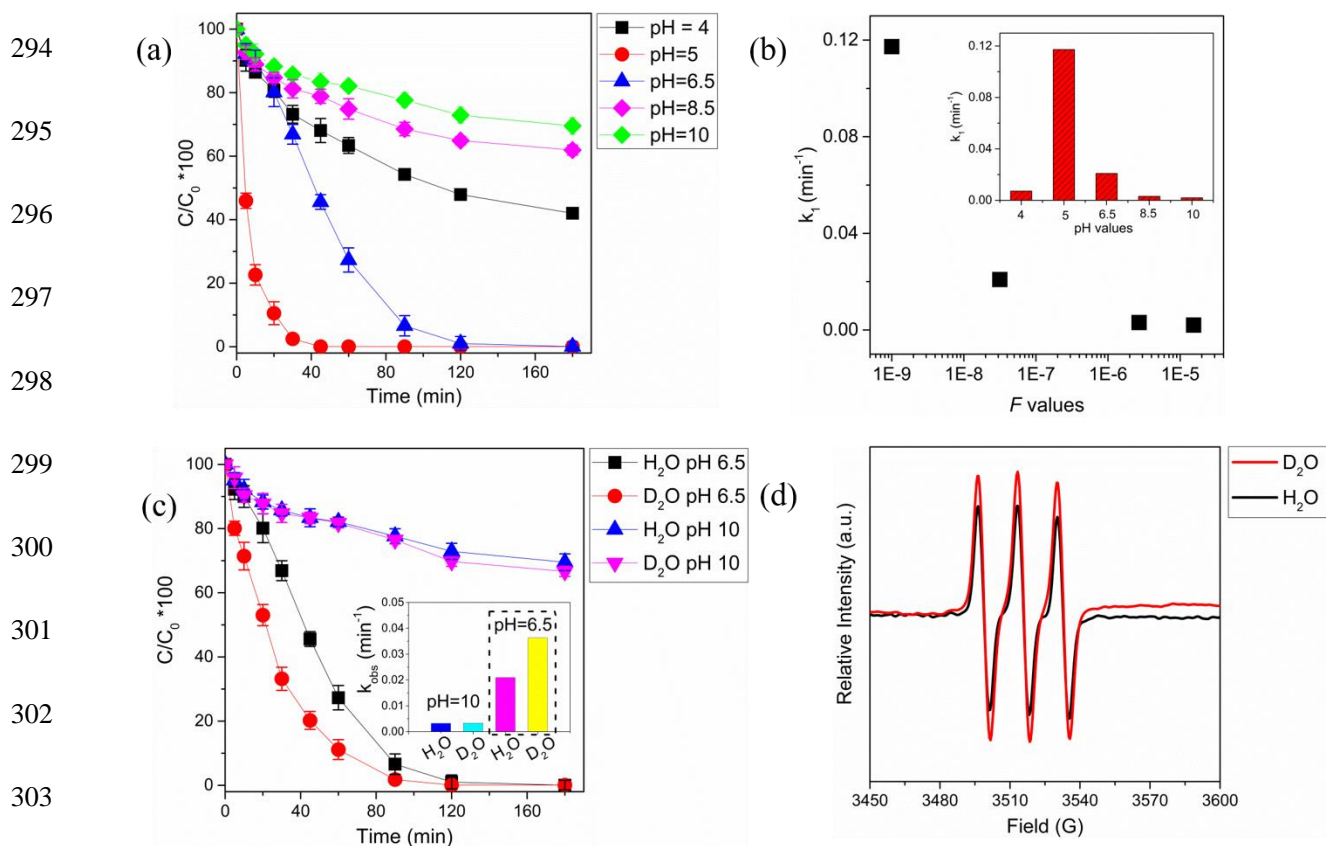
258 **Mechanism of singlet oxygen evolution.** The impacts of solution pH and reaction substrates were
259 investigated on ¹O₂ generation from β -MnO₂/PDS. In Figure 5a, phenol degradation rates were
260 significantly improved by decreasing the buffered pH from 10 to 5. At pHs 5 and 6.5, complete phenol
261 oxidation can be achieved in 45 and 120 min, respectively, whereas only 38.1% and 31.5% of organic
262 removals were yielded at pHs 8.5 and 10 in 180 min, respectively. Intriguingly, only 57.9% of phenol
263 was oxidized at a lower pH of 4. At the extreme low pH region (≤ 4), significant Mn dissolution (Figure
264 S2) was experienced and the leached Mn²⁺ is inactive for PDS activation. Moreover, surface structure
265 of MnO₂ was destroyed, which would decrease the catalytic performance. Since the zero potential
266 point of crystal MnO₂ was around 3.5,^{46, 47} a higher pH (8.5 - 10) would cause phenomenal

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

275 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})
276 to estimate the impact of solution pH. A positive linearity between the F values and peroxide activation
277 indicates that the reaction is pH-dependent and dominated by the persulfate ionization or base
278 activation.³⁰ In this study, the nonlinear correlation between phenol degradation rate and F (Figure 5b)
279 suggested that the reaction under neutral condition followed a heterogeneously catalytic process,
280 whereas surface electrostatic charge may gradually impede the reaction under extreme pH conditions.
281 ⁴⁹ Nevertheless, base activation of PDS (Figure S16) may take place at high pH to generate a minor
282 amount of hydroxyl radicals. However, the radical was less effective than the ¹O₂-based oxidation
283 because the electron-rich phenolic compounds were more susceptible to ¹O₂.^{31, 50}

284 Additionally, different solvents were applied to confirm the existence of ¹O₂. The lifetime of ¹O₂ in
285 D₂O (20 - 32 μs) was more than 10-fold longer than in H₂O (2 μs),⁵¹ which can kinetically accelerate
286 the oxidation in ¹O₂ based systems.^{34, 42} In this study, when the solvent H₂O was completely replaced
287 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.



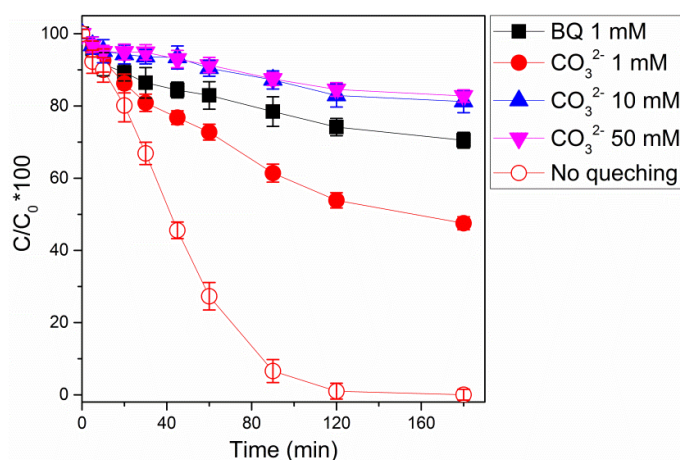
305 **Figure 5.** The insightful identification of singlet oxygen generation in $\beta\text{-MnO}_2/\text{PDS}$. (a) Phenol
 306 oxidation degradation in $\beta\text{-MnO}_2/\text{PDS}$ under different buffered pH conditions, (b) the relation of F
 307 values and degradation rates at different pH values,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

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

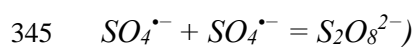
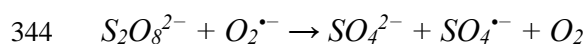
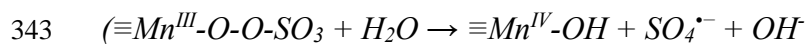
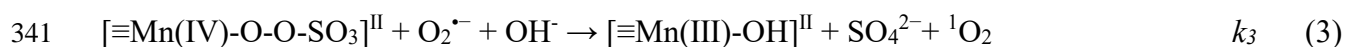
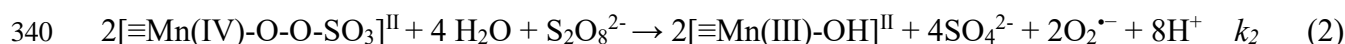
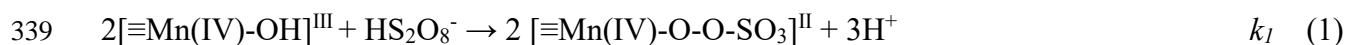
312 Typically, singlet oxygen can be generated from several pathways such as the reaction between
313 persulfate (PMS/PDS) and ketonic groups on carbonaceous materials,⁵² photo-excitation of oxygen
314 molecules (in a triplet ground state) via an energy-transfer process.²⁸ In this study, the $^1\text{O}_2$ 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

368 intermediates (reaction 1) was a catalytic process, primarily relying on MnO₂, while the final step in
 369 evolution of ¹O₂ may be determined by the existence form of persulfate anions. Based on PDS
 370 decomposition with manganese dioxide surface with/without phenol, the reaction rates of Eqs 1 and 2
 371 were confirmed in Text S7. We used the Langmuir–Hinshelwood model (Text S9) to identify the role
 372 of the metastable manganese intermediates. The well fitted Langmuir–Hinshelwood model curve of
 373 PDS ($R^2 = 0.942$, Figure S22) indicated that the surface-mediated reaction of PDS on the MnO₂ was
 374 enhanced by increasing the PDS concentration. The enhanced surface-mediated reaction by PDS was
 375 resulted from the formation of metastable manganese-PDS intermediates, which further led to ¹O₂
 376 generation. Furthermore, the reaction rate from O₂^{•-} to ¹O₂ in Eq 3 was calculated as $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
 377 (K_3), which is three-magnitude higher than the reaction rate between superoxide and phenol (5.8×10^2
 378 $\text{M}^{-1} \text{ s}^{-1}$).⁵⁸ This suggested that generated O₂^{•-} in this system was primarily consumed for ¹O₂ generation
 379 rather than direct contributing to phenol degradation. Moreover, based the singlet oxygen-mediated
 380 degradation of FFA, we can calculate the amount of generated ¹O₂ by the equation of $[\text{}^1\text{O}_2] = k_{obs} /$
 381 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
 382 higher than the amount in the typical ¹O₂-based system of Rose Bengal/irradiation (FFA 0.27 mM,
 383 $0.05 \times 10^{-11} \text{ M}$).⁵⁹

384 The simplified kinetic models were proposed as follows:

$$385 \quad -\frac{d[\text{organic}]}{dt} = k [\text{organic}]_0 \quad (6)$$

$$386 \quad \ln \left(\frac{[\text{organics}]_t}{[\text{organics}]_0} \right) = -K_{1,obs} t = -C k_1 K_2 K_3 (\text{or } K_4) K_5 [\text{MnO}_2]^{n1} [\text{PDS}]^{n2} t \quad (7)$$

387 For apparent first-order rate constant,

$$388 \quad K_{obs} = C K_1 K_2 K_3 (\text{or } K_4) K_5 [\text{MnO}_2]^{n1} [\text{PDS}]^{n2} \quad (8)$$

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 to be 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

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

414

415 **ASSOCIATED CONTENT**

416 **Supporting Information**

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

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431 **Notes**

432 The authors declare no competing financial interest.

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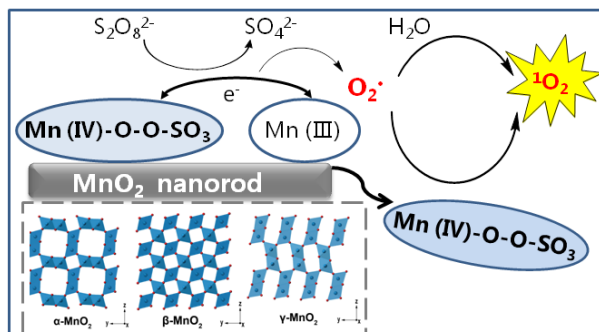
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