

Treatment of Coking Wastewater by α -MnO₂/Peroxymonosulfate Process via Direct Electron Transfer Mechanism

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Text S1. Details of synthesis procedures of α -MnO₂

KMnO₄ (3.88 g) and MnSO₄ (1.690 g) were dissolved in 40 ml DI water, respectively. These two solutions were mixed, and then transferred to a Teflon-lined autoclave and heated at 160 °C for 12 hours. The resulting product was washed with DI water several times and then dried in air at 60 °C overnight.

Text S2. Identification of dominated ROS.

To identify the dominated ROS, quenching studies by MeOH, TBA, FFA and CO₃²⁻ were carried out in parallel assays of phenol removal. Furthermore, PMSO was employed as a probe to certify the presence or absence of Fe(IV). In this assay, phenol was replaced by PMSO as the target compound. After the oxidation assays, PMSO and PMSO₂ were analyzed by this HPLC with UV detection at 230 and 215 nm, respectively. Chromatographic separations were performed on a Waters symmetry C18 column (150 mm × 4.6 mm, 5 μ m) using a binary mixture of acetonitrile and water (containing 0.1% acetic acid) as the mobile phase at a flow rate of 1 mL/min.

EPR tests were further conducted. DMPO and TEMP were employed as a spin-trapping agent for the EPR study. A solution containing 10 mM DMPO or TEMP, 2.0 mM PMS was prepared, and then a proper catalyst (if needed) was added to initiate the reaction. After 5 min of reaction, samples were taken out and analyzed on a FA200 spectrometer (196-0025, JEOL Ltd., Akishima-shi, Tokyo, Japan) at room temperature. EPR measurements were conducted using a radiation of 9.147 GHz (X band) with a modulation frequency of 100 kHz, modulation width of 0.1 mT, sweep width of 20 mT, center field of 326.0 mT, scan time of 60 s, time constant of 0.03 s, and microwave power of 5 mW.

Text S3. Details of the detection of PMS concentration.

First, 1 mL reaction solution was transferred into a 10 mL glass tube containing 1 mL DPD (12.5 mM), 1 mL phosphate buffer (250 mM, pH = 7), and 2 mL deionized water. Afterward, the mixture was vortex-mixed and left standing for 10 min, and then analyzed on a UV-Vis spectrophotometer at 510 nm.

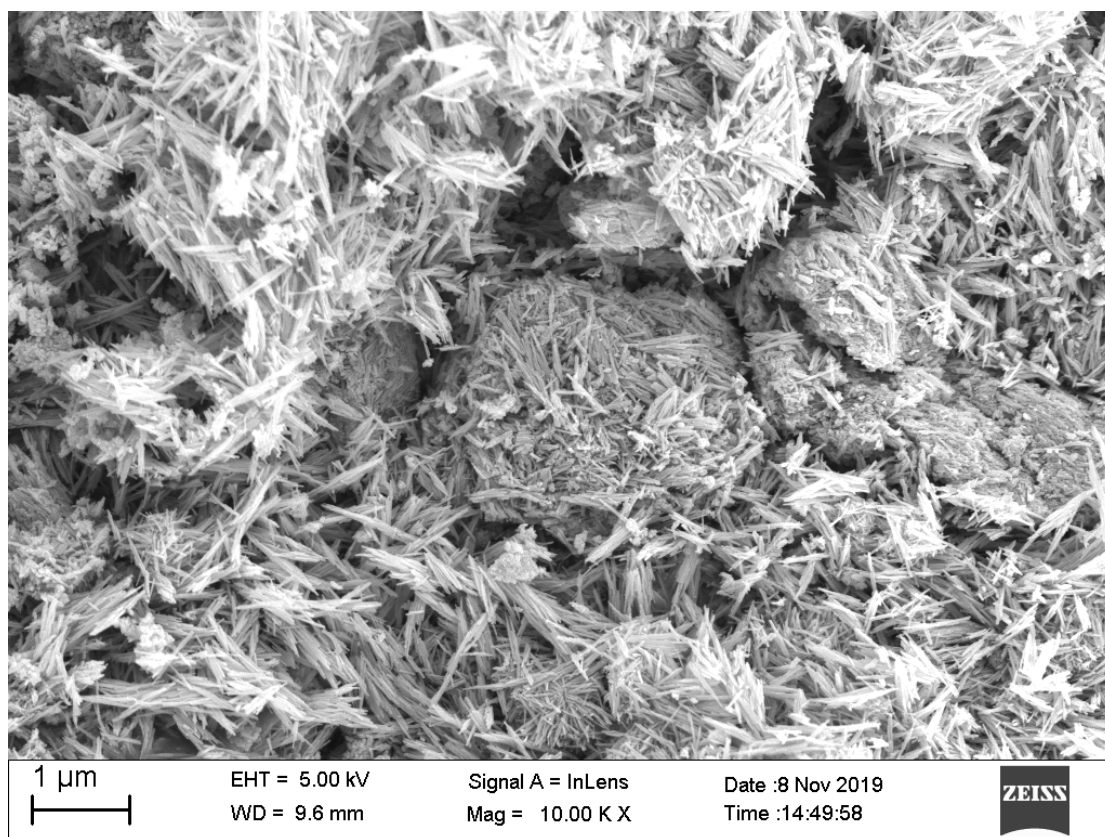


Figure S1. SEM image of α -MnO₂.

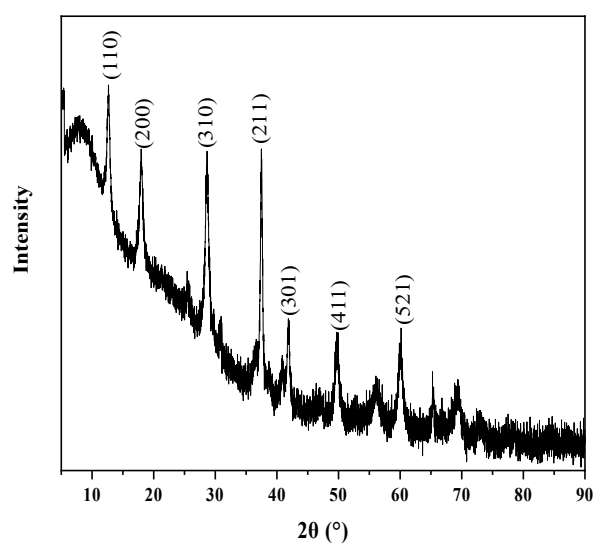


Figure S2. XRD pattern of α -MnO₂.

Peaks of crystal face (110), (200), (310), (211), (301), (411) and (521) were found in the XRD pattern, suggesting the successful synthesis of α -MnO₂ (JCPDS 29-1020) [1].

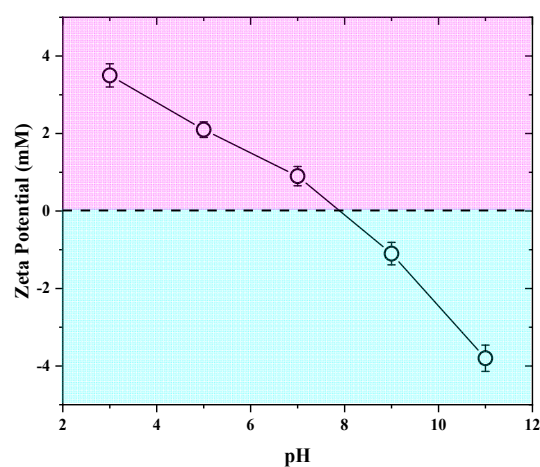


Figure S3. Zeta potential in the pH range from 3.0 to 11.0.

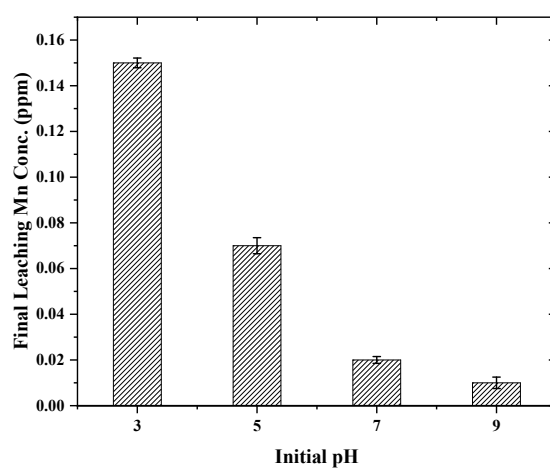


Figure S4. Leaching of Mn in pH window of 3.0 to 9.0. Reaction conditions: $[\alpha\text{-MnO}_2]_0 = 0.2$ g/L, $[\text{PMS}]_0 = 1.5$ mM, $[\text{phenol}]_0 = 20$ mg/L, $\text{pH}_0 = 3.0\text{-}9.0$, Temperature = 30 °C.

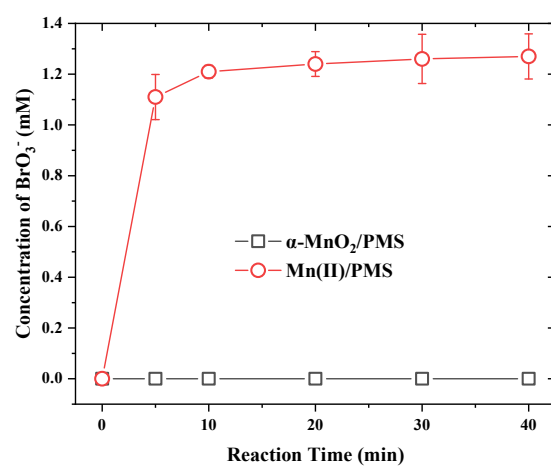


Figure S5. Formation of BrO_3^- in the presence of Br⁻. Reaction conditions: $[\alpha\text{-MnO}_2]_0 = 0.2$ g/L, $[\text{Mn(II)}]_0 = 1.5$ mM, $[\text{PMS}]_0 = 1.5$ mM, $[\text{phenol}]_0 = 20$ mg/L, $[\text{Br}^-]_0 = 1.5$ mM, $\text{pH}_0 = 7.0$, Temperature = 30 °C.

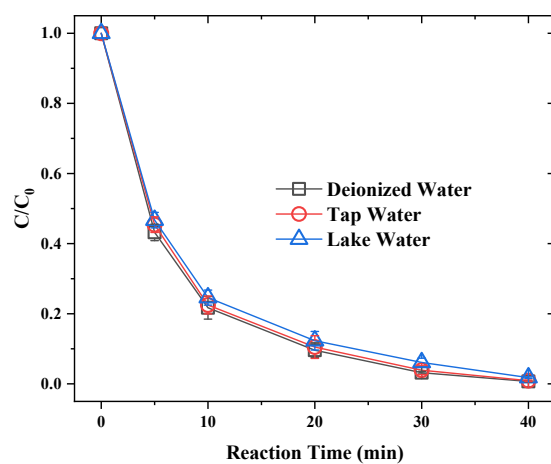


Figure S6. Removal of phenol by α -MnO₂/PMS system in deionized water, tap water or lake water. Reaction conditions: $[\alpha\text{-MnO}_2]_0 = 0.2$ g/L, $[\text{PMS}]_0 = 1.5$ mM, $[\text{phenol}]_0 = 20$ mg/L, $\text{pH}_0 = 7.0$, Temperature = 30 °C.

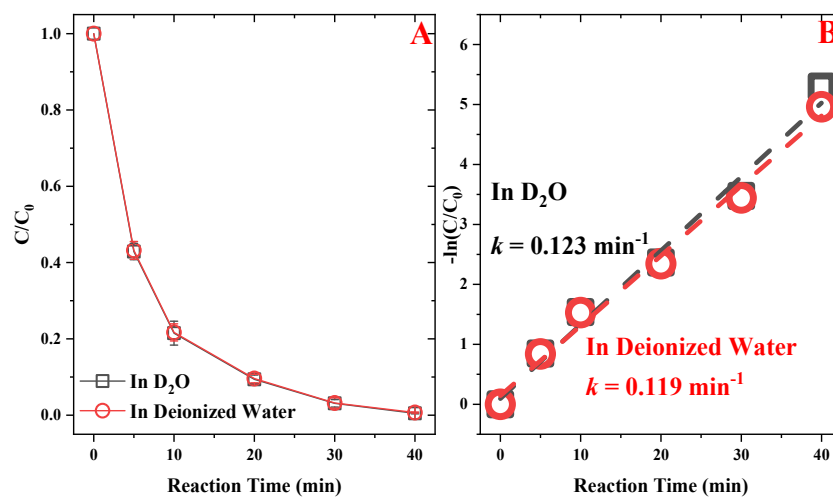


Figure S7. Phenol removal in D₂O and deionized water (A) and first-order kinetic model fitting results of the phenol removal (B). Reaction conditions: $[\alpha\text{-MnO}_2]_0 = 0.2$ g/L, $[\text{PMS}]_0 = 1.5$ mM, $[\text{phenol}]_0 = 20$ mg/L, $\text{pH}_0 = 7.0$, Temperature = 30 °C.

Table S1. Box–Behnken design and results of COD removal.

Run	X ₁ : Dosage of Cat. (g/L)	X ₂ : Dosage of PMS (mM)	X ₃ : Initial pH	Y: COD Removal (%)
1	30	35	3	44.8
2	30	35	9	45.9
3	50	20	6	67.5
4	10	35	3	23.4
5	50	50	6	72.9
6	50	35	3	72.9
7	30	50	3	59.8
8	30	20	3	35.4
9	30	35	6	46.8
10	10	50	6	32.4
11	30	35	6	46.8
12	30	20	9	36.7
13	10	20	6	17.8
14	10	35	9	24.5
15	50	35	9	73.8
16	30	50	9	71.4
17	30	35	6	46.9

Table S2. Physico-chemical properties of the tap water.

Parameter	Average	Standard Deviation
pH	7.3	±0.4
Suspended Solid (mg/L)	0.98	±0.01
COD (mg/L)	1.12	±0.02
Total Phosphorus (mg/L)	6.3	±0.2
Electrical conductivity (mS/cm)	0.078	±0.011
Alkalinity (mg/L, calculated as CaCO ₃)	9.5	±0.6
NH ₄ ⁺ (mg/L)	-	-
PO ₄ ³⁻ (mg/L)	13.7	±1.7
NO ₃ ⁻ (mg/L)	16.8	±2.1
SO ₄ ²⁻ (mg/L)	4.1	±0.3
Cl ⁻ (mg/L)	6.8	±0.5

Table S3. Physico-chemical properties of the lake water.

Parameter	Average	Standard Deviation
pH	7.9	±0.2
Suspended Solid (mg/L)	10.3	±1.1
COD (mg/L)	12.1	±0.25
Total Phosphorus (mg/L)	10.9	±0.93
Electrical conductivity (mS/cm)	0.35	±0.03
Alkalinity (mg/L, calculated as CaCO ₃)	16.8	±1.2
NH ₄ ⁺ (mg/L)	1.2	±0.08
PO ₄ ³⁻ (mg/L)	23.7	±3.3
NO ₃ ⁻ (mg/L)	31.6	±3.7
SO ₄ ²⁻ (mg/L)	8.9	±1.1
Cl ⁻ (mg/L)	21.3	±2.3

Reference

- Shen, S.; Zhou, X.; Zhao, Q.; Jiang, W.; Wang, J.; He, L.; Ma, Y.; Yang, L.; Chen, Z. Understanding the nonradical activation of peroxymonosulfate by different crystallographic MnO₂: The pivotal role of Mn-III content on the surface. *J. Hazard. Mater.* **2022**, *439*, 129613.