Supplementary Material

Degradation of Phenol in Water by Manganese-Loaded Biochar Activated Peroxymonosulfate

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Text S1. Information on experimental materials

Phenol ($C_6H_6O_2$, ≥99%), citric acid monohydrate ($C_6H_8O_7$ H_2O, ≥99.5%), potassium permanganate ($KMnO_4$, ≥99.5%), manganese(II) sulfate monohydrate ($MnSO_4$ H_2O, ≥99.0%), potassium peroxymonosulfate ($KHSO_5$ $0.5KHSO_4$ $0.5K_2SO_4$, PMS, ≥42%), methanol (CH_3OH, 99.9%), tert-butanol ($C_4H_{10}O$), furfuryl alcohol ($C_5H_6O_2$, 98%), sodium fluoride (NaF), sodium chloride (NaCl, ≥99.5%), sodium hydroxide (NaOH, ≥96%), sodium bicarbonate ($NaHCO_3$), sodium dihydrogen phosphate dihydrate (NaH_2PO_4 $2H_2O$, ≥99.0%), sodium sulfate (Na_2SO_4), anhydrous calcium chloride ($CaCl_2$, ≥96%), magnesium chloride hexahydrate ($MgCl_2$ $6H_2O$, ≥99.0%), ferroferric oxide (Fe_3O_4, 99%), and calcium nitrate tetrahydrate ($Ca(NO_3)_2$ $4H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Humic acid (HA, ≥90%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, ≥97%), and 2,2,6,6-tetramethylpiperidine (TEMP, ≥95%) were purchased from Aladdin Biotechnology Co., Ltd. (China).

Text S2. Details of the characterization

The biochar pyrolysis process was carried out using a programmable temperature-controlled muffle furnace. Material dispersion was achieved using an ultrasonic cleaner (40 kHz, 100 W). The reaction stirring and temperature control were performed using a magnetic stirrer equipped with a heating function. The solution pH was adjusted and measured using a pH meter with an accuracy of ±0.01. Phenol concentration was analyzed using high-performance liquid chromatography (HPLC) equipped with a UV detector. The morphology and surface element distribution of the samples were characterized using a scanning electron microscope (SEM) equipped with an EDS probe. Crystal structure analysis was performed using an X-ray diffractometer (XRD) with a Cu-Kα radiation source (λ = 0.15406 nm), a scanning range of 5°-80°, and a scanning speed of 5° min^{-1}. Surface elemental composition and chemical valence states were analyzed using X-ray photoelectron spectroscopy (XPS) with a monochromatic Al-Kα source (hν = 1486.6 eV). Specific surface area and pore size distribution were measured using a specific surface area analyzer (BET) via N_2 adsorption at -196 ℃. Reactive oxygen species were detected using electron paramagnetic resonance (EPR) under ambient temperature and pressure conditions. Surface functional group analysis was conducted using a Fourier-transform infrared spectrometer (FTIR) equipped with an attenuated total reflection (ATR) accessory, with a wavenumber range of 4000-400 cm^{-1}.

Text S3. Heterogeneous verification of the system

When the degradation efficiency reached 50% (Fig S2), the composite was removed and PMS was replenished to verify whether the degradation reaction would continue. The experimental results showed that after the removal of BMnC, the degradation reaction almost ceased regardless of the presence of PMS, indicating that the reaction is a heterogeneous catalytic process and the presence of BMnC is indispensable for activating PMS to degrade pollutants.

Table S1:

BET specific surface area and pore characteristics of BC and BMnC.

Samples	Specific surface area (m^2 g^{-1})	Average pore size (nm)	Pore volume (cm^3 g^{-1})
BC	337.5	5.80	0.0897
BMnC	342.3	6.23	0.1215

Figure S1 :

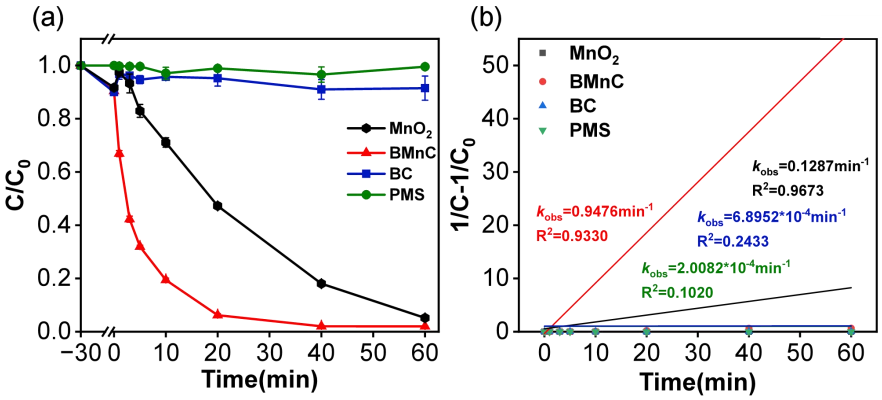

Figure S1 Degradation efficiency of phenol by different catalysts activating PMS (a); Kinetics

Figure S2 :

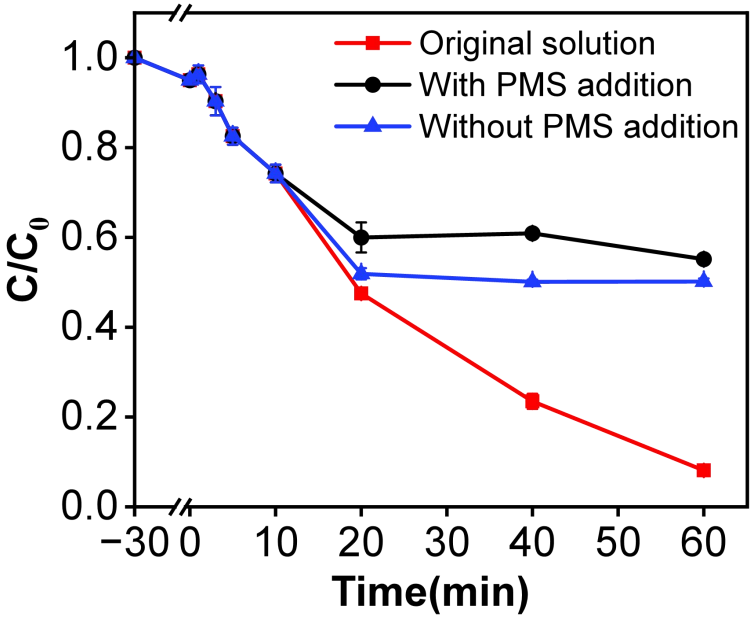

Figure S2 Heterogeneous verification of system

Equations:

$$BC\text{-}COOH+Mn^{2+}\rightarrow BC\text{-}COO\text{-}Mn^{+}+H^{+} \quad (S1)$$

$$BC\text{-}COO\text{-}Mn^{+}+O_2\rightarrow BC\text{-}COO\text{-}Mn\text{-}O\text{-}O^{-} \quad (S2)$$

$$\equiv Mn^{II}+HSO_5^{-}\rightarrow\equiv Mn^{III}+SO_4^{\bullet-}+OH^{-} \quad (S3)$$

$$\equiv Mn^{III}+HSO_5^{-}\rightarrow\equiv Mn^{IV}+SO_4^{\bullet-}+OH^{-} \quad (S4)$$

$$\equiv Mn^{IV}+HSO_5^{-}\rightarrow\equiv Mn^{III}+SO_5^{\bullet-}+H^{+} \quad (S5)$$

$$\equiv Mn^{III}+HSO_5^{-}\rightarrow\equiv Mn^{II}+SO_5^{\bullet-}+H^{+} \quad (S6)$$

$$SO_4^{\bullet-}+H_2O\rightarrow SO_4^{2-}+{}^{\bullet}OH+H^{+} \quad (S7)$$

$$SO_4^{\bullet-}+OH^{-}\rightarrow SO_4^{2-}+{}^{\bullet}OH \quad (S8)$$

$$^{\bullet}OH+H_2O_2\rightarrow HO_2^{\bullet}+H_2O \quad (S9)$$

$$HO_2^{\bullet}\rightleftharpoons O_2^{\bullet-}+H^{+} \quad (S10)$$

$$\equiv MnIII+O_2\rightarrow\equiv MnIV+O_2^{\bullet-} \quad (S11)$$

$$C_6H_5OH+SO_4^{\bullet-}/{}^{\bullet}OH\rightarrow{}^{\bullet}C_6H_4OH+HSO_4^{-}/H_2O \quad (S12)$$