

Supporting Information

Reinvestigation of the Role of Humic Acid in the Oxidation of Phenols by Permanganate

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Text S1

Separation was accomplished with an UPLC BEH C 18 column (2.1×50 mm, 1.7 μm; Waters) at 35±1 °C and a mobile phase of methanol-0.1% formic acid aqueous solution (from 30:70 to 70:30). The flow rate was 0.5 mL·min⁻¹ and the largest volume injection was 10 μL. Concentrations of phenols were determined by comparing the peak area at 270-305 nm with that of the corresponding phenol standards.

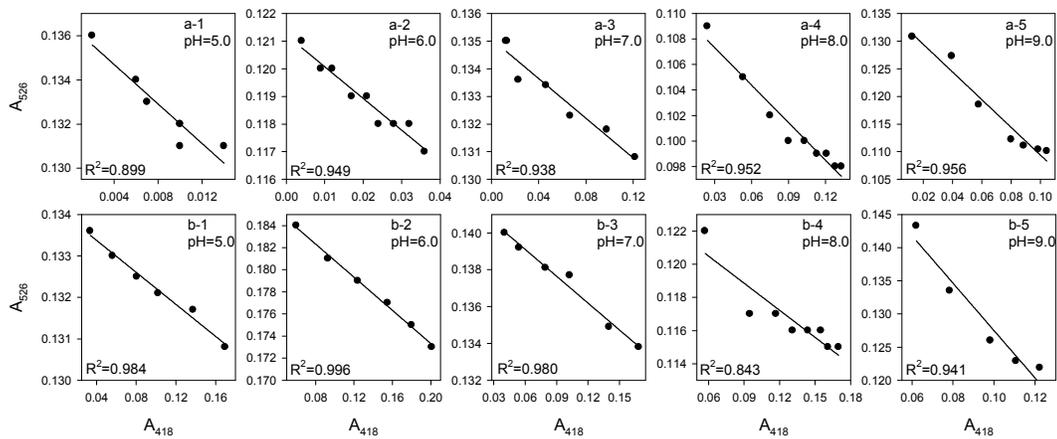


Figure S1. Absorbance at 526 nm vs. absorbance at 418 nm for the reduction of permanganate a) by phenol; b) by phenol in the presence of HA. Experimental conditions: $[\text{KMnO}_4]_0=50 \mu\text{M}$, $[\text{phenol}]_0=5 \mu\text{M}$, $T=25 \text{ }^\circ\text{C}$.

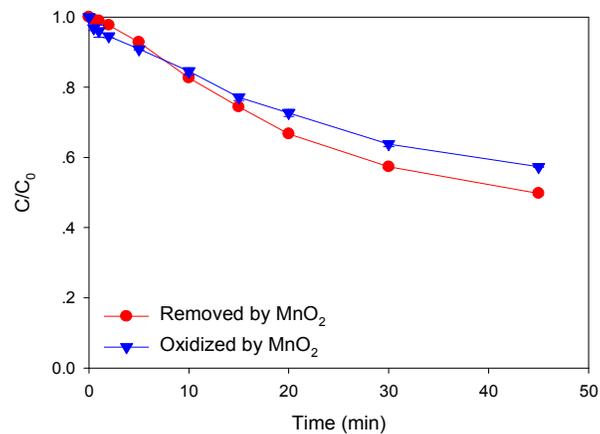


Figure S2. The role of MnO₂ in phenol removal. Reaction conditions: [phenols]₀=5 μM, [MnO₂]₀=25 μM, pH=5.0. Oxidized by MnO₂: After the sample was transferred into the beaker, excess sodium thiosulfate was added into the beaker immediately and the pH was adjusted to 2.0-3.0 by adding concentrated HCl, then the MnO₂ was reduced to Mn²⁺ and the phenol adsorbed by MnO₂ was released into the solution.

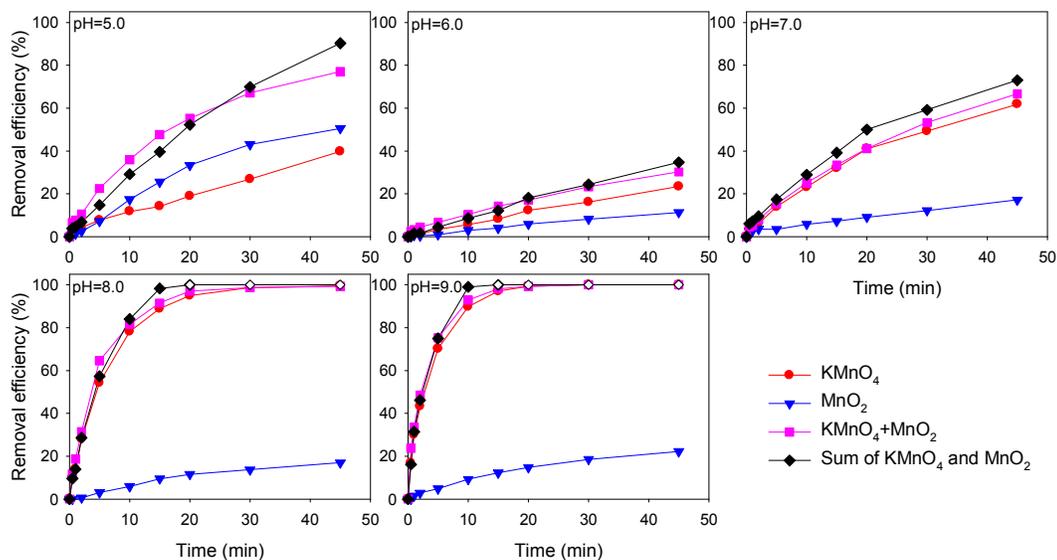


Figure S3. Removal efficiency of phenols by MnO_2 , KMnO_4 , $\text{KMnO}_4+\text{MnO}_2$ over the pH range of 5.0-9.0. The black symbols show the sum of phenol removal by KMnO_4 and MnO_2 , respectively. When the sum exceeded 100%, 100% (represented by the \blacklozenge symbols) was plotted in this figure since the maximum removal efficiency of phenol could not exceed 100%. Reaction conditions: $[\text{phenols}]_0=5 \mu\text{M}$, $[\text{MnO}_2]_0=25 \mu\text{M}$, $[\text{KMnO}_4]_0=50 \mu\text{M}$.

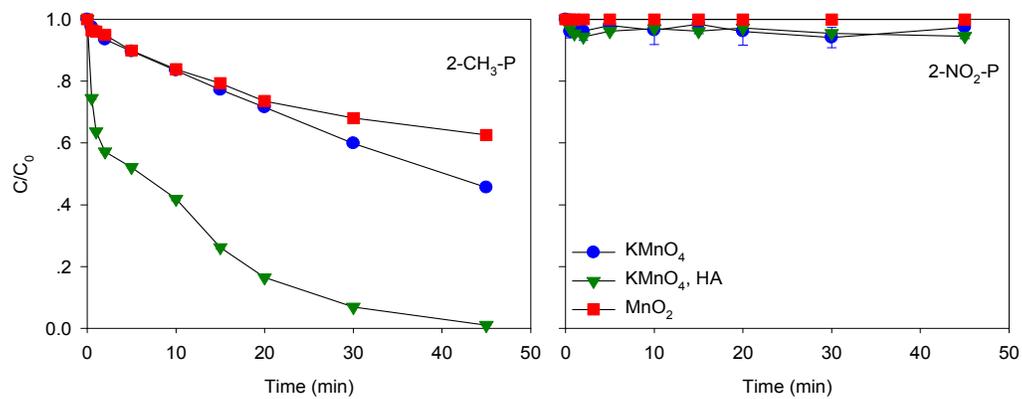


Figure S4. Oxidation of 2-CH₃-P and 2-NO₂-P by MnO₂ or KMnO₄ in the presence or absence of HA at pH 5.0. Reaction conditions: [phenols]₀=5 μM, [KMnO₄]₀=50 μM, [MnO₂]₀=25 μM, [HA]₀=1.0 mg L⁻¹ as DOC.

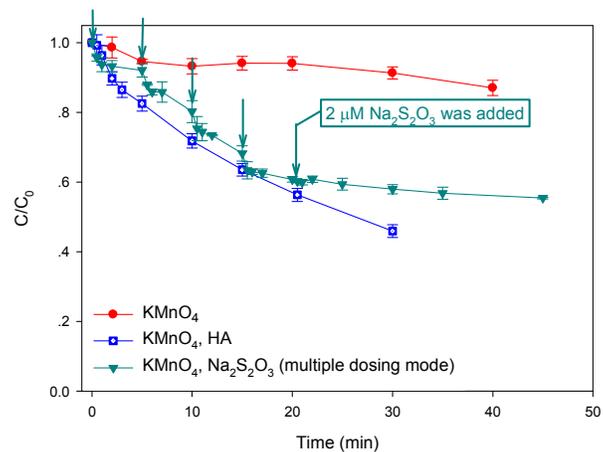


Figure S5. Influence of $\text{Na}_2\text{S}_2\text{O}_3$ applied at multiple dosing mode on 3,4-DCP oxidation by permanganate at pH 6.0. The kinetics of 3,4-DCP oxidation by permanganate in the absence or presence of HA was also present in this figure as references. Multiple dosing mode: $\text{Na}_2\text{S}_2\text{O}_3$ of $2 \mu\text{M}$ was applied every 5 minutes for 5 times. Reaction conditions: $[\text{3,4-DCP}]_0=5 \mu\text{M}$, $[\text{KMnO}_4]_0=50 \mu\text{M}$, $[\text{HA}]_0=1.0 \text{ mg/L}$ as DOC.

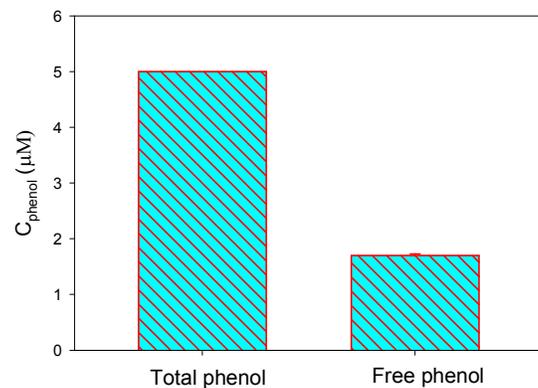


Figure S6. The proportion of phenol bonded to HA at pH 9.0. $[\text{HA}] = 10.0 \text{ mg/L}$ as DOC. HA and phenol were mixed and stirred for 2 hours in a volumetric flask. The mixture was then filtrated through a membrane with an average molecular weight exclusion point of 4000 Daltons. The phenol in the filtrate was referred to free phenol.

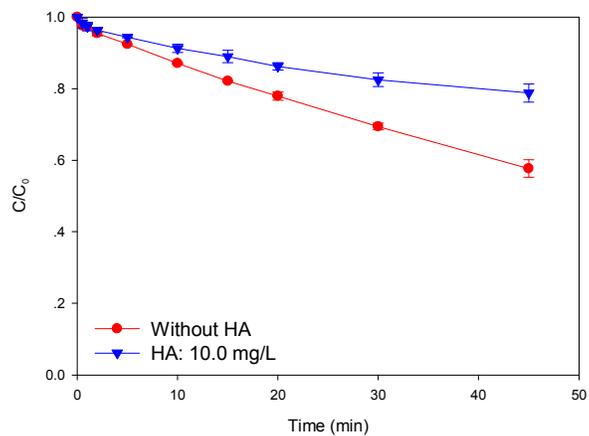


Figure S7. Influence of HA on the oxidation of 2,6-DCP by permanganate at pH 9.0.

Reaction conditions: $[2,6\text{-DCP}]_0 = 5 \mu\text{M}$, $[\text{KMnO}_4]_0 = 50 \mu\text{M}$.