

## Supporting Information

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

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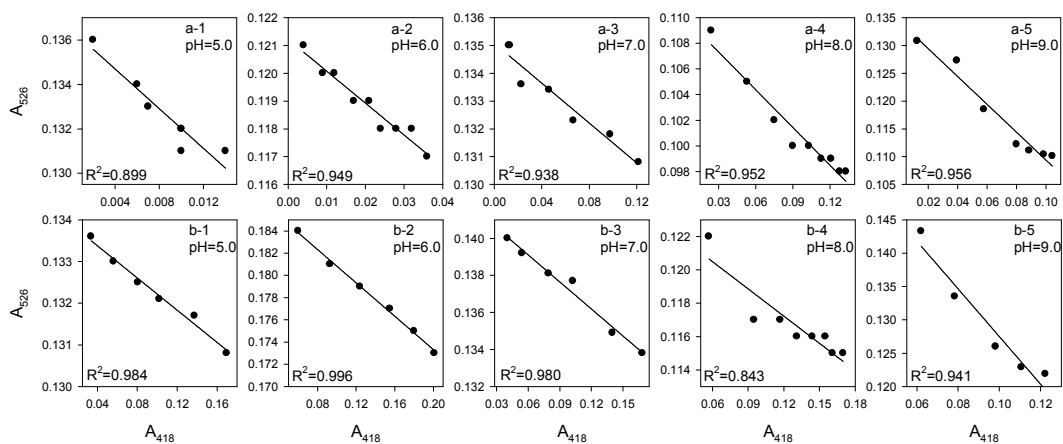
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**Text S1**

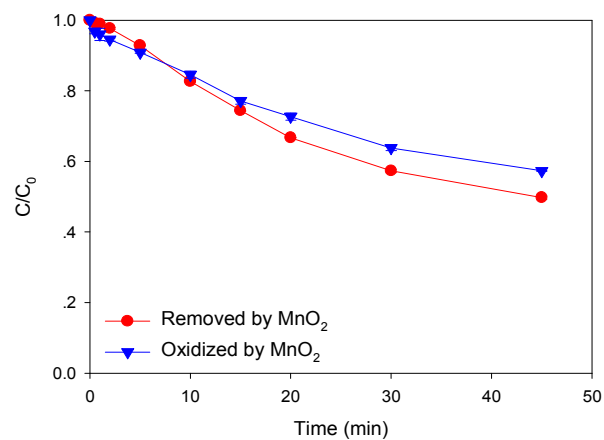
Separation was accomplished with an UPLC BEH C 18 column (2.1×50 mm, 1.7 μm; Waters) at 35±1 °C and a mobile phase of methanol-0.1% formic acid aqueous solution (from 30:70 to 70:30). The flow rate was 0.5 mL·min<sup>-1</sup> and the largest volume injection was 10 μL. Concentrations of phenols were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



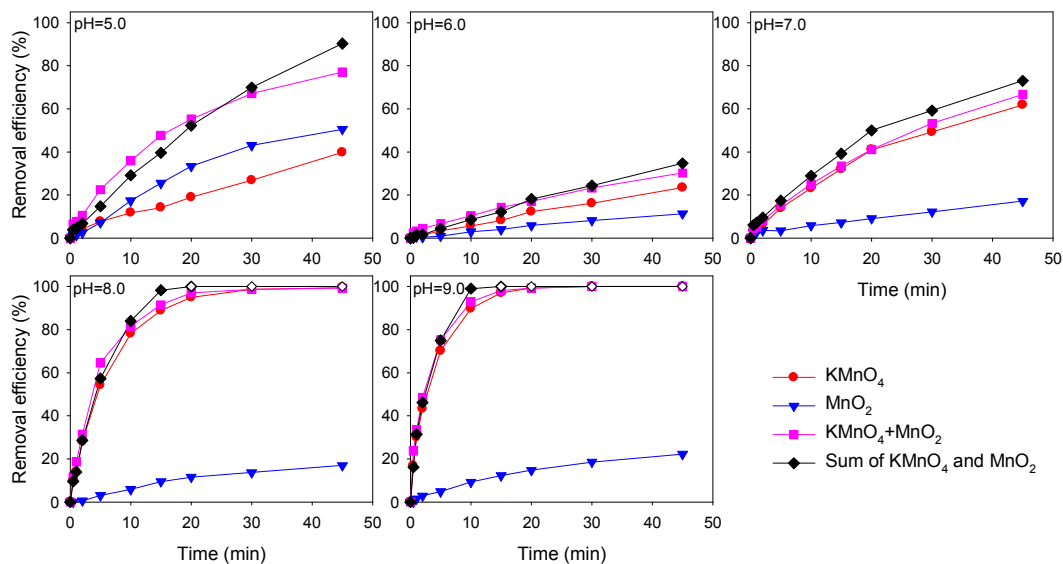
**Figure S1.** Absorbance at 526 nm vs. absorbance at 418 nm for the reduction of

permanganate a) by phenol; b) by phenol in the presence of HA. Experimental

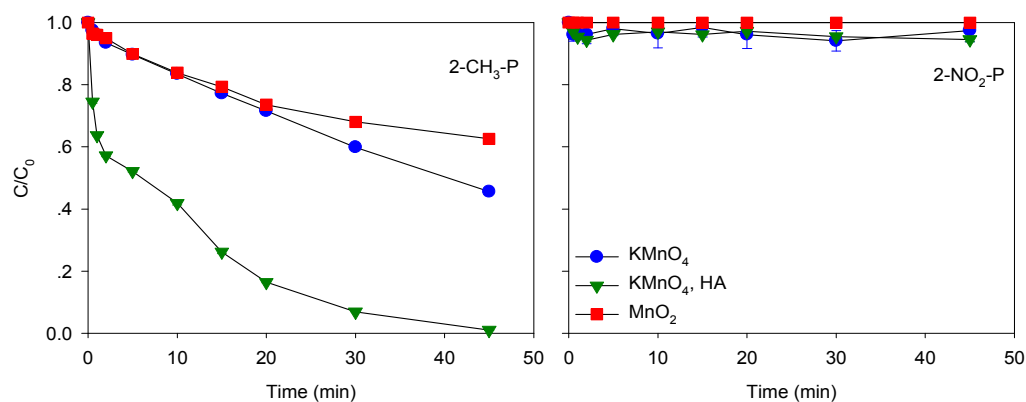
conditions:  $[\text{KMnO}_4]_0 = 50 \mu\text{M}$ ,  $[\text{phenol}]_0 = 5 \mu\text{M}$ ,  $T = 25^\circ\text{C}$ .



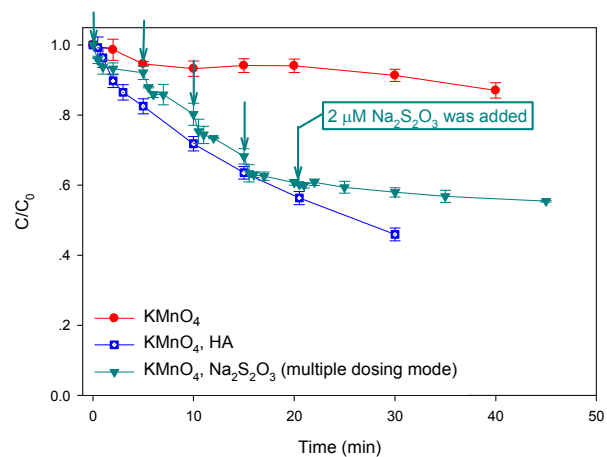
**Figure S2.** The role of MnO<sub>2</sub> in phenol removal. Reaction conditions: [phenols]<sub>0</sub>=5 μM, [MnO<sub>2</sub>]<sub>0</sub>=25 μM, pH=5.0. Oxidized by MnO<sub>2</sub>: After the sample was transferred into the beaker, excess sodium thiosulfate was added into the beaker immediately and the pH was adjusted to 2.0-3.0 by adding concentrated HCl, then the MnO<sub>2</sub> was reduced to Mn<sup>2+</sup> and the phenol adsorbed by MnO<sub>2</sub> was released into the solution.



**Figure S3.** Removal efficiency of phenols by  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{KMnO}_4+\text{MnO}_2$  over the pH range of 5.0-9.0. The black symbols show the sum of phenol removal by  $\text{KMnO}_4$  and  $\text{MnO}_2$ , 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:  $[\text{phenols}]_0=5\text{ }\mu\text{M}$ ,  $[\text{MnO}_2]_0=25\text{ }\mu\text{M}$ ,  $[\text{KMnO}_4]_0=50\text{ }\mu\text{M}$ .

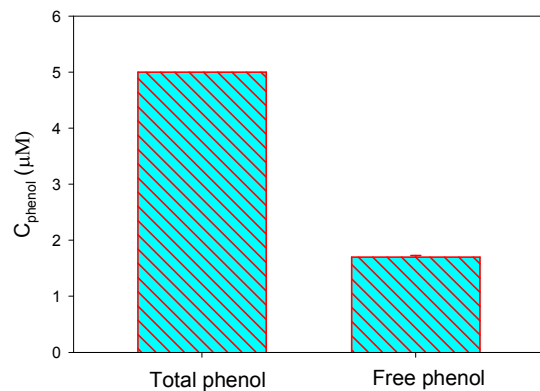


**Figure S4.** Oxidation of 2-CH<sub>3</sub>-P and 2-NO<sub>2</sub>-P by MnO<sub>2</sub> or KMnO<sub>4</sub> in the presence or absence of HA at pH 5.0. Reaction conditions: [phenols]<sub>0</sub>=5  $\mu$ M, [KMnO<sub>4</sub>]<sub>0</sub>=50  $\mu$ M, [MnO<sub>2</sub>]<sub>0</sub>=25  $\mu$ M, [HA]<sub>0</sub>=1.0 mg L<sup>-1</sup> as DOC.

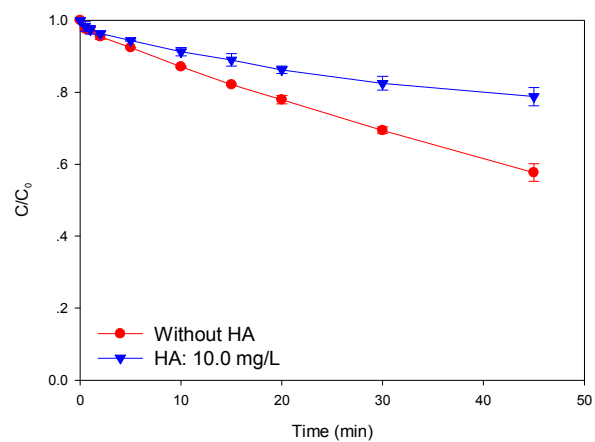


**Figure S5.** Influence of  $\text{Na}_2\text{S}_2\text{O}_3$  applied at multiple dosing mode on 3,4-DCP oxidation by permanganate at pH 6.0. The kinetics of 3,4-DCP oxidation by permanganate in the absence or presence of HA was also present in this figure as references. Multiple dosing mode:  $\text{Na}_2\text{S}_2\text{O}_3$  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:  $[2,6\text{-DCP}]_0 = 5 \mu\text{M}$ ,  $[\text{KMnO}_4]_0 = 50 \mu\text{M}$ .