

## Supplementary Material

### Impacts of environmental levels of hydrogen peroxide and oxyanions on the redox activity of MnO<sub>2</sub> particles

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9 Figures, 13 pages

**Acid birnessite synthesis.** Acid birnessite (AB) was prepared following the procedures of McKenzie.<sup>1</sup> 166 mL of concentrated HCl was added dropwise to 2.5 L of 0.4 M KMnO<sub>4</sub>. The suspension was stirred vigorously and kept at 90°C during the HCl addition. The reaction was continued at 90 °C for a further 10 min. Then, the obtained slurry was stirred vigorously at room temperature for 15 h. The precipitate was collected by centrifugation, washed with ultrapure water repeatedly until the conductivity was close to 0.6 μS cm<sup>-1</sup>. The suspensions were stored in polypropylene containers at 4 °C for further use.

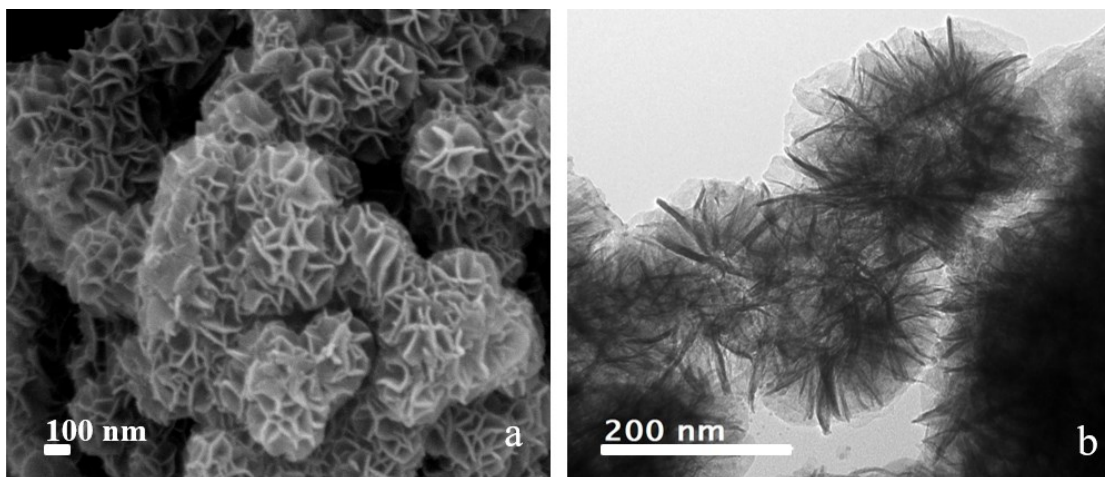
**Preparation of Mn(III)-rich birnessite.** Mn(III)-rich MnO<sub>2</sub> was synthesized according to previous published methods.<sup>2,3</sup> Briefly, about 2 g of acid birnessite was incubated with 80 mL of 10 mM HEPES and 10 mM NaCl solutions at pH 6.5 ±0.05 at a temperature of 25 °C for 48h. The precipitate was collected by centrifugation and washed with ultrapure water.

**Oxalic acid-permanganate back-titration method.** 0.1 g of the acid birnessite was dissolved in 2.5 mL of 0.5 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and 5 mL of 1 M H<sub>2</sub>SO<sub>4</sub> to reduce all highly charged manganese ions to Mn( II ). After all samples to be dissolved, the excess C<sub>2</sub>O<sub>4</sub><sup>2-</sup> was back titrated with standardized 0.02 M KMnO<sub>4</sub> solution at 75–85 °C until the color of solution turned into reddish and lasted for 30 seconds without fading, to obtain the oxidation number of Mn. Then, 0.1 g of the acid birnessite sample was dissolved in 20 mL 0.25 M hydroxylamine hydrochloride and diluted to 2 L with ultrapure water. AAS was used to determine the total Mn content, and the Mn content of the synthesized acid

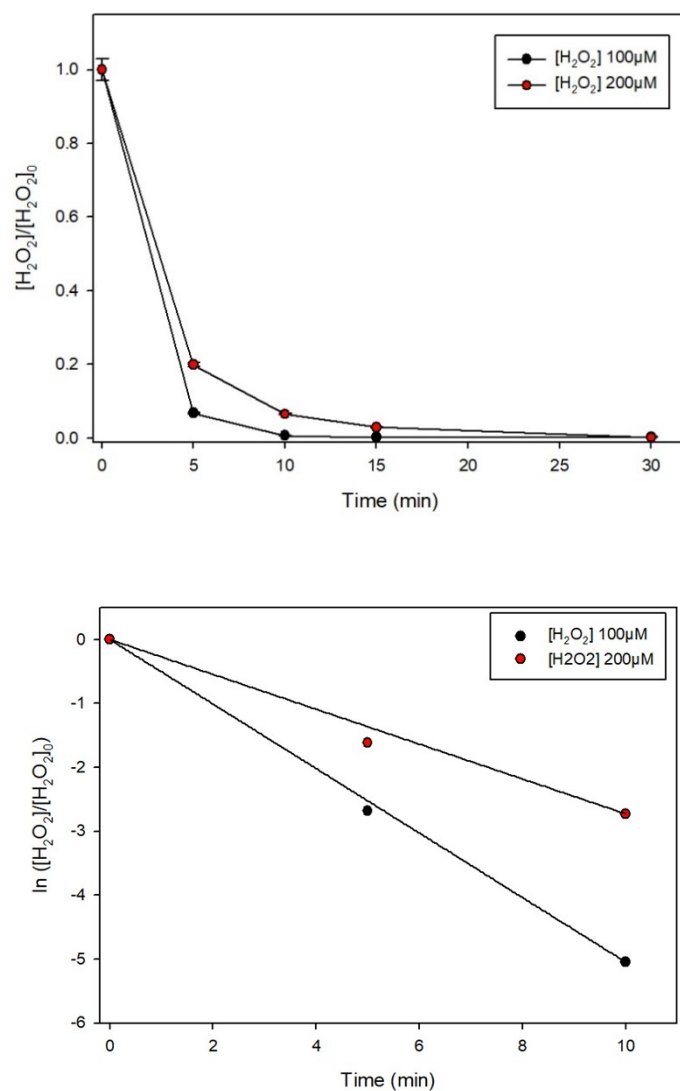
birnessite is 51.42 ( $\pm$  2.6) wt%. Then, according to the titration result and total Mn content, the AOS of acid birnessite was calculated. Triplicates were performed for each sample and the mean AOS value can be calculated.

$$\text{AOS} = 2 + 54.94 * \frac{n(\text{the oxidation number, mol})}{m(\text{the total Mn content, g})}$$

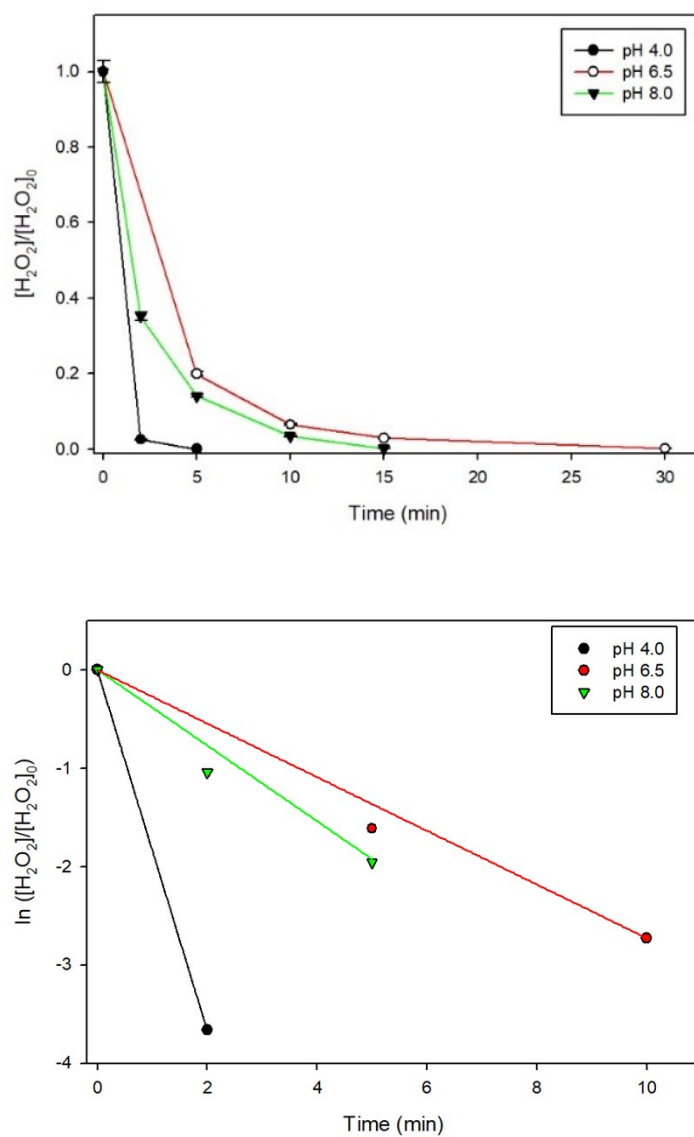
**Hydroxyl radical detection method.** Potential generation of hydroxyl radical was monitored by using a fluorescence method using terephthalic acid (TA) as a probe.<sup>4</sup> The detection mechanism is that nonfluorescence TA reacts with hydroxyl radical to generate fluorescent 2-hydroxyterephthalic acid which can be measured at 425 nm under the excitation of 320 nm. Specifically, in this work, 345  $\mu$ M of acid birnessite was mixed with TA (1 mM) and H<sub>2</sub>O<sub>2</sub> (200  $\mu$ M) in the 100mL ultrapure water. At different time interval, 2 mL of sample was withdrawn and detected by a fluorescence spectrophotometer (Varian Cary Eclipse, USA). The limit of detection for hydroxyl radicals using fluorescence method was in the low nano-molar range.



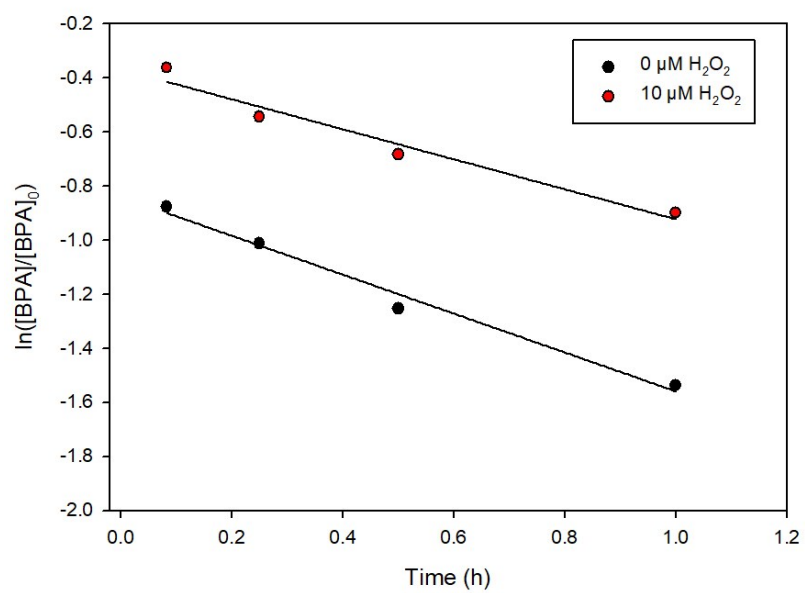
**Figure S1.** SEM (a) and TEM (b) images of the synthesized acid birnessite.



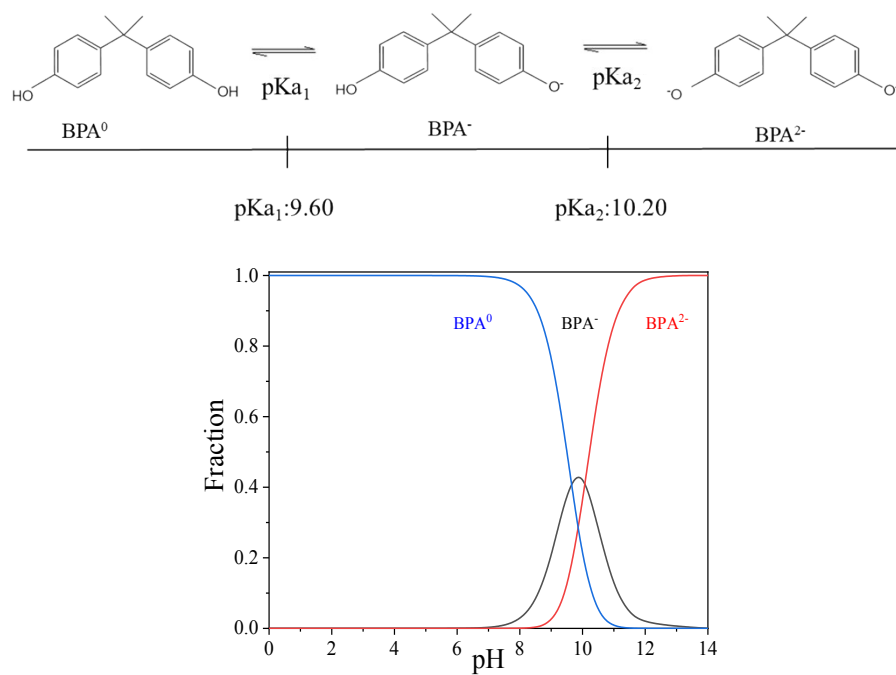
**Figure S2.** H<sub>2</sub>O<sub>2</sub> decomposition versus time with two H<sub>2</sub>O<sub>2</sub> concentrations and linear regression of  $\ln [H_2O_2] / [H_2O_2]_0$  versus time. Experimental conditions: [AB] = 345 μM, [BPA] = 25 μM, [H<sub>2</sub>O<sub>2</sub>] = 100 and 200 μM, pH = 6.5. H<sub>2</sub>O<sub>2</sub>/MnO<sub>2</sub> ratio = 0.3 and 0.6.



**Figure S3.**  $\text{H}_2\text{O}_2$  decomposition vs time at pH 4, 6.5 and 8, and linear regression of  $\ln [\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0$  versus time. Experimental conditions:  $[\text{H}_2\text{O}_2] = 200 \mu\text{M}$ ;  $[\text{AB}] = 345 \mu\text{M}$ ;  $[\text{BPA}] = 25 \mu\text{M}$ .  $\text{H}_2\text{O}_2/\text{MnO}_2$  ratio = 0.6.

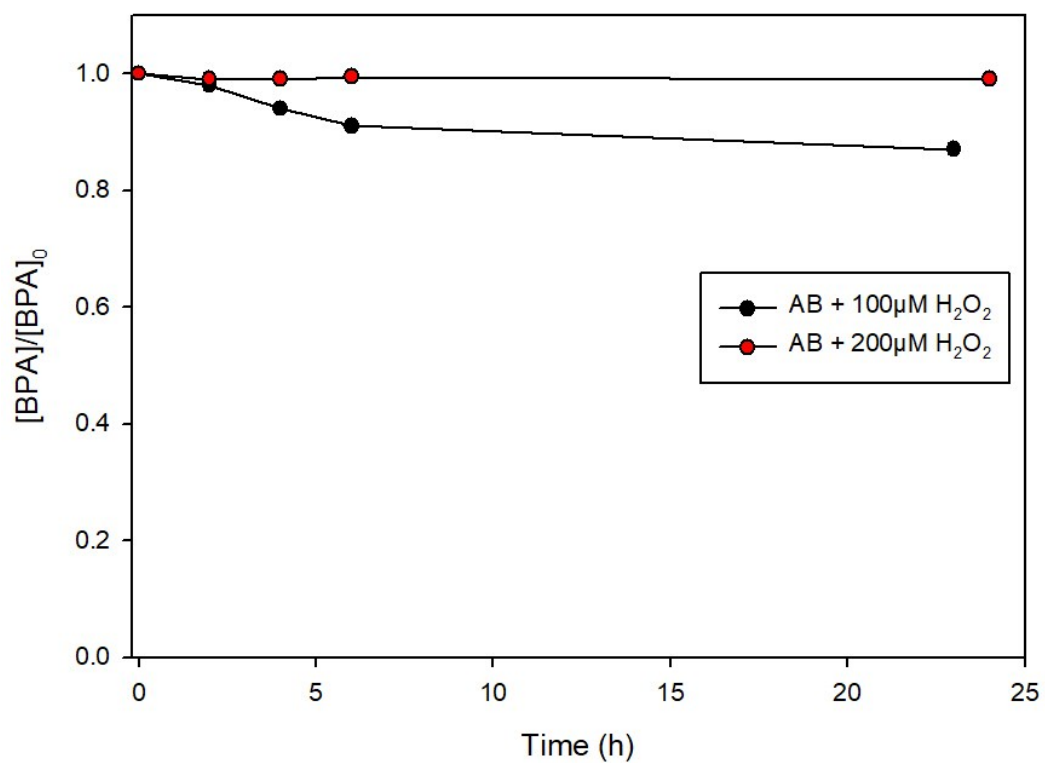


**Figure S4.** Linear regression of  $\ln [BPA]/[BPA]_0$  versus time. Experimental conditions: pH 6.5,  $[AB] = 345 \mu\text{M}$ ,  $[BPA] = 25 \mu\text{M}$ .  $\text{H}_2\text{O}_2/\text{MnO}_2$  ratio 0 and 0.03.

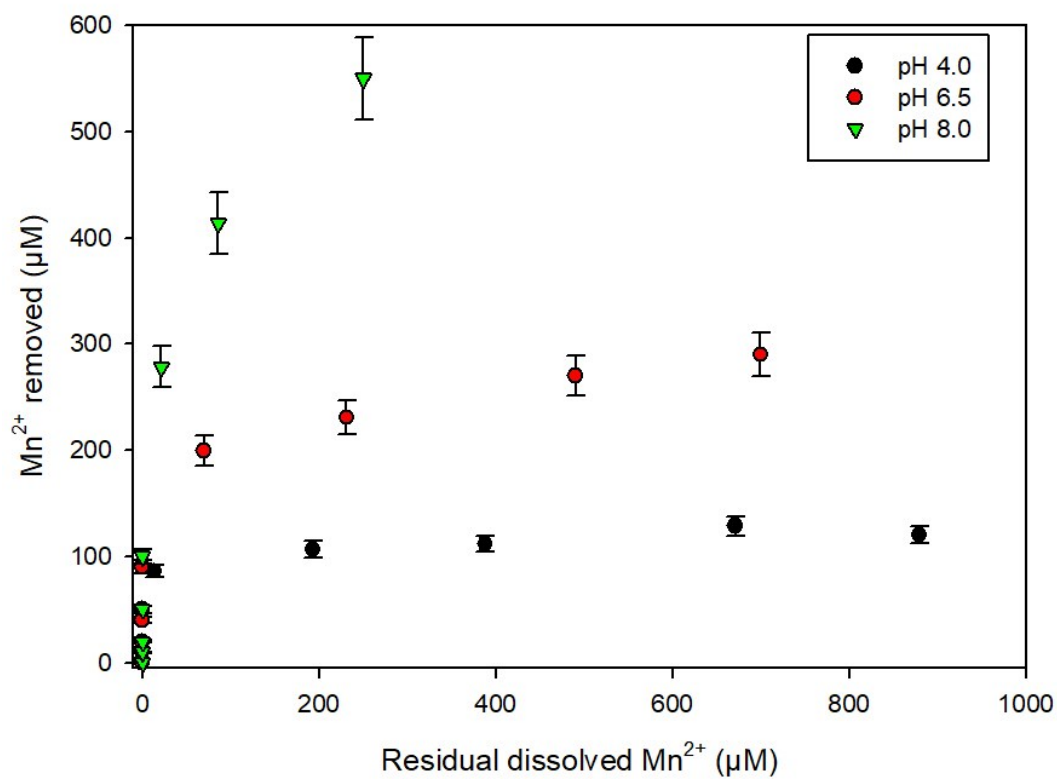


**Figure S5.** Chemical speciation of BPA vs pH. Ionic strength: 10 mM NaCl. pK<sub>as</sub> of BPA (pK<sub>a,1</sub> = 9.60 and pK<sub>a,2</sub> = 10.20) at infinite dilution were obtained from conditional pK<sub>a</sub> values and the Davies equation.

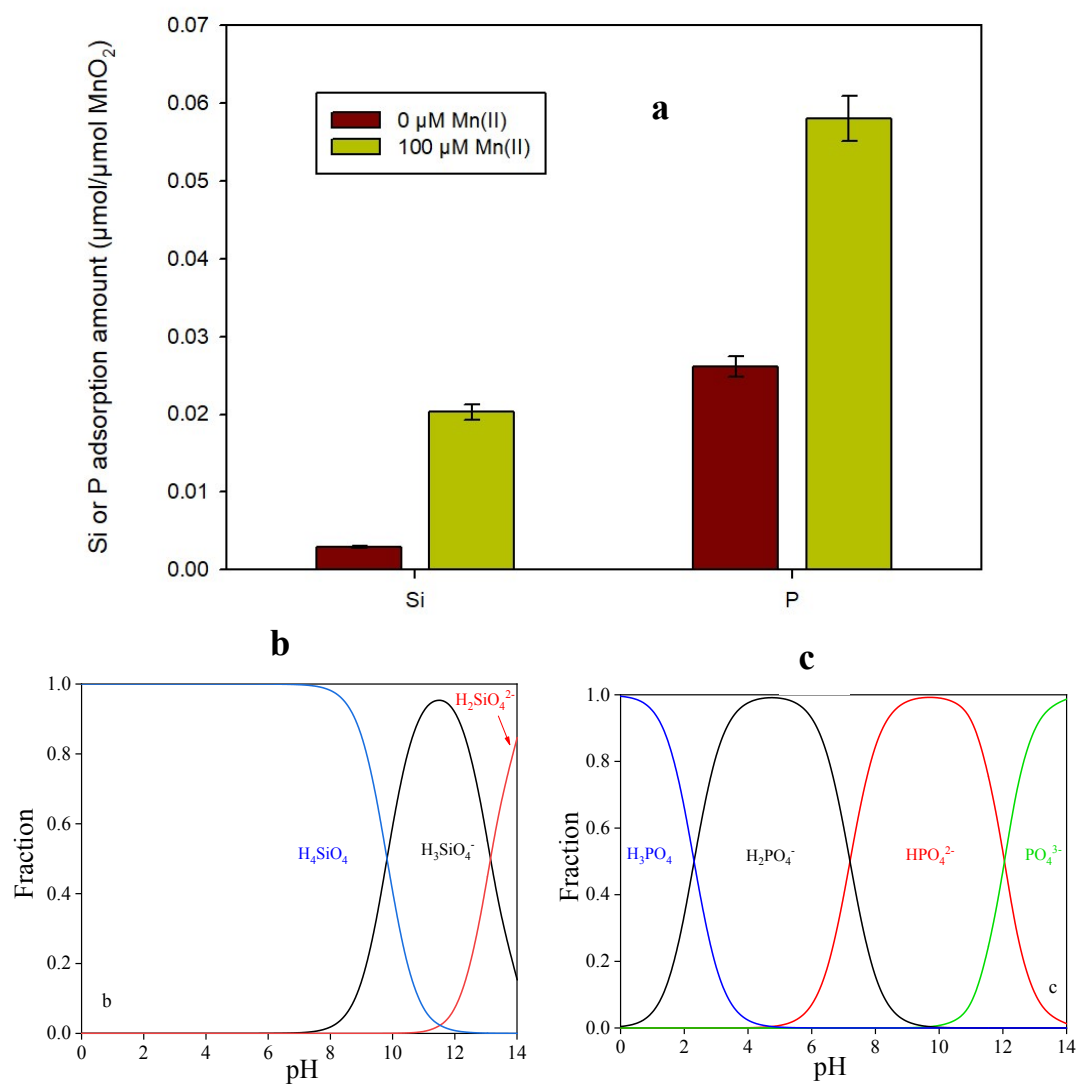




**Figure S6.** Effect of pre-equilibration  $H_2O_2/MnO_2$  on the BPA removal. Experimental conditions:  $[AB] = 345 \mu M$ ,  $[BPA] = 25 \mu M$ .

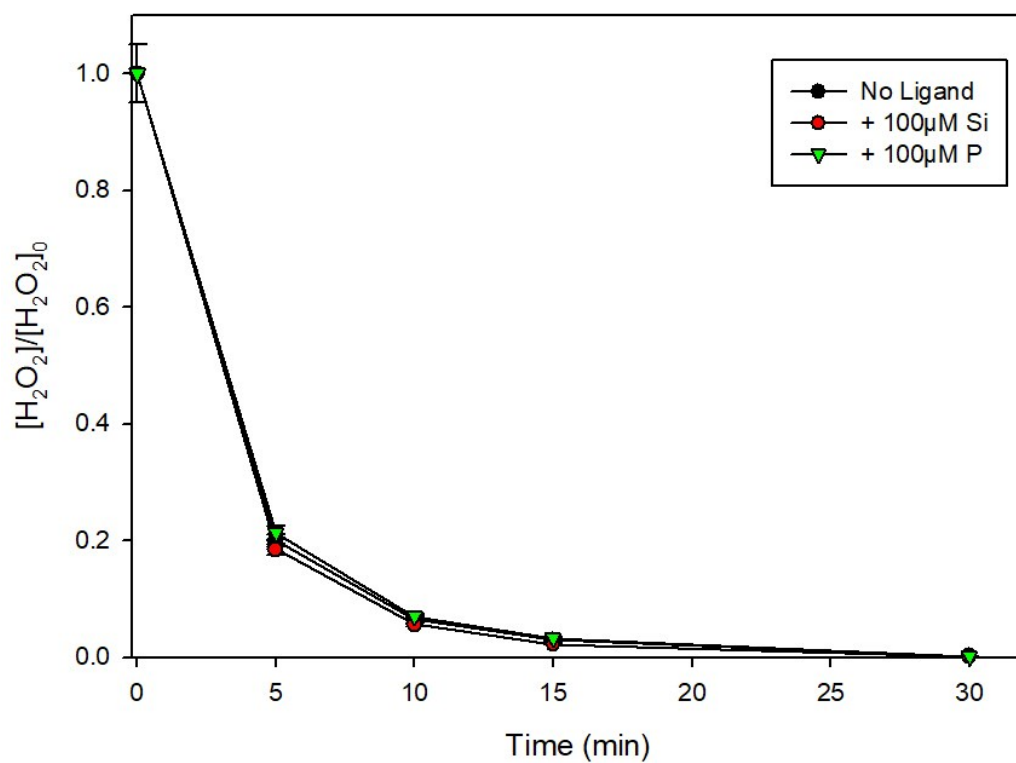


**Figure S7.** Mn(II)-birnessite sorption isotherms at three pH values. Experimental conditions: [AB] = 345 µM; T = 20 ± 1°C; reaction time = 48 h; aerobic conditions.



**Figure S8.** (a) Adsorption of Si or P at pH 6.5 in presence or absence of dissolved Mn(II). Chemical speciation of (b) silicates Si ( $\text{Na}_2\text{SiO}_3$ ) and (c) phosphates P ( $\text{NaH}_2\text{PO}_4$ ) versus pH.  $\text{pK}_{\text{as}}$  of silicate ( $\text{pK}_{\text{a},1} = 9.82$  and  $\text{pK}_{\text{a},2} = 13.45$ ) and phosphate ( $\text{pK}_{\text{a},1} = 2.12$ ,  $\text{pK}_{\text{a},2} = 7.21$  and  $\text{pK}_{\text{a},3} = 12.31$ ) at infinite dilution were obtained from conditional  $\text{pK}_{\text{a}}$  values and the Davies equation. Experimental conditions:  $[\text{AB}] = 345 \mu\text{M}$ ;  $[\text{Mn}(\text{II})] = 100 \mu\text{M}$ ;  $[\text{Na}_2\text{SiO}_3] = 100 \mu\text{M}$ ;  $[\text{NaH}_2\text{PO}_4] = 100 \mu\text{M}$ ; reaction time = 24 h.





**Figure S9.** Decomposition of  $\text{H}_2\text{O}_2$  ( $200 \mu\text{M}$ ) versus time in presence or absence of silicate or phosphate ( $100 \mu\text{M}$ ).

## References

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