

Electronic Supplementary Information for  
Impact of bisphenol A influent concentration  
and reaction time on MnO<sub>2</sub> transformation in a  
stirred flow reactor

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**Contents (10 pages): Figures: S1-S10, Tables: S1-S3**

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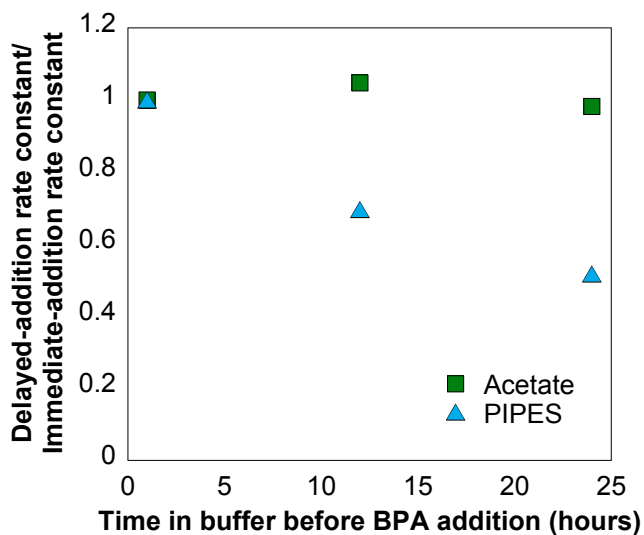
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## S1: Materials

**Purchased Chemicals.** Acetonitrile (HPLC grade), methanol (HPLC grade), formic acid (ACS, 88%), calcium chloride dihydrate (ACS, 100%), sodium acetate trihydrate (ACS, 100%), sodium chloride (ACS, 100%), polyvinylpyrrolidone (Molecular Biology Grade), and potassium permanganate (ACS) were purchased from Fisher Chemical. Boric acid (ACS) was purchased from Amresco, Inc. Bisphenol A ( $\geq 99\%$ ) and L-ascorbic acid ( $\geq 99\%$ ) were purchased from Sigma Aldrich. Manganese(II) nitrate tetrahydrate (analytical grade) and piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES, 99%) were purchased from Acros Organics. Sodium hydroxide (98%) was purchased from Sigma Chemical Co.

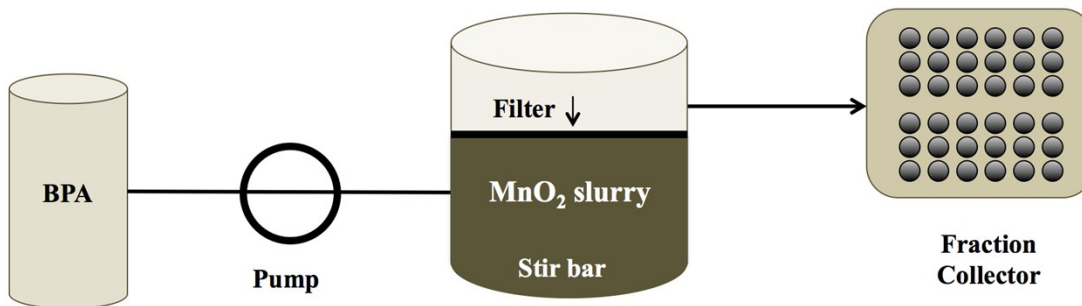
**Preparation and Characterization of  $\delta$ -MnO<sub>2</sub>.**  $\delta$ -MnO<sub>2</sub> was prepared by dissolving 11.29 g Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in 100 mL of ultrapure water, followed by dropwise addition to a 100 mL solution containing 2.4 g NaOH and 4.74 g KMnO<sub>4</sub> and stirring for at least twelve hours. The resulting slurry was centrifuged and washed five times in ultrapure water. The solids were then suspended in ultrapure water, stored at 4°C, and used within 10 days of synthesis. The slurry concentration was determined by gravimetric analysis. The starting material was characterized by X-ray diffraction (XRD; Rigaku Rapid II, Mo K $\alpha$  source;  $\lambda = 0.7093 \text{ \AA}$ ), showing that  $\delta$ -MnO<sub>2</sub> was the only crystalline phase produced. This synthesis yielded a mineral with an average valence state of  $3.94 \pm 0.11$  v.u. determined by oxalate titration,<sup>1</sup> indicating that the mineral is predominantly Mn(IV).

## S2: Buffer Selection

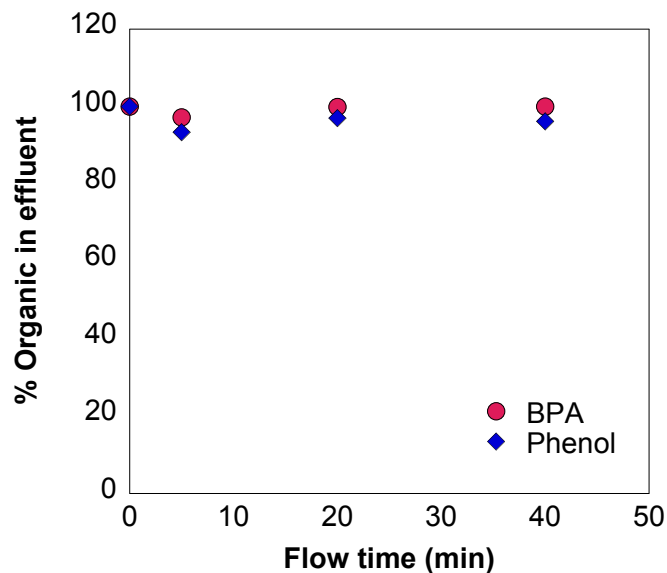


**Figure S1:** BPA oxidation rate constants with  $\delta$ -MnO<sub>2</sub>, where the reaction begins after  $\delta$ -MnO<sub>2</sub> is stirred with the buffer for a designated time. These delayed-addition rate constants are plotted as a fraction of the initial rate constant. Buffers used are PIPES (10 mM; pH 7) and acetate (10 mM; pH 5).

## S3: Stirred Flow Reactors



**Figure S2:** Schematic of stirred flow reactors.



**Figure S3:** Percentages of initial BPA and phenol concentrations (initial concentration = 20  $\mu$ M) in effluent when pumped through a line of Pt-cured silicone tubing.

#### **S4: XANES Analysis**

XANES data was collected at beamline 10-BM at the Advanced Photon Source at Argonne National Laboratory. This beamline has a bending magnet source equipped with a Si(111) double crystal monochromator, which was detuned by 40%. Data was collected at room temperature in transmission mode. Successive XANES scans were identical, indicating no change in Mn oxidation state during data collection. XANES data was processed using SIXPack<sup>2</sup> and was fit using the multi-standard Combo method<sup>3</sup> by fitting the first derivative of the spectra with restriction to a non-negative fit.

#### **S5: HCA Yield Calculations**

The steady-state approximation is used in stirred flow reactors that have reached a plateau in BPA and HCA concentrations. These reactors are not truly at steady-state since manganese oxide is still oxidizing both BPA and HCA, but the reaction has reached a

point where the oxidation rate is changing very little from one data point to the next. The steady-state approximation assumes that the concentration of any intermediates remain the same throughout the duration of the reaction, which is what is observed when the plateau is reached (i.e., BPA and HCA concentrations are generally constant throughout the reaction). When steady-state is assumed, the following mass balance equation can be used:

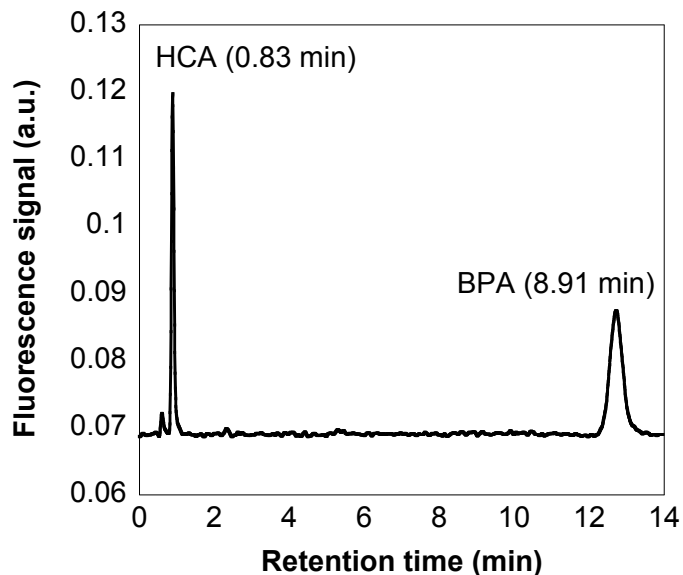
$$\frac{d[HCA]}{dt}V = -Q[HCA] + F_{HCA}k_1[BPA]V - k_2[HCA]V = 0 \quad (\text{S1})$$

where  $Q$  is the flow rate of the reactor (1 mL/min),  $V$  is the volume of the reactor (12.7 mL),  $[BPA]$  and  $[HCA]$  are the concentrations of BPA and HCA, respectively, and  $k_1$  and  $k_2$  are the oxidation rate constants of BPA and HCA, respectively.  $F_{HCA}$  is the fraction of BPA converted to HCA. This equation can be rearranged to form equation 2 in the manuscript. The BPA oxidation rate constant,  $k_1$ , is calculated using the following mass balance equation:

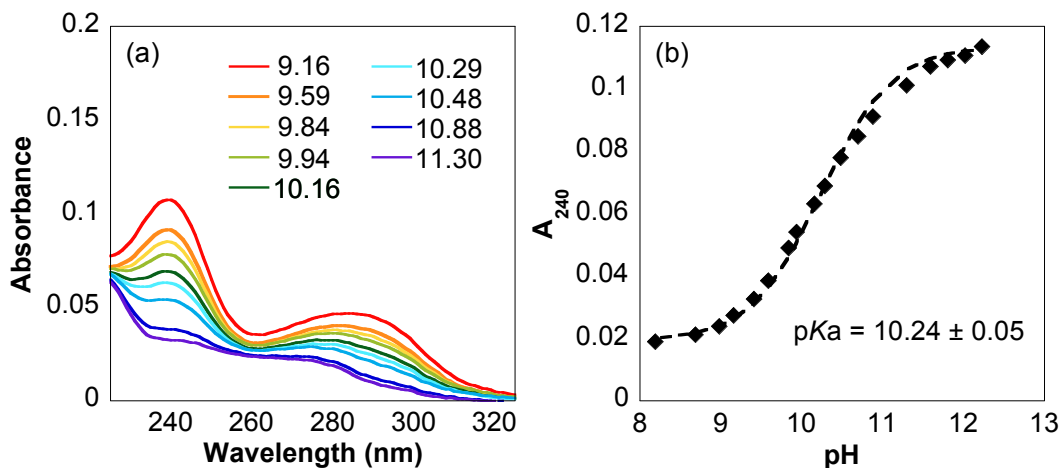
$$\frac{d[BPA]}{dt}V = Q[BPA]_0 - Q[BPA] - k_1[BPA]_0V = 0 \quad (\text{S2})$$

where  $[BPA]_0$  is the initial BPA concentration. This equation can be rearranged to form equation 3 in the manuscript. Separate batch reactors comparing BPA and HCA oxidation rate constants at each condition are used to determine  $k_2$ , the HCA oxidation rate constant in each stirred flow reactor.

## S6: HCA Identification and Acid Dissociation Constant ( $pK_a$ ) Determination



**Figure S4:** Example HPLC chromatogram from a batch reactor with 0.1 g/L  $\delta$ -MnO<sub>2</sub> and 40  $\mu$ M BPA in a 10 mM sodium acetate buffer. Both BPA and HCA peaks are identified and their retention times were confirmed using authentic standards.



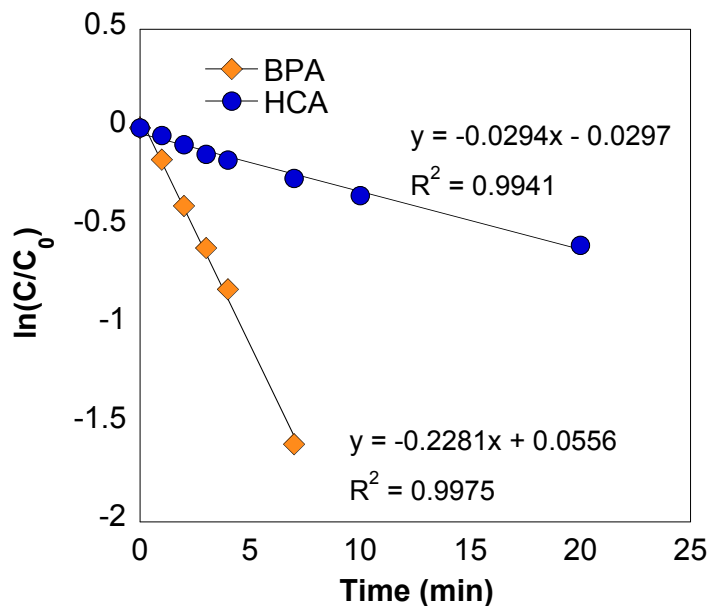
**Figure S5:** HCA (a) absorbance spectra at the pH values indicated in the legend and (b) absorbance at 240 nm versus pH. The dashed line represents the fit of the data using least squares minimization to determine the  $pK_a$ .

## S7: Batch Reactor Experiments

Sorption was determined by quantifying BPA and HCA concentrations in a quenched sample (10.8 mM ascorbic acid) and in a filtered sample (0.2  $\mu\text{m}$  polytetrafluoroethylene). The difference between these concentrations was used to quantify the HCA or BPA associated with the solid.

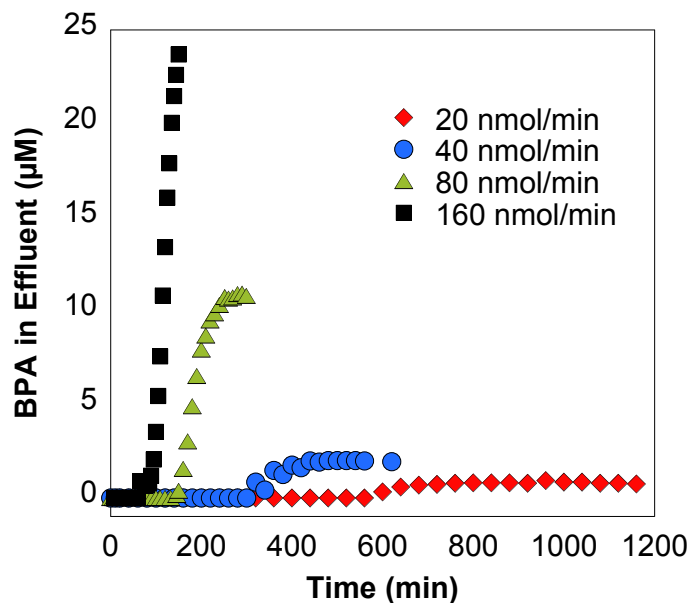
**Table S1:** BPA and HCA oxidation rate constants and percent sorption in identical batch reactors containing 0.1 g/L  $\delta\text{-MnO}_2$  and 40  $\mu\text{M}$  of the added phenol. Solutions contained 10 mM acetate buffer at pH 5 and were brought to an ionic strength of 25 mM using NaCl.

	Rate Constant ( $\text{min}^{-1}$ )	Sorption (%)
<b>BPA</b>	$0.228 \pm 0.005$	$13.57 \pm 18.45$
<b>HCA</b>	$0.029 \pm 0.000$	$-0.72 \pm 3.61$

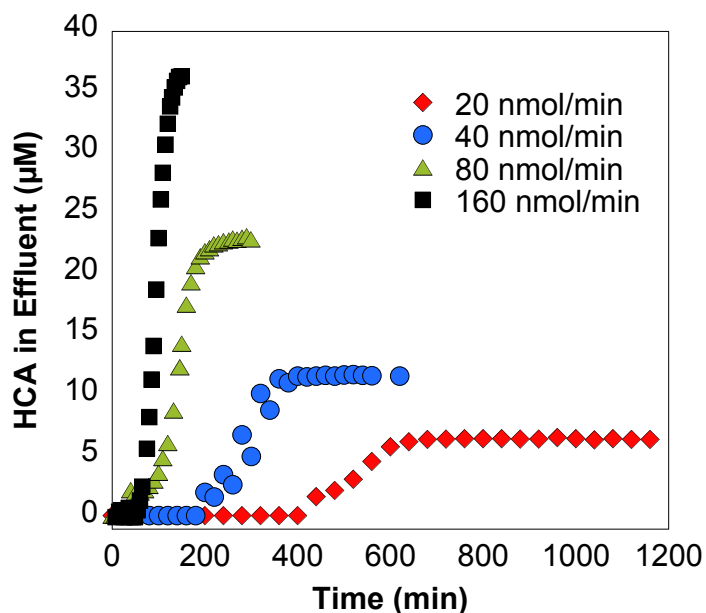


**Figure S6:** Pseudo-first-order rate analysis for BPA and HCA in identical batch reactors containing 0.1 g/L  $\delta\text{-MnO}_2$  and 40  $\mu\text{M}$  of the added phenol at pH 5. All solutions contained 10 mM acetate and were brought to an ionic strength of 25 mM using NaCl.

## S8: Stirred Flow Experiments

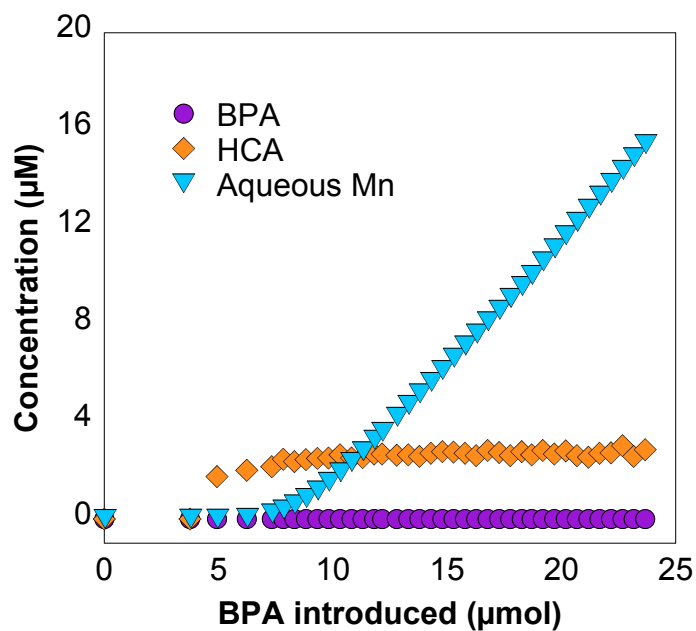


**Figure S7:** BPA present in the effluent as a function of time in stirred flow reactors containing 1.58 g/L  $\delta\text{-MnO}_2$  (10 mM acetate; pH 5) containing variable initial BPA concentrations.

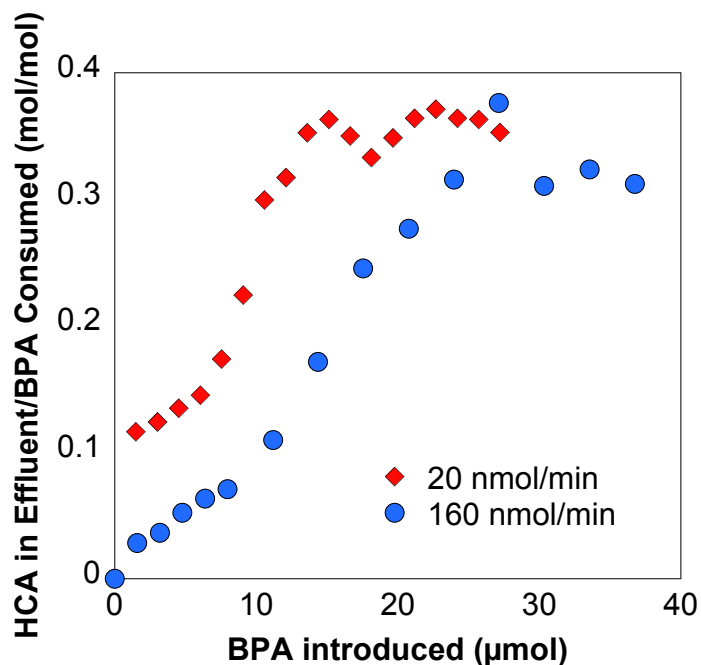


**Figure S8:** HCA present in the effluent as a function of time in stirred flow reactors containing 1.58 g/L  $\delta\text{-MnO}_2$  (10 mM acetate; pH 5) containing variable initial BPA concentrations.





**Figure S9:** Concentrations of BPA, HCA, and aqueous Mn in the effluent of a stirred flow reactor containing 1.58 g/L  $\delta$ -MnO<sub>2</sub> containing 5  $\mu$ M BPA and 10 mM acetate (pH 5) over 83 hours.



**Figure S10:** Ratios of HCA produced to BPA consumed in stirred flow reactors containing 1.58 g/L  $\delta$ -MnO<sub>2</sub> in 10 mM acetate (pH 5).

### S9: Solids Characterization

**Table S2:** Average manganese oxidation numbers and speciation of solids recovered from stirred flow reactors containing 1.58 g/L  $\delta$ -MnO<sub>2</sub> (10 mM acetate; pH 5) containing variable initial BPA concentrations, as determined by XANES spectroscopy.

Sample	AMON (v.u.)	% Mn(IV)	%Mn(III)	%Mn(II)
Starting Material	3.85	90	5	5
20 nmol/min	3.66	77	12	11
40 nmol/min	3.67	78	12	10
80 nmol/min	3.68	78	12	10
160 nmol/min	3.67	78	12	10

**Table S3:** Estimated net electron transfer from organic compounds to  $\delta$ -MnO<sub>2</sub> calculated for each reactor using the method described in Wang et al.<sup>4</sup>

Sample	Net Electron Transfer ( $\mu$ mol)
20 nmol/min	79.7
40 nmol/min	72.0
80 nmol/min	64.9
160 nmol/min	50.7

### References

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- (2) Webb, S. M. SIXpack: A Graphical User Interface for XAS Analysis Using IFEFFIT. *Phys. Scr.* **2005**, *2005* (T115), 1011–1014.
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- (4) Wang, Q.; Yang, P.; Zhu, M. Structural Transformation of Birnessite by Fulvic Acid under Anoxic Conditions. *Environ. Sci. Technol.* **2018**, *52* (4), 1844–1853.