1	ELECTRONIC SUPPORTING INFORMATION
2	for
3	Peroxi-electrocoagulation for simultaneous oxidation of trace organic compounds and
4	removal of natural organic matter at neutral pH
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12 ESI S1. Liquid Chromatography Mass Spectrometry Operating Conditions

13	TOrCs were quantified using a liquid chromatography-mass spectrometer (LC-MS,
14	Shimadzu LC-MS 2020). The HPLC and chromatography conditions for pCBA analysis were
15	adapted from Vanderford et al. (2007), as summarized in Table S1. The m/z ratios used for
16	pCBA was 155. Gradient flow was used for pCBA separation (Table S1). The mobile phase was
17	ultrapure water with 0.1% formic acid and the organic phase was HPLC grade methanol.
18	Eluent conditions are provided in Table S1 and other instrument parameters and column
19	information are in Table S2. Ten-point standard curves were used with concentrations ranging
20	from 4 μ g/L to 400 μ g/L. Each standard curve was prepared in the respective water matrix to
21	normalize the LC-MS response to ionic interference in each matrix. The limit of quantification
22	used for analyses was 4 $\mu\text{g/L}$ for all TOrCs because it was the lowest concentration that met the
23	10:1 signal-to-noise requirement for quantification.

Time (min)	Organic Phase (% of flow) ^a
0 - 5	10
5.0-5.5	60
5.5 – 10	100
10-12	100
12-15	10
15-18	10
18	End of run

24 **Table S1.** LC-MS 2020 gradient flow time progression utilized to quantify pCBA.

25

^a The organic phase was HPLC-grade methanol.

Table S2. LC-MS 2020 instrument information for pCBA quantification.

Parameter	Value
Eluent Type	Gradient
Mobile Phase A	Milli-Q water + 0.1% formic acid
Mobile Phase B	Methanol
Flow Rate	0.2 mL min ⁻¹
Column Temperature	35°C
Detection	Electrospray Mass Spec (ESI-MS) at 40°C
Injection Volume	50 μL
Acquisition Mode	Single ion mode
Interface Temperature	350°C
DL Temperature	250°C
Nebulizer Gas Flow	1.5 L min ⁻¹
Heat Block	400°C
Drying Gas Flow	15 L min ⁻¹

30 ESI S2. Hydroxyl radical quantification using pCBA degradation

The hydroxyl radical concentrations during EC:H₂O₂ were estimated by the pseudo-first
order degradation of pCBA (Eqn. S1).

$$-ln\frac{pCBA_t}{pCBA_0} = k_{HO:pCBA}[HO\bullet] \times t$$
Eqn. S1

Where $k_{HO:pCBA}$ is the second order rate constant in units of M^{-1*}s⁻¹, HO• is the hydroxyl radical concentration over the course of treatment, and t is the treatment time in seconds. This method was adapted from Rosario-Ortiz and Canonica (2016).³⁷

37 ESI S3. Hydroxyl radical availability for pCBA oxidation

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38 Hydroxyl radical scavenging was estimated for EC: H_2O_2 using Eqn. S2 as a function of 39 H_2O_2 concentration to assess whether higher H_2O_2 could inhibit oxidation. It was assumed that 40 pCBA, H_2O_2 , and HCO_3^- were the primary constituents competing for the radicals. Results are 41 shown in Figure S1.

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$$\frac{d[HO\bullet]}{dt} = k_{HO\bullet:pCBA}C_{pCBA}[HO\bullet] + k_{HO\bullet:H2O2}C_{H2O2}[HO\bullet] + k_{HO\bullet:HCO3}C_{HCO3}[HO\bullet] = [HO\bullet](k_{HO\bullet:pCBA}C_{pCBA} + k_{HO\bullet:H2O2}C_{H2O2} + k_{HO\bullet:HCO3}C_{HCO3}) = [HO\bullet](k_{HO\bullet:pCBA}C_{pCBA} + k_{HO\bullet:H2O2}C_{H2O2} + k_{HO\bullet:HCO3}C_{HCO3}) = \frac{k_{HO\bullet:pCBA}C_{pCBA}}{k_{HO\bullet:pCBA}C_{pCBA} + k_{HO\bullet:H2O2}C_{H2O2} + k_{HO\bullet:HCO3}C_{HCO3}} = \frac{k_{HO\bullet:PCBA}C_{PCBA}}{k_{HO\bullet:PCBA}C_{PCBA} + k_{HO\bullet:H2O2}C_{H2O2} + k_{HO\bullet:H2O3}C_{HCO3}} = \frac{k_{HO\bullet:PCBA}C_{PCBA}}{k_{HO\bullet:PCBA}C_{PCBA} + k_{HO\bullet:H2O3}C_{HCO3}} = \frac{k_{HO\bullet:PCBA}C_{PCBA}}{k_{HO\bullet:PCBA}C_{PCBA} + k_{HO\bullet:H2O3}C_{HCO3}} = \frac{k_{HO\bullet:PCBA}C_{PCBA}}{k_{H$$

46 **Table S3.** Second order rate constant for hydroxyl radicals and target compounds ³⁸.

Target compound	Hydroxyl radical rate constant, $k_{HO*:i}$, 1/M-s
рСВА	5 x 10 ⁹
H ₂ O ₂	2.7 x 10 ⁷





Figure S1. The estimated fraction of hydroxyl radicals available for pCBA oxidation as a function of increasing H_2O_2 concentrations based on calculated values for Eqn. S3. Values were estimated using the second order rate constants for H_2O_2 (0 - 100 mg/L), pCBA (2.5 μ M), and HCO₃⁻ (4 mM) to quantify matrix interference.

54

55 ESI S4. Oxidant competition for ferrous iron

56 Oxidant competition for Fe²⁺ was estimated using the rate constants for H_2O_2 and O_2

57 oxidizing Fe²⁺. These theoretical calculations relied on the assumption that dissolved oxygen

- 58 was present at the saturation concentration (9.1 mg O₂/L) ³⁹. Competition was assessed for pH
- 59 6.3 to 14 to evaluate the influence of [OH⁻] on Fe²⁺ depletion. The kinetic rate constant for Fe²⁺

60 and O₂ was 1.1 x 10¹⁰ L³/mol³-min ⁹. The Fe²⁺ and H₂O₂ rate constant used for analyses was

61 3780 L/mol-min ⁴⁰. The rate constants and associated oxidant concentrations were input into

62 the rate equations (Eqn S6 and Eqn S7) and compared as a ratio with Eqn S8.

$$\frac{d[Fe^{2+}]}{dt} = k_{Fe^{2+}:H_2O_2}[Fe^{2+}][H_2O_2]$$
$$\frac{d[Fe^{2+}]}{dt} = k_{Fe^{2+}:O_2}[Fe^{2+}][O_2][OH^-]^2$$

63

Eqn. S6

Eqn. S7

$$ratio = \frac{k_{Fe^{2+}:H_2O_2}^{[H_2O_2]}}{k_{Fe^{2+}:O_2}^{[O_2][OH^-]^2}}$$
Eqn. S8



67

68 Figure S2. Relative ratio of Fe²⁺ oxidation due to H₂O₂ and dissolved oxygen. In all scenarios, dissolved

69 oxygen was assumed to be saturated (9.1 mg O₂/L) as a conservative assumption to maximize the

70 influence of dissolved oxygen on the model.

71

72 ESI S5. Pseudo-first order rate constants for EC:H₂O₂

73 Experiments were conducted at a range of current densities and $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$

74 ratios. Throughout experiments, samples were taken at t = 0, 2.5, 5, 7.5, 10, and 15 minutes to

75 quantify pseudo-first order rate constants, as shown in Table S4.

76 **Table S4.** Pseudo-first order rate constants resulting from reactor inputs (s^{-1}) for EC:H₂O₂ experiments 77 discussed in 3.2.

$[H_2O_2]_{initial}/$		Current Density, mA/cm ²							
[Fe ²⁺] _{generated}	3	5.5	7.4	11.1	15				
0	1.4 x 10 ⁻⁴	2.7 x 10 ⁻⁴	2.9 x 10 ⁻⁴	2.5 x 10 ⁻⁴	2.7 x 10 ⁻⁴				
0.35	-	1.1 x 10 ⁻³	1.5 x 10 ⁻³	1.6 x 10 ⁻³	1.5 x 10 ⁻³				
0.5	8.4 x 10 ⁻⁴	1.3 x 10 ⁻³	1.5 x 10 ⁻³	1.6 x 10 ⁻³	-				
0.7	-	1.1 x 10 ⁻³	-	1.3 x 10 ⁻³	-				

-

"-" indicates test was not conducted.

78

79 ESI S6. Statistical Analyses

80 ESI S6.1 Pearson Correlations

81 Pearson correlations were conducted on reactor inputs prior to multivariable linear

82 regressions to select parameters correlated to removal and rate and assess multicollinearity

-

83 between other parameters. The data included in these analyses are results from EC:H₂O₂

84 experiments at neutral pH and H_2O_2 and EC controls.

Table S5. Pearson correlations (R^2) for EC:H₂O₂ experiments at neutral pH. Data inputs also include H₂O₂ and EC-only controls. ** indicates p<0.05.

	Regression: $H_2O_2 0 - 40 \text{ mg/L}$; (H_2O_2 and EC Controls included)								
	Removal	Current	H_2O_2	H_2O_2 / Fe	Fe applied	H ₂ O ₂ /pCBA	Fe/pCBA		
Removal	1.00								
Current	0.47**	1.00							
H_2O_2	0.003	-0.04	1.00						
H_2O_2 / Fe	0.28	-0.06	0.64**	1.00					
Fe applied	0.46**	0.90**	0.23	0.16	1.00				
H ₂ O ₂ /pCBA	0.00	-0.04	1.00**	0.64**	0.23	1.00			
Fe/pCBA	0.46**	0.90**	0.23	0.16	1.00**	0.23	1.00		

87

Table S6. Pearson correlation (R^2) for EC:H₂O₂ experiments for H₂O₂ doses up to 40 mg/L. ** indicates p<0.05.

Regression: H₂O₂ 0 - 40 mg/L Fe H₂O₂/pCBA Removal Current H_2O_2 H_2O_2 / Fe Fe/pCBA applied 1.00 Removal Current 0.18 1.00 0.84** 0.23 1.00 H_2O_2 H_2O_2 / Fe 0.84** 0.77** -0.24 1.00 0.92** Fe applied 0.18 0.40 -0.15 1.00

	H ₂ O ₂ /pCBA	0.84**	0.23	1.00**	0.77**	0.40**	1.00	
	Fe/pCBA	0.18	0.92**	0.39	-0.15	1.00**	0.39**	1.00
00								

- 92 **Table S7.** Pearson correlation (R^2) for EC:H2O2 experiments for H_2O_2 doses of 40 200 mg/L H_2O_2 . **
- 93 indicates p<0.05.

	Regression: H ₂ O ₂ 40 - 200 mg/L							
	Removal	Current	H_2O_2	H_2O_2 / Fe	Fe applied	H ₂ O ₂ /pCBA	Fe/pCBA	
Removal	1.00							
Current	0.84**	1.00						
H_2O_2	-0.38	0.01	1.00					
H_2O_2/Fe	0.10	0.08	0.40	1.00				
Fe applied	0.77**	0.97**	0.09	0.13	1.00			
H ₂ O ₂ /pCBA	-0.38	0.01	1.00**	0.40	0.09	1.00		
Fe/pCBA	0.77**	0.97**	0.10	0.13	1.00**	0.10	1	

95 **Table S8.** Pearson correlation (R^2) for EC:H₂O₂ experiments for current densities up to 7.4 mA/cm².

96 Regression only contains data for EC:H₂O₂ experiments. EC only experiments are excluded from

97 regression due to poor removal. ** indicates p<0.05.

	Regression: Current density < 7.4 mA/cm ²								
	Removal	Current	H_2O_2	H_2O_2 / Fe	Fe applied	H ₂ O ₂ /pCBA	Fe/pCBA		
Removal	1.00								
Current	0.63**	1.00							
H_2O_2	-0.42	-0.06	1.00						
H_2O_2 / Fe	-0.59**	-0.38	0.90**	1.00					
Fe applied	0.29	0.57	0.64**	0.31	1.00				
H ₂ O ₂ /pCBA	-0.42	-0.06	1.00**	0.90**	0.64**	1.00			
Fe/pCBA	0.30	0.57	0.64**	0.31	1.00**	0.64**	1.00		

98

99	Table S9. Pearson correlation	n (R ²) for EC:H ₂ O	2 experiments for curren	t densities ranging from 7.4
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100 mA/cm² to 15 mA/cm². Regression only contains data for EC: H_2O_2 experiments. EC only experiments are

101 excluded from regression due to poor removal. ** indicates p<0.05.

	Regression: Current density = 7.4 mA/cm ² to 15 mA/cm ²								
	Removal	Current	H_2O_2	H_2O_2 / Fe	Fe applied	H ₂ O ₂ /pCBA	Fe/pCBA		
Removal	1.00								
Current	0.14	1.00							
H_2O_2	-0.67**	0.09	1.00						
H_2O_2/Fe	-0.69**	-0.16	0.96**	1.00					
Fe applied	-0.05	0.80**	0.47	0.23	1.00				
H ₂ O ₂ /pCBA	-0.67**	0.09	1.00**	0.96**	0.47	1.00			
Fe/pCBA	-0.05	0.80**	0.47	0.23	1.00**	0.47	1.00		

ESI S6.2. Multivariable Analysis Tables

$\label{eq:table_signal} \textbf{Table S10.} Normalized multivariable linear regressions for EC: H_2O_2 experiments.$

Title	Scenario	Current Density (β1)	H ₂ O ₂ / Fe ²⁺ (β ₂)	рН (β₃)	Model R ²	Akaike information Criterion (AIC)	Number of points
			Removal vs. react	tor inputs			
%R, neutral	Reactor Inputs All [H ₂ O ₂] _{initial} /[Fe ²⁺] _{generated} (Neutral pH only)	0.5±0.15 (p=0.0012)	0.31±0.14 (<i>p=0.032</i>)	-	0.31	265	39
%R, low	Reactor Inputs vs. Removal ([H ₂ O ₂] _{initial} /[Fe ²⁺] _{generated} =0- 0.77), neutral pH	0.43±0.07 (p=0.0010)	0.77±0.06 (p<0.0001)	-	0.86	177.4	33
%R, high	Reactor Inputs vs. Removal $([H_2O_2]_{initial}/[Fe^{2+}]_{generated} = 0.33$ - 1.6	0.41±0.12 (p=0.002)	-0.42±0.11 (p=0.0008)	-	0.60	173	28
%R, all	Reactor inputs vs. pCBA removal (all [H ₂ O ₂] _{initial} /[Fe ²⁺] _{generated)} , all pH	0.36±0.09 (p=0.008)	0.22±0.09 (p=0.0219)	-0.91±0.15 (p<0.0001)	0.58	270	45
		Pseudo	o first order rate v	s. reactor inputs			
k, all	All $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$, all pH	0.063±0.075 (<i>p=0.40)</i>	0.033±0.08 (<i>p=0.68)</i>	-0.977±0.12 (p<0.0001)	0.63	235	42
k, low, neutral pH	[H ₂ O ₂] _{initial} /[Fe ²⁺] _{generated} 0- 0.77, rate, neutral pH	0.33±0.16 (<i>p=0.0045)</i>	0.76±0.11 (<i>p<0.0001)</i>	-	0.68	186	30
k, EC: H ₂ O ₂ only, neutral pH	$[H_2O_2]_{initial}/[Fe^{2+}]_{generated} = 0.33$ - 1.6, neutral pH	0.32±0.11 (p = 0.009)	-0.59±0.11 (p<0.0001)	-	0.68	170	28

103 ESI S7 H₂O₂ depletion during EC:H₂O₂

104 The hydrogen peroxide levels during EC:H₂O₂ at pH 3 and pH 6.3 conditions were

105 measured at the reaction stagnation points after 5 minutes, as shown in Table S11. Additionally,

106 the residual iron following no electricity controls was measured to better assess the iron

107 following treatment that entered solution via non-faradaic dissolution of the electrodes.

108

109 **Table S11.** H_2O_2 remaining after 5 minutes of EC: H_2O_2 at pH = 3 and pH = 6.3. Tests were conducted in 110 triplicate.

Treatment	Residual H	₂ O ₂ Concentration, mg/L	H ₂ O ₂ Removal		
	Average	Standard Deviation	Average	Standard Deviation	
EC: H ₂ O ₂ pH 3	1.5	0.2	95.1	0.8	
No electricity (H ₂ O ₂ + electrodes) pH 3 ^a	0.73	0.12	97.5	0.4	
EC: H ₂ O ₂ pH 6.3	9.7	1.5	67.8	5.1	

¹¹¹ ^a The treatment time for this no electricity control was 15 minutes to match experiments.

112

113 **Table S12.** Residual iron following no electricity control experiments of 30 mg/L H₂O₂ and iron

114 electrodes in pH = 3 and pH = 6.3 tests. Tests were conducted in triplicate.

No electricity (H ₂ O ₂ + electrodes)	Resi	dual Iron, mg/L	$[H_2O_2]_{initial} / [Fe^{2+}]_{generated}$		
	Average	Standard Deviation	Average	Standard Deviation	
рН 3	32.2	0.4	1.53	0.02	
pH 6.3	1.01	0.4	50.6	10.7	

116 ESI S8 Pearson Correlation and Multivariable Analysis: the impact of water quality on pCBA

117 removal

- 118 Pearson correlations and multivariable analyses were conducted to assess the role of
- 119 water quality on pCBA removal following EC:H₂O₂. Results are shown in Table S13 S8.4.

120 Table S13. Pearson correlation of the impact of water quality on E_{EO} and pseudo-first order rate for all

121 matrices ** indicates p<0.05.

	DOC	Alkalinity	Alkalinity nH		рСВА	DOC
	initial	Aikaiiiity	рп	demand	Removal	removal
DOC initial	1.00					
Alkalinity	-0.57**	1.00				
рН	-0.26	-0.01	1.00			
H_2O_2 demand	0.89**	-0.58**	-0.25	1.00		
pCBA Removal	-0.53**	0.35	-0.60**	-0.47**	1.00	
DOC removal	0.54**	-0.78**	-0.30	0.62**	-0.47**	1.00

122

123 **Table S14.** Pearson correlation of the impact of water quality on E_{EO} and pseudo-first order rate for all 124 matrices with the exception of the primary influent ^{**} indicates p<0.05.

		1 /				
	DOC initial	Alkalinity	рН	H_2O_2 demand	pCBA Removal	DOC removal
DOC						
initial	1.00					
Alkalinity	-0.39**	1.00				
рН	-0.20	-0.16	1.00			
H_2O_2						
demand	0.13	-0.31	-0.11	1.00		
pCBA Removal	0.12	0.00	0.01**	0.07	1.00	
	0.12	0.09	-0.91	0.07	1.00	
removal	-0.10	-0.72**	-0.18	0.36	0.08	1.00

125

127 **Table S15.** Pearson correlation of the impact of water quality on E_{EO} and pseudo-first order rate. This 128 regression includes all waters tested ^{**} indicates p<0.05.

Matrices	DOC _{initial} (β ₁)	Alkalinity (β_2)	pΗ (β ₃)	H_2O_2 demand (β_4)	Model R ²	AIC	Number of points
All	-0.72±0.18	-0.11±0.08	-0.81±0.08	-0.11±0.17	0.00	107	20
Matrices	(p<0.0001)	(p=0.0013)	(p<0.0001)	(p<0.0001)	0.88	171	20

- 130 Table S16. Multivariable linear regression of the impact of water quality on E_{EO} and pseudo first order
- 131 rate. This regression includes all waters tested with the exception of the "Primary effluent test" **
- 132 indicates p<0.05.

Matrices	DOC _{initial} (β ₁)	Alkalinity (β ₂)	pΗ (β ₃)	Model R ²	AIC	Number of points
All Source water Matrices	-0.07±0.07 (p<0.34)	-0.08±0.09 (<i>p=0.393)</i>	-0.80±0.09 (p<0.0001)	0.88	112	17

134 ESI S9. Lack of flocculation following EC:H2O2 for SR-NOM at pH 8.3

- 135 Following EC:H₂O₂ of SR-NOM at pH 8.3, the treated solution was orange (Figure S3),
- 136 indicating the presence of iron, and no visible floc formation, indicating unsuccessful
- 137 coagulation and flocculation. Accordingly, DOC was not measured for this experiment.



138

139 **Figure S3**. Unsuccessful floc precipitation following $EC:H_2O_2$ of SR-NOM at pH 8.3 in 4 mM HCO_3^- . 140

141 ESI S10 Multivariable analysis: Electrical Energy per Order

- 142 The multivariable regressions for electrical energy per order are shown in Table S17 and for
- 143 water quality impacts, they are shown in Table S19. Additionally, the Pearson correlations are
- 144 provided for water quality impacts in Table S18.
- 145

146 **Table S17.** Multiple regression of process inputs on E_{EO} .

Matrices	H ₂ O ₂ /Fe (β ₁)	Current Density (β ₂)	Model R ²	AIC	Number of points
All ratios	-0.13±0.09 (<i>p=0.16</i>)	0.36±0.09 (p<0.0001)	0.40	214	36

147

148 Table S18. Pearson correlation of the impact of water quality on E_{EO} and pseudo-first order rate. **

149 indicates p<0.05.

		Rate	DOC			
	EEO	Constant	initial	Alkalinity	рН	Conductivity
EEO	1.00					
Rate Constant	-0.73**	1.00				
DOC initial	0.58**	-0.55**	1.00			
			-			
Alkalinity	-0.18	0.46**	0.55**	1.00		
рН	0.46**	-0.66**	-0.13	-0.27	1.00	
Conductivity	0.06	-0.44**	0.59**	-0.39**	-0.12	1.00

150

151 Table S19. Multivariable linear regression of water quality impact on E_{EO}.

Matrices	DOC _{initial} (β ₁)	Alkalinity (β ₂)	pΗ (β ₃)	Conductivity (β₄)	Model R ²	AIC	Number of points
All	1.2±0.15	0.45±0.11	0.63±0.09	-0.29±0.1	0.96	172	20
Matrices	(p<0.0001)	(p=0.0013)	(p<0.0001)	(p<0.0001)	0.86	123	20

152