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## Peroxi-electrocoagulation for treatment of trace organic compounds and natural organic matter at neutral pH†

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Iron-based oxidation technologies can be advantageous for mitigating trace organic compounds (TOCs) during water and wastewater treatment due to their production of hydroxyl radicals. However, iron-based oxidation often occurs at acidic pH to promote Fenton's reaction, which limits the processes' feasibility for treatment applications. This study focused on utilizing iron-electrocoagulation (EC) paired with *ex situ* H<sub>2</sub>O<sub>2</sub> addition (peroxi-electrocoagulation [EC:H<sub>2</sub>O<sub>2</sub>]) to promote oxidative reactions at neutral pH conditions. The hydroxyl radical probe *para*-chlorobenzoic acid (*p*CBA) was used to gauge oxidant activity and serve as a representative TOC. The impact of water pH, current density, iron dose, H<sub>2</sub>O<sub>2</sub> dose (*i.e.*, [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub>/[Fe<sup>2+</sup>]<sub>generated</sub> ratio), and the presence of natural organic matter (NOM) were evaluated. Multivariable regressions showed that high levels of H<sub>2</sub>O<sub>2</sub> relative to iron (*i.e.*, [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub>/[Fe<sup>2+</sup>]<sub>generated</sub> ratio >0.7) inhibited the rate of *p*CBA oxidation, likely due to additional radical quenching from extra H<sub>2</sub>O<sub>2</sub>. Oxidation of *p*CBA was confirmed at neutral pH conditions, indicating that EC:H<sub>2</sub>O<sub>2</sub> may potentially serve as a multi-mechanistic treatment technology capable of oxidation. Experiments were also conducted in real-world water samples to gauge EC:H<sub>2</sub>O<sub>2</sub> applications for treating groundwater, river water, and primary treated wastewater. Overall, H<sub>2</sub>O<sub>2</sub> addition enhanced the oxidative degradation of TOCs while still removing NOM. The one exception was the primary effluent sample, which had the highest degree of oxidant scavenging of all matrices tested. The electrical energy per order (*E*<sub>EO</sub>) metric demonstrated that EC:H<sub>2</sub>O<sub>2</sub> is competitive with other TOC oxidation technologies, with the added benefit of NOM mitigation in the same unit process.

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### Environmental significance

As trace organic compounds are increasingly being monitored in drinking water, technologies are needed that can mitigate their risks. Iron-electrocoagulation paired with hydrogen peroxide can potentially serve as an oxidative technology for these contaminants, and can simultaneously remove trace organics and bulk organics such as natural organic matter within the same unit process. This combined process can be particularly advantageous for rural and decentralized systems due to multiple treatment processes occurring within the same reactor and favorable energy requirements as compared to oxidation technologies such as UV-H<sub>2</sub>O<sub>2</sub> and ozonation.

## 1. Introduction

Iron has expansive applications for water and wastewater treatment. Different iron-based treatment pathways proceed depending on the valence state of the iron (*e.g.*, ferrous [Fe<sup>2+</sup>] or ferric [Fe<sup>3+</sup>]). Iron speciation varies as a function of pH and the presence of dissolved oxygen in water. Ferric iron predominates

in the oxygen-rich neutral and basic pH conditions that are typical for water and wastewater treatment. During coagulation, iron is dosed as ferric chloride or ferric sulfate targeting removal of turbidity and natural organic matter (NOM).<sup>1</sup> Alternately, Fe<sup>2+</sup> predominantly exists in acidic conditions, and can mediate oxidative treatment *via* Fenton's reaction, which produces hydroxyl radicals (HO<sup>•</sup>) that can oxidize trace organic compounds (TOCs).<sup>2–4</sup> Accordingly, iron-based treatments typically feature either non-destructive removal or oxidative destruction due to dominant pathways under different pH conditions.<sup>5</sup> Research is needed to simultaneously promote both non-destructive and oxidative destructive pathways through Fenton's reaction at circumneutral pH for treating multiple classes of contaminants such as bulk organics (*i.e.*,

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NOM) and TOCs in a single unit process, which can be beneficial for water and wastewater treatment facilities.

Fenton's reaction relies on non-complexed  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  as reagents to form  $\text{HO}^\bullet$  (Reaction 1, Table 1). Hydroxyl radicals are highly reactive (2.8 V vs. standard hydrogen electrode) and can react with Fenton's reagents (Reactions 4 and 5) at faster rates ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) than the radicals are generated ( $40\text{--}80 \text{ M}^{-1} \text{ s}^{-1}$ ), which terminates Fenton's reaction due to oxidant and reagent depletion and hinders treatment effectiveness. However, in acidic conditions (pH 2–4), soluble  $\text{Fe}^{3+}$  can be recycled into  $\text{Fe}^{2+}$  (Reaction 2), thereby continuing  $\text{HO}^\bullet$  generation without reagent depletion.

At neutral pH conditions in water and wastewater treatment, the feasibility of Fenton's reaction is limited for several reasons:

1. Iron speciation shifts toward  $\text{Fe}^{3+}$ , which is less soluble and more prone to floc formation compared to  $\text{Fe}^{2+}$ , resulting in termination of the Fenton's reaction cycle by inhibiting regeneration of  $\text{Fe}^{2+}$  required for oxidant generation.

2. Dissolved oxygen readily oxidizes  $\text{Fe}^{2+}$  in neutral and basic pH conditions (Reaction 3). Each increase in pH unit increases the oxidation rate of  $\text{Fe}^{2+}$  100-fold, leading to less available Fenton's reagents.<sup>9,10</sup>

3. Anionic ligands in natural waters (e.g.,  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ ) form complexes with  $\text{Fe}^{2+}$ , which decreases the amount of non-complexed  $\text{Fe}^{2+}$  available to react with  $\text{H}_2\text{O}_2$  to generate oxidants.<sup>6</sup>

Accordingly, pH limitations restrict Fenton applications to a narrow pH range (pH 2–4), which impedes implementation in water and wastewater treatment due to the intensive pH adjustments to acidify and neutralize waters before and after treatment. Additionally, acidic waters can enhance corrosion of infrastructure and shift the pH of natural waters following discharge.<sup>6</sup>

To facilitate Fenton oxidation at neutral pH, the key premise relies on generating or stabilizing the  $\text{Fe}^{2+}$  needed to react with  $\text{H}_2\text{O}_2$  to form  $\text{HO}^\bullet$ . Accordingly, electrochemical water treatment processes, such as electrocoagulation (EC), may be used for Fenton oxidation at neutral pH by generating non-complexed  $\text{Fe}^{2+}$  via anodic dissolution of iron electrodes.<sup>11</sup>

Continuous generation of  $\text{Fe}^{2+}$  can be advantageous for Fenton oxidation at neutral pH by minimizing the need for  $\text{Fe}^{3+}$  reduction to  $\text{Fe}^{2+}$  via  $\text{H}_2\text{O}_2$  (Reaction 2). Prior research has also shown that EC alone can generate  $\text{HO}^\bullet$  to treat TOCs through the *in situ* generation of  $\text{Fe}^{2+}$  at the anode and  $\text{H}_2\text{O}_2$  production at the cathode.<sup>12–14</sup> During electrolysis, the microenvironment near the anode surface is acidic.<sup>15</sup> Consequently, Fenton reactions may occur at the vicinity of the anode surface even if the bulk solution pH is circumneutral, potentially leading to oxidative conditions at neutral pH between  $\text{H}_2\text{O}_2$  and the iron anode surface. Supplemental addition of  $\text{H}_2\text{O}_2$  as a radical promotor, known as peroxi-electrocoagulation (EC: $\text{H}_2\text{O}_2$ ), can further enhance EC's oxidizing capacity and serve as a multi-mechanistic process. During EC: $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  is continually generated at low concentrations ( $\text{nM s}^{-1}$  based on Faraday's law) over the course of electrolysis, such that non-complexed  $\text{Fe}^{2+}$  is available for oxidation by  $\text{H}_2\text{O}_2$ . As a result, less  $\text{Fe}^{2+}$  is “wasted” as a Fenton's reagent by non-radical generating side reactions such as ligand complexation or oxygenation.<sup>11</sup> This combination of  $\text{Fe}^{2+}$  reagent generation and minimal reliance on  $\text{Fe}^{3+}$  reduction to  $\text{Fe}^{2+}$  can make EC: $\text{H}_2\text{O}_2$  an advantageous dosing method compared to *ex situ* reagent dosing in Fenton applications. Of note, while *in situ*  $\text{Fe}^{2+}$  dosing can be advantageous, *ex situ*  $\text{H}_2\text{O}_2$  dosing may still be needed, depending on EC: $\text{H}_2\text{O}_2$  reactor design.

Pratap and Lemley (1998, 1994)<sup>8,16</sup> demonstrated point-of-concept use of EC: $\text{H}_2\text{O}_2$  for remediation of the herbicides atrazine and metalochlor at neutral pH conditions. Since the inception of EC: $\text{H}_2\text{O}_2$ , research has primarily focused on coagulation/flocculation during industrial wastewater treatment for removing bulk organic pollutants (such as chemical oxygen demand) at high concentrations ( $\text{mg L}^{-1}$  levels).<sup>5,17–22</sup> However, these high-strength wastewater studies do not translate well to municipal wastewater and drinking water treatment applications. For example, environmental waters have lower conductivity, fewer oxidant scavengers, higher dissolved oxygen, and neutral pH conditions, all of which impact the oxidative efficiency of EC: $\text{H}_2\text{O}_2$  and speciation of iron in water. Considering iron's treatment capabilities, EC: $\text{H}_2\text{O}_2$  may also

Table 1 Fenton's reaction. Iron species are color-coded to reflect the valence state: blue represents ferrous iron ( $\text{Fe}^{2+}$ ) and orange represents ferric iron ( $\text{Fe}^{3+}$ )<sup>a</sup>

Reaction	Chemical reaction	Role
1	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{OH}^-$	Radical production
2	$\text{Fe}_{(\text{aq})}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^\bullet + \text{H}^+$	Ferrous regeneration via ferric reduction
3	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\text{OH}^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3(\text{s})$	Oxygenation of ferrous iron, reagent quenching
4	$\text{Fe}^{2+} + \text{HO}^\bullet \rightarrow \text{Fe}^{3+} + \text{OH}^-$	Radical quenching, reagent quenching
5	$\text{H}_2\text{O}_2 + \text{HO}^\bullet \rightarrow \text{HO}_2^\bullet + \text{H}_2\text{O}$	Radical quenching, reagent quenching

<sup>a</sup> Reactions adapted from ref. 2, 3 and 6–9.



offer an opportunity for simultaneous treatment of TORCs and bulk organics (e.g., NOM and chemical oxygen demand) in a single unit process as the  $\text{Fe}^{3+}$  produced following Fenton's reaction can subsequently contribute to physical removal (i.e., non-destructive removal) of contaminants through coagulation, flocculation, and sedimentation processes.

The goal of this research was to evaluate EC:H<sub>2</sub>O<sub>2</sub> for simultaneous treatment of both TORCs and NOM at neutral pH conditions. To vet oxidation, *para*-chlorobenzoic acid (*p*CBAs) was selected as the representative TORC, and also served as a HO<sup>•</sup> probe for advanced oxidation process (AOP) effectiveness.<sup>23</sup> The relative impacts of current density (i.e., iron dosing rate), H<sub>2</sub>O<sub>2</sub> dose, and the corresponding  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio were tested in synthetic matrices. Experiments were conducted to differentiate non-destructive removal *via* EC-only from oxidative destructive removal and to assess the contribution of potential oxidants generated in EC:H<sub>2</sub>O<sub>2</sub> such as HO<sup>•</sup> and H<sub>2</sub>O<sub>2</sub>. Experiments were also conducted using surface water, groundwater, and wastewater sources to evaluate the influence of water quality parameters (i.e., dissolved organic carbon [DOC], pH, conductivity, and ions) and the feasibility of EC:H<sub>2</sub>O<sub>2</sub> for different treatment applications. Finally, electrical energy per order of magnitude reduction ( $E_{\text{EO}}$ ) was calculated for all matrices to provide a means of comparing EC:H<sub>2</sub>O<sub>2</sub> energy requirements relative to other advanced oxidation processes.

## 2. Materials and methods

### 2.1. Experimental protocols for EC:H<sub>2</sub>O<sub>2</sub> tests of *p*CBAs removal

The EC:H<sub>2</sub>O<sub>2</sub> batch experiments were conducted for 15 minutes of electrolysis with 150 rpm mixing ( $G = 180 \text{ s}^{-1}$ ) in 4 mM  $\text{HCO}_3^-$  buffer solutions containing 400  $\mu\text{g L}^{-1}$  *p*CBAs. The *p*CBAs concentration of 400  $\mu\text{g L}^{-1}$  was selected based on reliable analytical quantification of >90% removal at a target *p*CBAs concentration below that of mg L<sup>-1</sup>-level background oxidant scavengers (i.e., NOM). Electrolysis was performed in 200 mL polypropylene beakers using 1020 steel iron electrodes (VMetals, Milwaukee, WI), which were sanded and wet polished with 320 grit silicon carbide sandpaper prior to experiments. An XPH 75-2D Dual DC power supply (Sorenson Electronics, Cedar City, UT) was used to carry out electrolysis at currents ranging from 40 mA to 200 mA through a submerged electroactive surface area of 13.5 cm<sup>2</sup>, as described in Ryan *et al.* (2020).<sup>24</sup> The power supply was equipped with a polarity reversal device to alternate the anode and cathode every 30 seconds based on prior works.<sup>25</sup> For evaluating oxidative treatment, *p*CBAs (99%, Sigma Aldrich, St. Louis, MO) was selected as the HO<sup>•</sup> probe due to its resistance to sorption on iron flocs and frequent use as a radical probe to demonstrate the treatability of TORCs by HO<sup>•</sup> exposure.<sup>23,26–28</sup> Compared to other TORCs, *p*CBAs is classified as having “moderate reactivity” with HO<sup>•</sup>, as reported by Gerrity *et al.* (2012),<sup>23</sup> which is similar to TORCs of concern such as atrazine and 1,4-dioxane.<sup>23</sup>

Three reactor inputs – current density, H<sub>2</sub>O<sub>2</sub> dose, and the corresponding  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio – were evaluated

to gauge their relative influence on treatment. For EC experiments, the current density was synonymous with the iron loading rate. The iron applied in each test was varied by adjusting the current density (and consequently the iron loading rate). For these experiments, the current density ranged from 3 to 15 mA cm<sup>-2</sup> (charge loading rate = 12–60 Coulomb L<sup>-1</sup> min<sup>-1</sup>, iron loading rate = 3.5–17.3 mg-Fe<sup>2+</sup> per L-min). The H<sub>2</sub>O<sub>2</sub> stock (ACS reagent grade, Sigma Aldrich, St. Louis, MO) was added at the beginning of EC:H<sub>2</sub>O<sub>2</sub> experiments at levels ranging from 10 to 200 mg H<sub>2</sub>O<sub>2</sub> per L to assess *p*CBAs treatment resulting from a fixed amount of H<sub>2</sub>O<sub>2</sub> available for Fe<sup>2+</sup> to generate radicals. The corresponding  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  was 0.3–1.6 based on current density and H<sub>2</sub>O<sub>2</sub> inputs. Notably, the  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio reflects the total H<sub>2</sub>O<sub>2</sub> added at the beginning of the reaction, divided by the amount of Fe<sup>2+</sup> generated by EC (estimated by Faraday's Law) by the end timepoint when *p*CBAs removal ceased due to H<sub>2</sub>O<sub>2</sub> depletion. The end timepoint of the *p*CBAs degradation reaction was determined as the time point at which less than 10% difference in *p*CBAs removal compared to the preceding time point was observed, likely indicating depletion of H<sub>2</sub>O<sub>2</sub>. Samples were collected every 2.5 minutes for 10 minutes, with a final sample at 15 minutes for kinetic analyses. Kinetic curves were fit to at least four data points ( $R^2 > 0.95$  for all) to calculate first order rate constants for *p*CBAs degradation for samples collected prior to H<sub>2</sub>O<sub>2</sub> depletion, assessed as noted above.

### 2.2. Removal pathway control experiments

Experiments were conducted under the same electrolysis and current density conditions described in Section 2.1 to isolate the impact of different system inputs and delineate the potential treatment pathways in EC:H<sub>2</sub>O<sub>2</sub>, including oxidation by HO<sup>•</sup> and H<sub>2</sub>O<sub>2</sub> as well as physical removal by sorption to iron flocs. For HO<sup>•</sup> oxidation controls, methanol was spiked in stoichiometric excess (12 mM MeOH) of *p*CBAs and H<sub>2</sub>O<sub>2</sub> to quench HO<sup>•</sup> that would otherwise react with *p*CBAs. In this case, H<sub>2</sub>O<sub>2</sub> is reactive with electron-dense compounds and unlikely to react with unsaturated alcohols such as methanol. For no electricity controls (e.g., H<sub>2</sub>O<sub>2</sub> controls), 30 mg-H<sub>2</sub>O<sub>2</sub> per L was spiked into the reactors containing the iron electrodes and stirred for 15 minutes to assess the potential *p*CBAs removal due to H<sub>2</sub>O<sub>2</sub> under treatment conditions without electricity in addition to potential losses *via* sorption to the electrode surface.

Kinetic analyses were conducted to estimate the competition between H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> as a function of H<sub>2</sub>O<sub>2</sub> inputs and water chemistry conditions (H<sub>2</sub>O<sub>2</sub> dose, O<sub>2</sub>, and pH). These tests assessed the feasibility of HO<sup>•</sup> generation under neutral pH conditions and informed mechanistic analyses (oxidation by O<sub>2</sub> limits HO<sup>•</sup> production by generating Fe<sup>3+</sup>). The relative rates of oxidation and associated rate constants are provided in the ESI S4.†

### 2.3. Water quality conditions

All EC:H<sub>2</sub>O<sub>2</sub> experiments were conducted in 4 mM bicarbonate solution (with the exception of the environmental waters) to simulate buffered conditions for neutral pH environmental



Table 2 Water quality parameters

Water matrix	Initial pH	H <sub>2</sub> O <sub>2</sub> demand, <sup>a</sup> mg L <sup>-1</sup> (% H <sub>2</sub> O <sub>2</sub> removal)	DOC, mg-C per L	Alkalinity, mg L <sup>-1</sup> as CaCO <sub>3</sub>	Conductivity, μS cm <sup>-1</sup>	Ca <sup>2+</sup> , mg L <sup>-1</sup>	Mg <sup>2+</sup> , mg L <sup>-1</sup>
Bicarbonate buffer <sup>b</sup>	8.3 <sup>c</sup>	0 (0%)	0, 7.5 <sup>d</sup>	210	370 <sup>e</sup>	0	0
Groundwater	7.30	10 (33%)	3.3	400	1430	70	40
River water	8.4	5 (15%)	7.0	240	755	30	20
Primary wastewater effluent	7.1	23 (75%)	55	280	1400	40	15

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> demand is reported as the decrease in H<sub>2</sub>O<sub>2</sub> concentration after 15 minutes (the length of batch experiments), where the initial concentration was 30 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>. <sup>b</sup> All model waters were prepared in Milli-Q water with 4 mM HCO<sub>3</sub><sup>-</sup>. <sup>c</sup> pH varied from 3 to 10.3 depending on the experiment. The unadjusted pH was 8.3. <sup>d</sup> For NOM tests, NOM was added as International Humic Substance Society Suwannee River NOM. <sup>e</sup> Conductivity varied for pH tests due to the addition of acid (HCl) or base (NaOH) for pH adjustment. At pH 3, conductivity = 920 μS cm<sup>-1</sup>. At pH 6.3, conductivity = 450 μS cm<sup>-1</sup>. At pH 10.3, conductivity = 750 μS cm<sup>-1</sup>. For unadjusted pH, conductivity = 370 μS cm<sup>-1</sup>.

waters containing alkalinity, and to supply an electrolyte for electrochemical reactions (Table 2). Environmental waters were sampled to assess the impact of water quality and treatment performance in real waters relative to synthetic waters containing different NOM sources (Table 2). These analyses are important for informing the role of other environmentally relevant water quality parameters such as NOM characteristics and concentration, conductivity, and divalent cations, all of which can impact treatment efficacy. A sample from the Milwaukee River (Milwaukee, WI) was used to test the impact of NOM and mid-range conductivity water. Groundwater from a drinking water well in West Bend, WI, was tested to reflect low dissolved organic carbon (DOC) and high conductivity conditions. Finally, primary effluent from an urban water reclamation facility in Milwaukee, WI, was tested for the impact of high DOC due to anthropogenic NOM and other oxidant scavengers (such as bulk chemical oxygen demand). The wastewater also served as a point of comparison to previous EC:H<sub>2</sub>O<sub>2</sub> wastewater studies. For DOC quantification experiments, a sedimentation phase was required after EC:H<sub>2</sub>O<sub>2</sub> to allow the flocs to settle prior to DOC analysis. Batch tests were performed as described in Section 2.1 followed by an additional tapered flocculation phase (10 minutes at 40 rpm [ $G = 25 \text{ s}^{-1}$ ] and 10 minutes at 20 rpm [ $G = 9 \text{ s}^{-1}$ ]) and a 20 minute sedimentation period to remove flocs (method adapted from Ryan *et al.* (2020)).<sup>24</sup>

**2.3.1. Analytical measurements.** Liquid chromatography-mass spectrometry was utilized to quantify *p*CBA (method adapted from Vanderford *et al.* (2007)<sup>28</sup>). All *p*CBA samples were filtered through 0.22 μm PTFE syringe filters (Agela Technologies, Wilmington, DE) prior to analyses. Additional information on chromatography and mass spectrometry conditions is provided in ESI S1.† The H<sub>2</sub>O<sub>2</sub> concentrations before and after each experiment were measured using Hach Model Hyp-1 test kits. The DOC was measured *via* a Shimadzu TOC - V<sub>CSN</sub> based on U.S. EPA Method 415.3. All DOC samples were filtered through 0.45 μm PTFE filters (Agela Technologies) prior to analyses. ICP-MS (7700 series, Agilent Technologies, Santa Clara, CA) was used to measure cations in real-world water samples. Alkalinity was measured *via* titration using Hach Model 2443-89 test kits.

**2.3.2. Electrical energy per order.** Electrical energy per order of magnitude removal ( $E_{EO}$ ), as shown in eqn (1), was estimated to provide a figure of merit for comparing energy requirements (kW h m<sup>-3</sup>-order) for EC:H<sub>2</sub>O<sub>2</sub> to other oxidative treatment technologies.<sup>29</sup> The voltage reading was recorded for each current density during each test to calculate power (power = voltage × current). Pseudo-first order rate constants were used to normalize treatment times across experiments as different reactor inputs and water quality conditions required different treatment times for 90% *p*CBA removal.

$$E_{EO} = \frac{P}{V \times 0.4343k \times 3600 \times 1000} \quad (1)$$

where  $P$  is power in W,  $V$  is volume in m<sup>3</sup>, and  $k$  is the pseudo-first order rate constant for *p*CBA removal in s<sup>-1</sup>. The coefficient of 0.4343 = log( $C_0/C_i$ ) for one order of magnitude reduction. The conversion factor 3600 is used to convert seconds to hours, and 1000 is used to convert W to kW.

**2.3.3. Data analysis and interpretation.** GraphPad Prism (version 9.5.1.) software was used to conduct one-way and two-way ANOVA followed with Tukey's multiple comparison post-hoc test, Pearson correlations, and multivariable linear regressions. Multivariable linear regressions were used as explanatory models to evaluate the contributions of system inputs (H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, and [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub>/[Fe<sup>2+</sup>]<sub>generated</sub>) and the impact of water quality parameters. Independent variables for the EC:H<sub>2</sub>O<sub>2</sub> process were selected based on Pearson correlations and normalized using the min-max method. This min-max normalization method was conducted to minimize the artificial impacts of independent variables on the dependent variable due to different scales and ranges of inputs (*e.g.*, rate constants were on the order of 10<sup>-4</sup> s<sup>-1</sup>, whereas H<sub>2</sub>O<sub>2</sub> ranged from 10 to 100 mg L<sup>-1</sup>).<sup>30</sup> The independent variables for reactor inputs (pH, [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub>/[Fe<sup>2+</sup>]<sub>generated</sub>, and current density) were selected for the multivariable linear regression model based on their correlation to the dependent variables: *p*CBA removal, pseudo-first order rate constant, and  $E_{EO}$ . For environmental waters, DOC<sub>initial</sub>, alkalinity, pH, and conductivity were selected as the independent water quality variables. All independent variables selected for multivariable linear regression were not multicollinear with other variables based on variance inflation factors <5 for all regressions.<sup>31</sup>



### 3. Results and discussion

#### 3.1. *Para*-chlorobenzoic acid removal for hydroxyl radical validation

Removal of *p*CBA during EC:H<sub>2</sub>O<sub>2</sub> primarily proceeded *via* oxidation at neutral pH conditions due to the system's combination of iron and H<sub>2</sub>O<sub>2</sub> (Fig. 1). EC-only controls yielded an average *p*CBA removal of approximately 15%, presumably due to the low levels of HO<sup>•</sup> that can be generated during EC alone.<sup>13,14</sup> For EC:H<sub>2</sub>O<sub>2</sub> + MeOH experiments, the high MeOH concentration (12 mM) scavenged the oxidants and resulted in negligible *p*CBA degradation. This scavenging indirectly underscores the role of homogeneous oxidants (such as HO<sup>•</sup>). Negligible *p*CBA removal in the EC:H<sub>2</sub>O<sub>2</sub> + MeOH test further indicates that *p*CBA does not sorb to iron flocs. The 'No Electricity Control' experiments demonstrated that potential reactions between H<sub>2</sub>O<sub>2</sub> and the iron electrode surface had minimal removal relative to the EC:H<sub>2</sub>O<sub>2</sub> conditions with electricity ( $p < 0.0001$ , one-way ANOVA) at circumneutral pH conditions. Overall, these data demonstrate that the addition of H<sub>2</sub>O<sub>2</sub> can enhance oxidant production in EC:H<sub>2</sub>O<sub>2</sub> relative to EC alone and induce oxidative processes at neutral pH conditions.

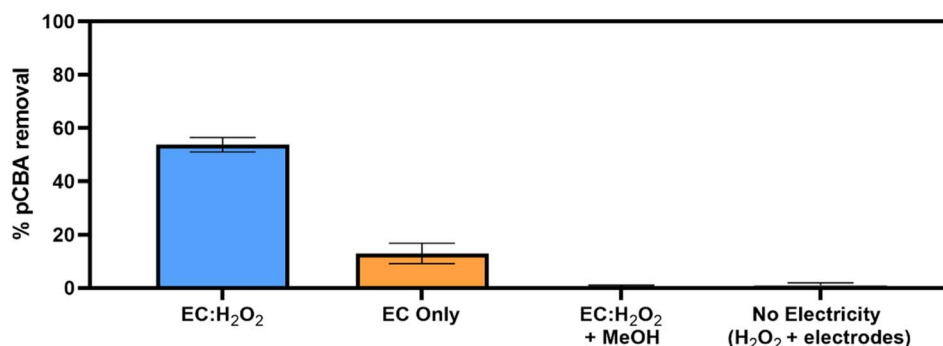
The occurrence of oxidation at neutral pH conditions during EC:H<sub>2</sub>O<sub>2</sub> is important in the context of Fenton literature since traditional Fenton oxidation proceeds at highly acidic pH 3 conditions. These conventional Fenton conditions limit the feasibility of EC:H<sub>2</sub>O<sub>2</sub> applications as the high acidity can damage infrastructure, enhance corrosion, and incur chemical costs for acidifying and neutralizing water during treatment.

#### 3.2. The impact of reactor inputs on *p*CBA degradation during EC:H<sub>2</sub>O<sub>2</sub>: removal and kinetics

Following oxidant verification, the impact of EC:H<sub>2</sub>O<sub>2</sub> reactor inputs and water quality were assessed. The discussion centers on the role of  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios, current density, and pH. Multivariable linear regressions were used to parameterize the contribution of all inputs.

**3.2.1. The impact of H<sub>2</sub>O<sub>2</sub> dose, current density, and iron dose on *p*CBA removal at neutral pH conditions.** The efficacy of H<sub>2</sub>O<sub>2</sub> dose for *p*CBA removal varied as a function of the  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio (Fig. 2A). The presence of H<sub>2</sub>O<sub>2</sub> only improved treatment when Fe<sup>2+</sup> was also present in the system ( $R_{\text{H}_2\text{O}_2\text{-all:removal}}^2 = 0.003$ ,  $p = 0.99$  Pearson correlation, Table S13<sup>†</sup>). With 10–40 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, there was a positive correlation between *p*CBA removal and H<sub>2</sub>O<sub>2</sub> dose during EC:H<sub>2</sub>O<sub>2</sub> when iron was also present in the system ( $R_{\text{H}_2\text{O}_2\text{:removal}}^2 = 0.84$ ,  $p < 0.05$  Pearson correlation, Table S14<sup>†</sup>). Once H<sub>2</sub>O<sub>2</sub> exceeded 30 mg L<sup>-1</sup> in the presence of Fe<sup>2+</sup>, *p*CBA removal began to plateau around 50–60% *p*CBA removal for  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios ranging from 0.3 to 0.7. In contrast, the higher  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio of 1.6 resulted in less *p*CBA removal compared to the same H<sub>2</sub>O<sub>2</sub> dose applied at lower ratios. Alternately, for H<sub>2</sub>O<sub>2</sub> concentrations greater than 40 mg L<sup>-1</sup>, the H<sub>2</sub>O<sub>2</sub> dose did not significantly correlate ( $R_{\text{H}_2\text{O}_2>40\text{:removal}}^2 = -0.377$ ,  $p = 0.136$ , Pearson correlation, Table S15<sup>†</sup>) and resulted in less *p*CBA removal. For example, 50 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> had approximately 60% *p*CBA removal when applied at  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}} = 0.35$ ; when the ratio increased to  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}} = 1.6$ , *p*CBA removal decreased to 40% for all H<sub>2</sub>O<sub>2</sub> doses. The inhibition of *p*CBA removal at higher H<sub>2</sub>O<sub>2</sub> levels aligns with the scavenging impact of H<sub>2</sub>O<sub>2</sub> and competition between matrix constituents. Although more H<sub>2</sub>O<sub>2</sub> can be beneficial for HO<sup>•</sup> generation *via* Fenton's reaction, higher H<sub>2</sub>O<sub>2</sub> levels lead to a higher degree of oxidant scavenging and decreased radical availability for *p*CBA removal (ESI S3).<sup>†</sup>

The key role of current density in this study was to adjust the iron loading rate to add Fe<sup>2+</sup> as Fenton's reagent (Fig. 2B). When no H<sub>2</sub>O<sub>2</sub> was present (*i.e.*, EC-only), *p*CBA removal was consistently less than 20% regardless of current density (Fig. 2C). Hence, EC offered effective *p*CBA removal only when H<sub>2</sub>O<sub>2</sub> was present, indicating that the  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio was the key driver of treatment efficacy. During EC:H<sub>2</sub>O<sub>2</sub>, *p*CBA removal improved with increases in current density up to 7.4 mA cm<sup>-2</sup> ( $R_{\text{current density}=3 \text{ to } 7.4 \text{ mA cm}^{-2}}^2 = 0.63$ ,  $p = 0.008$ ,



**Fig. 1** Mechanisms for *p*CBA removal during EC:H<sub>2</sub>O<sub>2</sub> at 7.40 mA cm<sup>-2</sup>. A series of controlled batch experiments were run in 4 mM bicarbonate buffer at pH 8.3 for 15 minutes. In "EC only," electrolysis was conducted using iron electrodes with no peroxide addition. For "EC:H<sub>2</sub>O<sub>2</sub> + MeOH", methanol was spiked in stoichiometric excess of *p*CBA (12 mM MeOH:2.5 μM *p*CBA) to quench oxidants that would otherwise degrade *p*CBA. In "No Electricity (H<sub>2</sub>O<sub>2</sub> + electrodes)", 30 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> was spiked into the solution with the iron electrodes and mixed for 15 minutes. All experiments were conducted in duplicate and error bars indicate ± 1 standard deviation. EC-only results are the average of all duplicate experiments for each EC-only control, including current densities of 3.5 mA cm<sup>-2</sup>, 5.5 mA cm<sup>-2</sup>, 11.1 mA cm<sup>-2</sup>, and 15 mA cm<sup>-2</sup>, where  $n = 8$ .



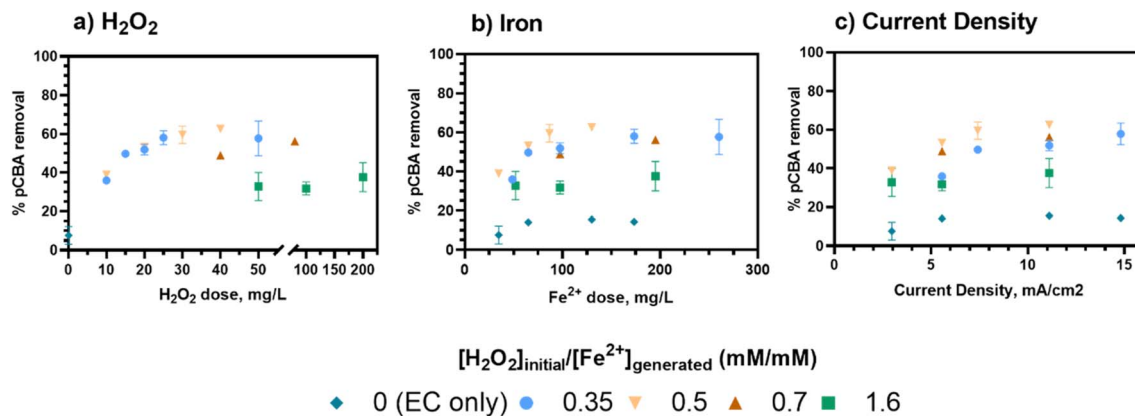


Fig. 2 *p*CBA removal after 15 minute EC:H<sub>2</sub>O<sub>2</sub> batch experiments as a function of (a) H<sub>2</sub>O<sub>2</sub> initially dosed into the system, (b) total ferrous iron generated (estimated by Faraday's law) over the course of the EC:H<sub>2</sub>O<sub>2</sub> experiment, and (c) current density, which is proportional to the iron loading rate (mg-Fe per L). Iron loading rates were estimated using Faraday's law, where 3 mA cm<sup>-2</sup> = 3.5 mg-Fe per L-min, 5.5 mA cm<sup>-2</sup> = 6.5 mg-Fe per L-min, 7.4 mA cm<sup>-2</sup> = 8.6 mg-Fe per L-min, 11.1 mA cm<sup>-2</sup> = 13 mg-Fe per L-min, and 15 mA cm<sup>-2</sup> = 17.4 mg-Fe per L-min. All experiments were conducted in duplicate and error bars indicate ± 1 standard deviation.

Pearson correlation, Table S16†) and plateaued after 7.4 mA cm<sup>-2</sup> ( $R_{\text{current density} > 7.4 \text{ mA cm}^{-2}} = 0.141$ ,  $p = 0.6$ , Pearson correlation). As treatment inputs increased, the higher ratio of  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}} = 1.6$  had the least *p*CBA removal for EC:H<sub>2</sub>O<sub>2</sub> regardless of current density. The plateau in *p*CBA removal for higher current density may suggest that a minimum level of iron is needed for this system, and beyond that level, additional iron no longer improves treatment. Here, the lowest Fe<sup>2+</sup> loading rate was 3.5 mg Fe per L-min (resulting from 3 mA cm<sup>-2</sup> current density).

In summary,  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios were the key driver for *p*CBA removal where lower ratios (0.33–0.7) had higher removal ( $\beta_{\text{H}_2\text{O}_2/\text{Fe}=0-0.7} = 0.77$ ,  $p < 0.0001$ , multivariable linear regression: “% *R*, low ratio, neutral pH”) from minimal HO<sup>•</sup> scavenging, and higher ratios (1.6) decreased removal ( $\beta_{\text{H}_2\text{O}_2/\text{Fe}=0.3-1.6} = -0.42$ ,  $p = 0.0008$ , multivariable linear regression: “% *R* EC: H<sub>2</sub>O<sub>2</sub> neutral pH”). This finding is important when considering material requirements including the *ex situ* H<sub>2</sub>O<sub>2</sub> additions and the power demands associated with iron generation. For this system, H<sub>2</sub>O<sub>2</sub> levels determined the treatment capacity because *p*CBA removal ceased after depletion of the one-time dose of H<sub>2</sub>O<sub>2</sub> at the start of the test, whereas the Fe<sup>2+</sup> was continually generated *via* electrolysis.

It is important to note that  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios do not translate to the actual ratio of H<sub>2</sub>O<sub>2</sub> relative to Fe<sup>2+</sup> at any timepoint during the test. During EC:H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> is initially in large excess to Fe<sup>2+</sup> as Fe<sup>2+</sup> is formed during EC, which may drive the rate of oxidant formation resulting from interactions between Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>. This excess is a result of Fe<sup>2+</sup> being generated at nM levels (e.g., 2500 nM s<sup>-1</sup> for 7.4 mA cm<sup>-2</sup> based on Faradays law) during electrolysis, which highlights the benefits of using iron electrolysis for Fe<sup>2+</sup> dosing to avoid side reactions and encourage efficient Fe<sup>2+</sup> utilization by H<sub>2</sub>O<sub>2</sub>.

**3.2.2. The impact of  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  and current density on *p*CBA oxidation rate during EC:H<sub>2</sub>O<sub>2</sub>.** Pseudo-first order kinetic modeling offered good data fits, enabled comparison to other AOP processes in the literature, and was

used in  $E_{\text{EO}}$  calculations. For a fixed current density of 5.5 mA cm<sup>-2</sup>,  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}} = 0.35, 0.5$ , and  $0.7$  had similar pseudo-first order rate constants ( $1.1 \times 10^{-3}$  to  $1.3 \times 10^{-3}$  s<sup>-1</sup>) before H<sub>2</sub>O<sub>2</sub> depletion (Fig. 3A and Table S5†). As the ratio increased, the rate of *p*CBA removal declined, which corroborates the removal findings in Section 3.2.1. Notably, for  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}} = 0.35$  and  $0.5$ , *p*CBA removal stagnated after 7.5 minutes and 10 minutes, respectively. Accordingly, H<sub>2</sub>O<sub>2</sub> should be continually dosed at lower concentrations in EC:H<sub>2</sub>O<sub>2</sub> operations in order to continue oxidative reactions without adding excess H<sub>2</sub>O<sub>2</sub> that can lead to quenching.

As shown in Fig. 3, for a fixed  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratio of  $0.5$ , the rate constants were comparable for current densities of  $5.5, 7.4$ , and  $11.1$  mA cm<sup>-2</sup> ( $1.3$  to  $1.6 \times 10^{-3}$  s<sup>-1</sup>, Table S5†). However,  $3$  mA cm<sup>-2</sup> had the lowest rate of removal ( $8.4 \times 10^{-4}$  s<sup>-1</sup>, Table S5†). This trend aligns with the removal data, in which the removal plateaued as current (*i.e.*, iron loading rate) increased, indicating that additional iron after a threshold level no longer improved treatment.

Overall, the ratio had the highest influence on rate of removal based on multivariable linear regressions ( $\beta_{[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]=0-0.77} = 0.76 \pm 0.11$ ,  $p < 0.0001$ , multivariable linear regression: “*k*, EC:H<sub>2</sub>O<sub>2</sub> low ratio, neutral pH”) (Fig. 3C). Considering both major inputs in terms of  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios, pseudo-first order rate constants were grouped into three clusters for a range of current densities at neutral pH conditions (Fig. 3C) to understand the general impact of different ratio levels. The clusters were EC-only conditions (*i.e.*, no H<sub>2</sub>O<sub>2</sub>),  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios =  $0.3$ – $0.7$ , and  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios greater than  $0.7$ . The lower  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios of  $0.3$ – $0.7$  had the highest rate constants, ranging from  $1.1 \times 10^{-3}$  to  $1.6 \times 10^{-3}$  s<sup>-1</sup>. The higher ratios of  $>0.7$  to  $1.6$  resulted in lower rate constants, ranging from  $5.8 \times 10^{-4}$  to  $7.7 \times 10^{-4}$  s<sup>-1</sup> ( $\beta_{[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]=0.3 \text{ to } 1.6} = -0.59 \pm 0.11$ ,  $p < 0.0001$ , multivariable linear regression: “*k*, EC:H<sub>2</sub>O<sub>2</sub> only, neutral pH”). For all cases, experiments containing H<sub>2</sub>O<sub>2</sub> had faster rates of *p*CBA removal compared EC-only controls ( $1.4 \times 10^{-4}$  to  $2.7 \times 10^{-4}$  s<sup>-1</sup>). However, higher levels of H<sub>2</sub>O<sub>2</sub> (greater than  $40$  mg L<sup>-1</sup>)



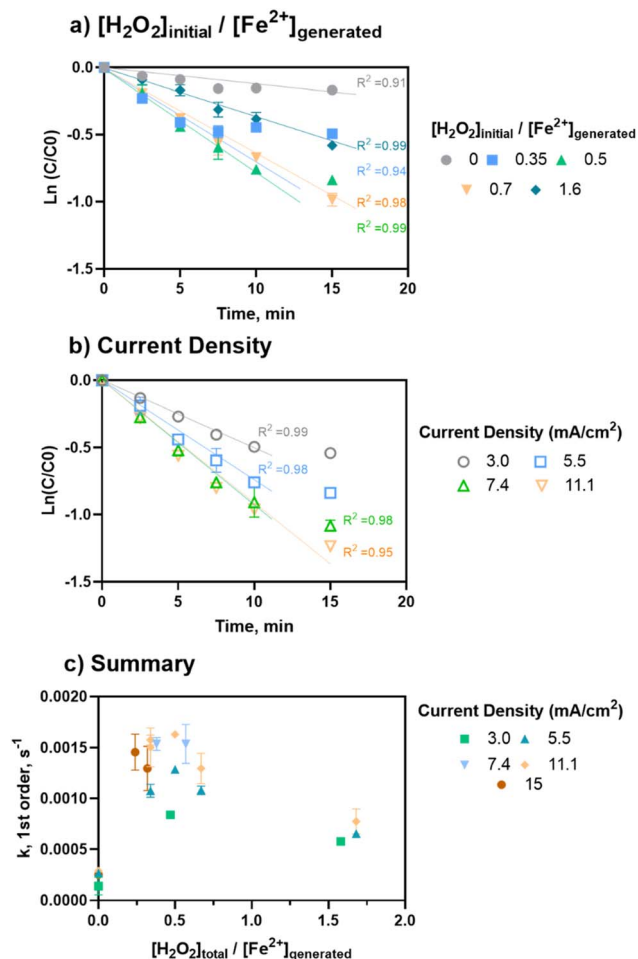


Fig. 3 Summary of pseudo-first order rate constants for degradation of *para*-chlorobenzoic acid (*pCBA*) following 15 minute EC:H<sub>2</sub>O<sub>2</sub> batch experiments. All experiments were conducted in 4 mM HCO<sub>3</sub><sup>-</sup> buffer at pH = 8.3. Samples were taken every 2.5 minutes for a total of 15 minutes. (a) Pseudo-first order kinetic curves showing the impact of  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  ratios for a fixed current density of 5.5 mA cm<sup>-2</sup>. (b) Pseudo-first order kinetic curves showing the impact of current density for a fixed  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  of 0.5. (c) Summary of pseudo-first order rate constants for all EC:H<sub>2</sub>O<sub>2</sub> batch experiments for all current density and  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  ratios. Pseudo-first order constants were determined and verified based on  $R^2 \geq 0.95$  over the course of treatment to capture the linear range prior to H<sub>2</sub>O<sub>2</sub> depletion. The end timepoint of the *pCBA* degradation reaction used in kinetic modeling was determined as the time point at which *pCBA* removal was less than 10% different than the preceding time point. Error bars show  $\pm 1$  standard deviation of duplicate experiments.

did not increase the rate of *pCBA* removal, likely due to radical quenching by H<sub>2</sub>O<sub>2</sub>. This is notable given that the effective H<sub>2</sub>O<sub>2</sub> doses found in this study are less than reagent demands in other EC:H<sub>2</sub>O<sub>2</sub> studies for industrial treatment applications.<sup>5,17–22</sup> Overall, these findings indicate that less H<sub>2</sub>O<sub>2</sub> may be required than previously thought for effective oxidation during EC:H<sub>2</sub>O<sub>2</sub>.

**3.2.3. The impact of pH on oxidation rate.** The impact of pH on *pCBA* oxidation was assessed to evaluate the interplay of Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>, and *pCBA* over a range of acid/base conditions. As pH decreased, *pCBA* removal increased and the rate of oxidation

accelerated (Fig. 4). At basic pH 10.3 conditions, minimal removal was observed. At pH 6.3, the maximum rate of *pCBA* degradation was observed (amongst the circumneutral pH levels tested),  $k = 4.6 \times 10^{-3} \text{ s}^{-1}$  (1.6 times faster than the rate at pH 8.3). Removal of *pCBA* ceased after 5 minutes (as indicated by the stagnation of the kinetic curve), likely due to depletion of H<sub>2</sub>O<sub>2</sub> at these conditions. Measurements of the H<sub>2</sub>O<sub>2</sub> remaining after 5 minutes demonstrated roughly 70% loss of the initial 30 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at pH 6.3 and 95% loss at pH 3 (ESI S7†). Depletion of the H<sub>2</sub>O<sub>2</sub> helps explain the stagnated *pCBA* removal, likely due to decreased formation of oxidants. Accordingly, H<sub>2</sub>O<sub>2</sub> should be continually dosed at lower concentrations in EC:H<sub>2</sub>O<sub>2</sub> to encourage continuous oxidative reactions and improve ToRC treatment.

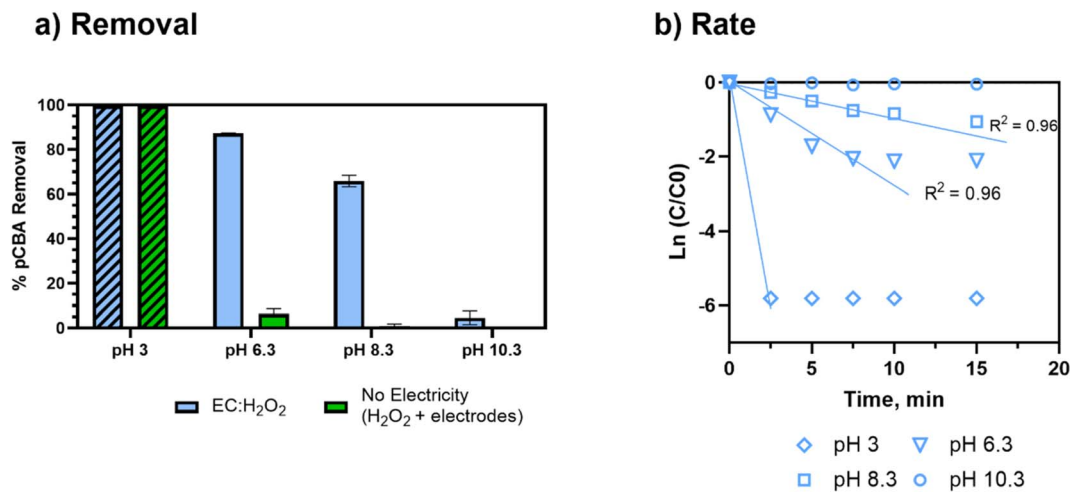
The acidic conditions (pH 3, encouraging Fenton's reactions) resulted in the greatest and fastest *pCBA* removal (>99% removal, to below the detectable limit). However, at pH 3, enhanced corrosivity led to >99% *pCBA* removal even without electricity, wherein increased iron dissolution was visually observed. For no electricity controls, *pCBA* removal was likely due to non-faradaic iron dissolving from the electrodes (30 mg Fe per L) and reacting with *ex situ* H<sub>2</sub>O<sub>2</sub> (98% H<sub>2</sub>O<sub>2</sub> removal; ESI S7†) to generate HO<sup>•</sup>. The no electricity control resulted in a  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  ratio of 1.5. Although this ratio was toward the upper end of ratios tested, the pH 3 conditions were expected to enhance the rate of reaction. For circumneutral conditions, the no-electricity controls had minimal *pCBA* removal, indicating no oxidant generation in the absence of electricity at the conditions tested.

Overall, the *pCBA* removal trends agree with the kinetic modeling performed to estimate the competition between H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> for oxidizing Fe<sup>2+</sup> (ESI S4†). The modeling scenarios included 0 to 200 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> concentrations. At pH 6.3, the rate of Fe<sup>2+</sup> oxidation by H<sub>2</sub>O<sub>2</sub> was up to 10 orders of magnitude higher than Fe<sup>2+</sup> oxidation by O<sub>2</sub>, suggesting that there was minimal competition for ferrous oxidation between H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>. Accordingly, these kinetic analyses support that HO<sup>•</sup> generation was driven by Fe<sup>2+</sup> oxidation *via* H<sub>2</sub>O<sub>2</sub> (not O<sub>2</sub>). Removal was minimal at pH 10.3, likely due to enhanced O<sub>2</sub> activity (Fig. 4). As pH increases, the inhibition of HO<sup>•</sup> generation due to O<sub>2</sub> becomes more apparent given that the oxidation of Fe<sup>2+</sup> by O<sub>2</sub> is second order with respect to [OH<sup>-</sup>] (based on Stumm and Lee, 1961<sup>9</sup>) and increases 100-fold for each pH unit increase (ESI S4†).

The pseudo-first order rate constants were used to estimate the HO<sup>•</sup> concentration (ESI S2†). For pH 8.3, [HO<sup>•</sup>] ranged from 2–4.1 × 10<sup>-13</sup> M for the  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  ratios of 0.33 to 0.7. At pH 6.3, when *pCBA* treatment was more effective, [HO<sup>•</sup>] was approximately 9 × 10<sup>-13</sup> M. These estimates of radical concentrations can be applied to future studies to compare the [HO<sup>•</sup>] yield for a range of ToRC oxidation technologies such as UV/H<sub>2</sub>O<sub>2</sub>.

**3.2.4. Multivariable linear regression analysis of EC:H<sub>2</sub>O<sub>2</sub> process inputs.** To evaluate the roles of independent variables, multivariable linear regressions were conducted to consider the influence of all reactor input experiments at neutral pH and for variable pH experiments. The key parameters incorporated into





**Fig. 4** Degradation of *p*CBA at different pH conditions prepared in 4 mM bicarbonate buffer. During EC:H<sub>2</sub>O<sub>2</sub>, current density = 7.4 mA cm<sup>-2</sup>, H<sub>2</sub>O<sub>2</sub> = 30 mg L<sup>-1</sup>, 15 minutes of treatment time. (a) Removal of *p*CBA as a function of pH. The no electricity control experiment shows removal due only to iron electrodes and the addition of 30 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>. Striped bars indicate concentrations below the limit of detection (4 μg L<sup>-1</sup>). (b) *p*CBA removal rate as a function of pH. *R*<sup>2</sup> correlations are not shown for pH 3 due to insufficient points above the limit of detection after treatment (removal at all pH 3 treatments was calculated using the limit of detection as the final concentration). *R*<sup>2</sup> is not shown for pH 10.3 due to no removal. The end timepoint of the *p*CBA degradation reaction used in kinetic modeling was determined as the time point at which *p*CBA removal was less than 10% different than the preceding time point. Error bars show ± 1 standard deviation of triplicate experiments. Of note, the error bars for b are not visible due to low standard deviation.

the regression were  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios, pH, and current density. These independent variables were selected based on preliminary Pearson correlations and were not multicollinear (ESI S6†).

Overall,  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios, pH, and current density were significantly correlated to *p*CBA removal ( $p = 0.028$ , 0.008, and <0.0001, respectively, multivariable regression “% *R* all”). The most influential parameter for *p*CBA removal was pH ( $\beta_{\text{pH}} = -0.91 \pm 0.15$ , multivariable linear regression: “% *R*, all”), where lower pH led to higher *p*CBA removal. The ratio of  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  and current density had smaller impacts relative to pH, but similar magnitude of contributions to one another ( $\beta_{[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]} = 0.22 \pm 0.09$ ,  $\beta_{\text{current density}} = 0.36 \pm 0.09$ , multivariable linear regression: “% *R*, all”).

A separate regression was performed for experiments with  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios = 0–0.77 to rank the inputs that yielded higher rate constants and higher *p*CBA removal. For these tests, pH still had the greatest influence ( $\beta_{\text{pH}} = -0.79 \pm 0.08$ ,  $p < 0.0001$ , multivariable linear regression: “*k*, all”) followed by  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios ( $\beta_{[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]} = 0.38 \pm 0.05$ ,  $p < 0.0001$ , multivariable linear regression: “*k*, all”). However, variations in current density alone had an insignificant influence on the rate of *p*CBA removal ( $\beta_{\text{current density}} = 0.09 \pm 0.05$ ,  $p = 0.073$ , multivariable linear regression: “*k*, all”), implying that pH and  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios are the key parameters influencing oxidant production.

### 3.3. Co-treatment of *p*CBA and NOM using EC:H<sub>2</sub>O<sub>2</sub> to treat environmental waters and synthetic matrices

**3.3.1. *p*CBA removal in NOM-containing waters.** In environmental source waters (*i.e.*, river water and groundwater), EC:H<sub>2</sub>O<sub>2</sub> oxidized *p*CBA, indicating that EC:H<sub>2</sub>O<sub>2</sub> can treat real

waters containing relatively low DOC levels typical of natural source waters in addition to synthetic matrices (Fig. 5A). The matrices with the lowest levels of DOC (groundwater and bicarbonate [no DOC]) had similarly high *p*CBA removal ( $p = 0.8$ , ANOVA: post hoc Tukey multiple comparison), whereas the matrices containing moderate DOC levels (river water and SR-NOM) had less *p*CBA removal and performed similarly to one another ( $p > 0.99$ , ANOVA: post hoc Tukey multiple comparison). Notably, the synthetic matrices had similar removal efficacy to the real waters in spite of increased complexity in real water sources.

The initial concentration of DOC had a small impact on *p*CBA removal ( $\beta_{\text{DOC}} = -0.07$ ,  $p = 0.34$ , not including primary effluent) for matrices containing low-to mid-range DOC levels (<10 mg-C per L) that reflect drinking water source matrices. This trend implies that the presence of NOM may not heavily impede *p*CBA oxidation when treating typical environmental source waters.

Compared to real-world waters and synthetic matrices, the primary effluent had the least *p*CBA removal. Decreased removal was likely due to high H<sub>2</sub>O<sub>2</sub> demand (Table 2) and high DOC levels. In this case, the high H<sub>2</sub>O<sub>2</sub> demand rapidly depleted the H<sub>2</sub>O<sub>2</sub> that was initially dosed into the reactor, which hindered HO<sup>•</sup> production. Thus, for EC:H<sub>2</sub>O<sub>2</sub> applications, the water's H<sub>2</sub>O<sub>2</sub> demand should be accounted for to gauge potential negative impacts on process performance. For example, Serra-Clusellas *et al.* (2021)<sup>32</sup> demonstrated TOC mitigation *via* EC:H<sub>2</sub>O<sub>2</sub> at pH 3 in municipal tertiary treated wastewater containing ng L<sup>-1</sup> TOCs by using elevated 220–440 H<sub>2</sub>O<sub>2</sub> mg L<sup>-1</sup> doses (resulting in  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios of 1.7 to 2 during treatment), which offset oxidant scavenging by wastewater constituents.





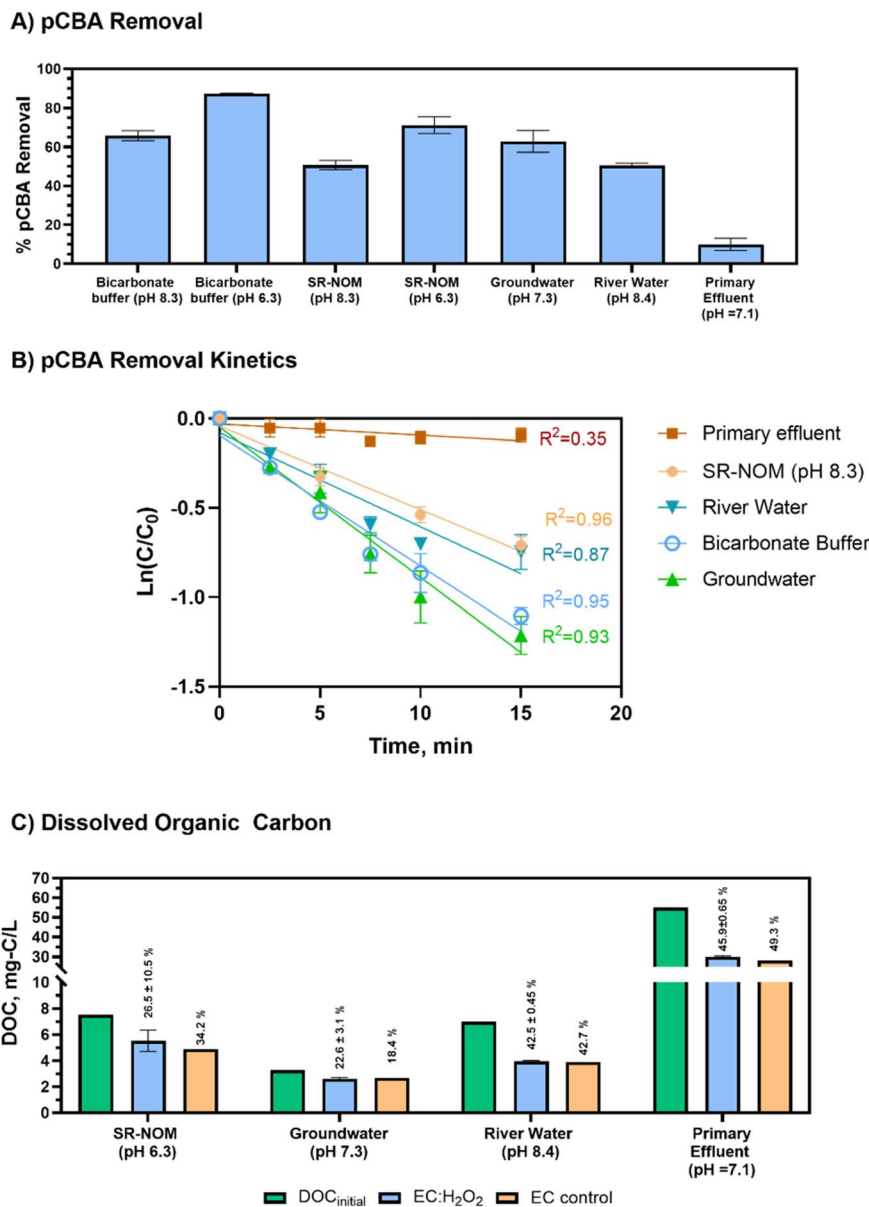


Fig. 5 Removal of *p*CBA and dissolved organic carbon (DOC) in synthetic and real-world waters following 15 minutes of EC:H<sub>2</sub>O<sub>2</sub> (7.40 mA cm<sup>-2</sup>, H<sub>2</sub>O<sub>2</sub> = 30 mg L<sup>-1</sup>). (A) *p*CBA removal following EC:H<sub>2</sub>O<sub>2</sub> (C<sub>i</sub> = 400 μg L<sup>-1</sup> for all matrices). (B) Pseudo-first order degradation of *p*CBA in EC:H<sub>2</sub>O<sub>2</sub> at [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub>/[Fe<sup>2+</sup>]<sub>generated</sub> ratio = 0.55 (7.4 mA cm<sup>-2</sup>, 30 mg H<sub>2</sub>O<sub>2</sub> per L) in synthetic and real-world waters. (C) DOC in the waters initially and remaining following EC:H<sub>2</sub>O<sub>2</sub> or EC-only treatment. A pH 6.3 test was conducted for SR-NOM to reflect enhanced coagulation conditions. Bicarbonate buffer is not included in panel (C) as there was no DOC in the synthetic matrix. The % DOC removal by EC:H<sub>2</sub>O<sub>2</sub> is shown in vertical text above each bar. All DOC and *p*CBA data are from the same batch experiments for the respective water matrix. Error bars show ± 1 standard deviation of triplicate experiments, with the exception of the "EC control" values in panel C, which are single replicates.

A multivariable regression of all test matrices showed that DOC<sub>initial</sub> and pH were the key water quality parameters that impacted *p*CBA removal ( $\beta_{\text{DOC}} = -0.72 \pm 0.18$ ,  $p = 0.008$  and  $\beta_{\text{pH}} = -0.81 \pm 0.08$ ,  $p < 0.0001$ , respectively). Pearson correlations showed that DOC<sub>initial</sub> and H<sub>2</sub>O<sub>2</sub> demand were multicol-linear ( $R_{\text{DOC vs. H}_2\text{O}_2 \text{ demand}}^2 = 0.893$ ,  $p < 0.05$ , Pearson correlations). As anticipated, higher DOC levels typical of wastewater impeded treatment efficacy, whereas lower DOC conditions improved radical yield and offered less competition for oxidants. However, it is important to note that other water

matrix constituents beyond DOC (including chemical oxygen demand, reduced metals, and sulfides, which were not assessed in this study) also likely contributed to H<sub>2</sub>O<sub>2</sub> depletion and impeded DOC removal.

**3.3.2. DOC removal in environmental waters.** In terms of bulk organics, EC:H<sub>2</sub>O<sub>2</sub> appeared to offer similar levels of DOC removal compared to EC-only, with the added benefit of TOC mitigation based on *p*CBA removal (Fig. 5C). The favorable reproducibility of DOC removal *via* EC:H<sub>2</sub>O<sub>2</sub> replicates relative to single EC-only as a point of reference suggests that DOC



removal primarily proceeds through non-destructive pathways as EC-only was previously shown to have minimal *p*CBA removal *via* oxidants at the conditions tested.

The river water and SR-NOM matrices are of particular interest for DOC removal given that they are representative of surface waters that could be treated for drinking water. Using EC:H<sub>2</sub>O<sub>2</sub>, DOC removal for the river water complied with recommendations in the US Environmental Protection Agency's Enhanced Coagulation Guidance manual (>30% DOC removal for matrices containing >120 mg L<sup>-1</sup> as CaCO<sub>3</sub> alkalinity).<sup>33</sup> The synthetic SR-NOM matrix only had effective DOC removal when pH was 6.3. At pH 8.3, EC:H<sub>2</sub>O<sub>2</sub> formed no flocs or precipitates in SR-NOM, indicating unsuccessful coagulation, precipitation, and subsequent sedimentation of flocs (ESI S9†). This difference between real and synthetic waters suggests that other constituents in environmental waters (such as divalent cations, *i.e.*, calcium and magnesium) may improve coagulation processes in real waters by promoting ionic interactions between NOM and ions that promote co-sorption to flocs, as shown for a calcium-fulvic acid-goethite iron mineral system.<sup>34</sup> Overall, the addition of H<sub>2</sub>O<sub>2</sub> during EC:H<sub>2</sub>O<sub>2</sub> can enhance treatment applications by simultaneously treating TOxCs such as *p*CBA as well as bulk organics such as DOC in a single unit process *in lieu* of a multi-stage treatment train such as coagulation/flocculation/sedimentation followed by filtration and oxidation to achieve both non-destructive removal and oxidative destruction of contaminants.

### 3.4. Engineering implications: rate constants and electrical energy per order

**3.4.1. Pseudo-first order rate constants for treating environmental waters.** Pseudo-first order rate constants are key figures of merit for evaluating operational parameters by accounting for matrix-specific scavengers. The pseudo-first order rates for *p*CBA removal were  $1.3 \times 10^{-3} \text{ s}^{-1}$  and  $1.6 \times 10^{-3} \text{ s}^{-1}$  for river water and groundwater, respectively (Fig. 5B and Table 4). These values satisfy the proposed breakeven point  $k = 2.1 \times 10^{-5} \text{ s}^{-1}$  for TOxC treatment technologies to be competitive based on technoeconomic analyses.<sup>35</sup>

**3.4.2. Electrical energy per order: impact of reactor inputs assessed in bicarbonate buffer.** In terms of energy requirements, higher current densities resulted in higher  $E_{\text{EO}}$  values ( $\beta_{\text{current density}} = -0.36 \pm 0.09$ ,  $p < 0.0001$ , multivariable regression: " $E_{\text{EO}}$ , all"), whereas  $[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$  ratios had less impact ( $\beta_{[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]} = -0.36 \pm 0.09$ ,  $p = 0.16$ ). For the lower current densities, 3 and 5 mA cm<sup>-2</sup>, the  $E_{\text{EO}}$  was 0.62 ±

0.02 and  $1.22 \pm 0.05 \text{ kW h m}^{-3}$ , respectively, when operated at pH 8.3 conditions. The higher current densities of 7.4 to 15 mA cm<sup>-2</sup> had  $E_{\text{EO}}$  values ranging from  $3.13 \pm 0.13$  to  $12.54 \pm 2.12 \text{ kW h m}^{-3}$  due to the additional electrical loading (Table 3). When pH decreased to 6.3, the  $E_{\text{EO}}$  decreased from  $2.86 \pm 0.2 \text{ kW h m}^{-3}$  to  $0.68 \pm 0.004 \text{ kW h m}^{-3}$  for the same current density of 7.4 mA cm<sup>-2</sup>. This improvement in energy efficiency was likely due to a combination of the faster rate of removal at pH 6.3 and the solution's increased conductivity due to chloride addition (HCl was used for pH adjustment).

At circumneutral pH, current densities above 3 mA cm<sup>-2</sup> thus exceeded the recommended  $1 \text{ kW h m}^{-3} E_{\text{EO}}$  threshold to be competitive with conventional HO<sup>•</sup>-mediated advanced oxidation processes (AOPs) such as UV/H<sub>2</sub>O<sub>2</sub> and ozone-based AOPs.<sup>36</sup> Accordingly, EC:H<sub>2</sub>O<sub>2</sub> may be operated at lower current densities for more favorable energy demands. However, the benchmark  $E_{\text{EO}}$  values for conventional AOPs rely on preliminary treatment technologies such as coagulation and membrane filtration to remove oxidant scavengers, primarily DOC. Additional DOC removal technologies add materials and energy demands to overall treatment of TOxCs that are not accounted for in standalone  $E_{\text{EO}}$  values for conventional AOPs. Alternately, EC:H<sub>2</sub>O<sub>2</sub> offers the benefit of simultaneous TOxC and DOC treatment, which can minimize preliminary treatment needs and decrease overall energy inputs compared to conventional AOP treatment trains.

Although EC:H<sub>2</sub>O<sub>2</sub> was higher than the  $E_{\text{EO}}$  benchmark for conventional AOPs under high current conditions, EC:H<sub>2</sub>O<sub>2</sub> generally resulted in a lower range of  $E_{\text{EO}}$  values (0.6 to 12.5 kW h kW h m<sup>-3</sup> [Table 3]) compared to *p*CBA mitigation using other electrochemical technologies such as boron-doped diamond electrooxidation. For example, Lanzarini-Lopes *et al.* (2017)<sup>37</sup> reported  $E_{\text{EO}}$  values for *p*CBA mitigation ranging from 39.3 kW h m<sup>-3</sup> to 332 kW h m<sup>-3</sup> for electro-oxidation current densities from 16.6 to 100 mA cm<sup>-2</sup>. Consistent with this study, increasing current density in the electrochemical treatment process yielded higher, less favorable  $E_{\text{EO}}$  values.

**3.4.3. Electrical energy per order: impact of water quality.** The  $E_{\text{EO}}$  values for different water matrices ranged from 0.7 to 7.5 kW h m<sup>-3</sup> (Table 4) as a function of water quality, *p*CBA removal, and the voltage input to achieve the fixed current of 7.4 mA cm<sup>-2</sup>. Of the environmental waters, groundwater had the lowest  $E_{\text{EO}}$  at  $1.0 \pm 0.13 \text{ kW h m}^{-3}$ , while the river water  $E_{\text{EO}}$  was  $1.91 \pm 0.21 \text{ kW h m}^{-3}$ . The matrix with the highest  $E_{\text{EO}}$  was SR-NOM ( $7.57 \pm 0.20 \text{ kW h m}^{-3}$ ) due to low *p*CBA

**Table 3** Electrical energy per order of magnitude *p*CBA removal (kW h m<sup>-3</sup>) for EC:H<sub>2</sub>O<sub>2</sub> operated in bicarbonate buffer. Values are the averages of duplicate experiments ± one standard deviation

$[\text{H}_2\text{O}_2]_{\text{initial}}/[\text{Fe}^{2+}]_{\text{generated}}$	Current density, mA cm <sup>-2</sup>				
	3	5.5	7.4	11.1	15
0.35		0.74 ± 0.04	3.13 ± 0.13	6.10 ± 0.21	12.54 ± 2.12
0.5	0.76 ± 0.03	0.62 ± 0.02	3.15 ± 0.39	5.89 ± 0.06	
0.7		0.74 ± 0.03		7.45 ± 0.84	
1.6	1.11 ± 0.08	1.22 ± 0.05		12.56 ± 2.01	



**Table 4** Figures of merit for *p*CBA treatment in varying water matrices, including pseudo-first order rate constants (*k*) and electrical energy per order ( $E_{EO}$ ) of magnitude removal values for EC:H<sub>2</sub>O<sub>2</sub>. For all experiments, current density = 7.4 mA cm<sup>-2</sup> and H<sub>2</sub>O<sub>2</sub> = 30 mg L<sup>-1</sup>. pH 3 is not included due to insufficient data points to model a pseudo-first order rate constant prior to H<sub>2</sub>O<sub>2</sub> depletion. pH 10.3 is not shown due to poor removal that did not provide viable data for pseudo-first order rate constants to estimate  $E_{EO}$  values

Water matrix	<i>k</i> , s <sup>-1</sup>	$E_{EO}$ , kW h m <sup>-3</sup>
Bicarbonate buffer (pH 8.3)	$1.2 \times 10^{-3}$	$2.86 \pm 0.20$
Bicarbonate buffer (pH 6.3)	$4.7 \times 10^{-3}$	$0.68 \pm 0.005$
Bicarbonate buffer + NOM	$6.3 \times 10^{-3}$	$7.57 \pm 0.20$
Bicarbonate buffer + NOM (pH 6.3)	$2.9 \times 10^{-3}$	$1.13 \pm 0.08$
Groundwater	$1.6 \times 10^{-3}$	$1.00 \pm 0.13$
River water	$1.3 \times 10^{-3}$	$1.91 \pm 0.21$
Primary effluent	$2.5 \times 10^{-4}$	$6.49 \pm 1.34$

removal and low matrix conductivity. Primary effluent had the second highest  $E_{EO}$  of  $6.49 \pm 1.34$  kW h m<sup>-3</sup>. Notably, primary effluent had the least *p*CBA removal of all waters tested (<20%); however, the water's high conductivity led to low voltage input, leading to a relatively low  $E_{EO}$  in spite of the poor *p*CBA treatment performance.

Multivariable regressions were used to assess how water quality in environmental and synthetic water matrices influenced  $E_{EO}$ . The  $E_{EO}$  trends followed the removal trends, where DOC concentration and alkalinity increased  $E_{EO}$  by decreasing *p*CBA removal and increasing treatment inputs ( $\beta_{DOC} = 1.2 \pm 0.15$ ,  $p < 0.0001$ ;  $\beta_{alkalinity} = 0.45 \pm 0.11$ ,  $p = 0.0013$ , multivariable regression: " $E_{EO}$ , water quality"). In terms of water quality parameters, DOC<sub>initial</sub> had the largest negative influence on  $E_{EO}$ . For parameters that improved  $E_{EO}$ , higher water matrix conductivity improved  $E_{EO}$  by reducing the electrochemical cell's power demands ( $\beta_{conductivity} = -0.29 \pm 0.1$ ,  $p < 0.0001$ , multivariable regression: " $E_{EO}$ , water quality" ESI S10†). Accordingly, groundwater required the lowest  $E_{EO}$  of the environmental waters likely due to the low DOC concentration and high conductivity. The energy demands of the EC:H<sub>2</sub>O<sub>2</sub> system operated at 7.4 mA cm<sup>-2</sup> were in the range of competitive performance (e.g., 1 kW h m<sup>-3</sup> according to Miklos *et al.* (2018)<sup>36</sup>) for several water matrices (Table 4), making EC:H<sub>2</sub>O<sub>2</sub> a promising option for scaled applications for treating TORCs in environmental waters such as groundwater and river water, with the added benefit of DOC removal in the same reactor.

### 3.5. Conclusions

The goal of this research was to evaluate EC:H<sub>2</sub>O<sub>2</sub> as a combined destructive and non-destructive treatment technology at neutral pH. This performance was assessed as a function of reactor inputs and solution pH. The treatment efficacy of environmental source waters containing varying levels of NOM, scavengers, and ionic constituents was also evaluated. Neither current density nor H<sub>2</sub>O<sub>2</sub> alone promoted *p*CBA oxidation, although the combination of these parameters heavily influence performance. At neutral pH conditions,  $[H_2O_2]_{initial}/[Fe^{2+}]_{generated}$  ratio was the key driver of oxidative performance,

where ratios <0.7 had higher *p*CBA removal and higher ratios (0.7–1.6) decreased *p*CBA removal, likely due to H<sub>2</sub>O<sub>2</sub> scavenging.

For water quality, pH was the key driver of improved removal, where lower pH conditions minimized the competition between H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> for oxidation of Fe<sup>2+</sup> to better encourage radical generation. When treating groundwater and river water, EC:H<sub>2</sub>O<sub>2</sub> had both oxidative treatment of TORCs and non-destructive treatment of DOC. The pseudo-first order rate constants and  $E_{EO}$  values demonstrated that EC:H<sub>2</sub>O<sub>2</sub> can be competitive with other AOPs for TORC treatment based on energy requirements and treatment performance (depending on current density and water quality, e.g., low DOC, high conductivity waters are easier to treat), with an added benefit of DOC removal due to coagulation and flocculation in the same reactor.

In real world treatment trains, EC:H<sub>2</sub>O<sub>2</sub> could be operated to promote both oxidative and non-destructive treatments in a single process, which could replace multiple conventional unit processes. However, post-EC:H<sub>2</sub>O<sub>2</sub> particle separation *via* sedimentation or rapid sand filtration would be needed to separate the iron flocs from solution. Additionally, a final disinfection step would likely be needed to ensure sufficient pathogen inactivation and maintain disinfectant residual. Future assessment of the performance of the full treatment train and the related energy efficiency can help to inform treatment train comparisons.

Future work is needed to evaluate EC:H<sub>2</sub>O<sub>2</sub> treatment trains from a systems-engineering perspective wherein the additional benefits such as DOC removal and *in situ* chemical generation are parameterized to compare against the treatment costs associated with conventional treatment trains. These findings are needed to quantify the benefits of utilizing EC:H<sub>2</sub>O<sub>2</sub> for combined treatment and provide a more comprehensive comparison of EC:H<sub>2</sub>O<sub>2</sub> to current AOP technologies as well as conventional treatment trains. Additionally, the byproducts generated during EC:H<sub>2</sub>O<sub>2</sub> should be evaluated. For example, the co-dissolution of regulated metals from iron electrodes (e.g., manganese) could add secondary contamination. *Ex situ* H<sub>2</sub>O<sub>2</sub> addition is another challenge for decentralized EC:H<sub>2</sub>O<sub>2</sub> treatment. Accordingly, research is needed to inform reactor setups for EC:H<sub>2</sub>O<sub>2</sub> and to explore H<sub>2</sub>O<sub>2</sub> dosing technologies such as air-diffusion cathodes that can promote *in situ* H<sub>2</sub>O<sub>2</sub> generation, thereby decreasing *ex situ* chemical additions and enhancing the process' potential as a small footprint decentralized treatment technology.

### Author contributions

DRR: conceptualization, data curation, methodology, laboratory analyses, investigation, visualization, writing – original draft; writing – review & editing. PJM: methodology, funding acquisition, project administration, supervision, resources, validation, visualization, writing – review & editing. CKB: investigation, laboratory analysis, writing – original outline, writing – review & editing. YW: funding acquisition, resources, writing – review & editing. BKM: methodology, funding



acquisition, project administration, supervision, resources, validation, visualization, writing – review & editing.

## Conflicts of interest

There are no conflicts of interest to declare.

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