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**Citric Acid-Modified Fenton's Reaction for the Oxidation of Chlorinated Ethylenes
in Soil Solution Systems**

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27

28 **Abstract**

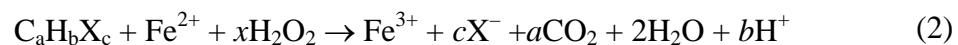
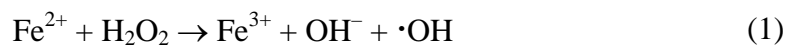
29 Fenton's reagent, a solution of hydrogen peroxide and ferrous iron catalyst, is used for an
30 in-situ chemical oxidation of organic contaminants. Sulfuric acid is commonly used to
31 create an acidic condition needed for catalytic oxidation. Fenton's reaction often involves
32 pressure buildup and precipitation of reaction products, which can cause safety hazards
33 and diminish efficiency. We selected citric acid, a food-grade substance, as an acidifying
34 agent to evaluate its efficiencies for organic contaminant removal in Fenton's reaction,
35 and examined the impacts of using citric acid on the unwanted reaction products. A series
36 of batch and column experiments were performed with varying H₂O₂ concentrations to
37 decompose selected chlorinated ethylenes. Either dissolved iron from soil or iron sulfate
38 salt was added to provide the iron catalyst in the batch tests. Batch experiments revealed
39 that both citric and sulfuric acid systems achieved over 90% contaminant removal rates,
40 and the presence of iron catalyst was essential for effective decontamination. Batch tests
41 with citric acid showed no signs of pressure accumulation and solid precipitations,
42 however the results suggested that an excessive usage of H₂O₂ relative to iron catalysts
43 (Fe²⁺/H₂O₂ < 1/330) would result in lowering the efficiency of contaminant removal by
44 iron chelations in the citric acid system. Column tests confirmed that citric acid could
45 provide suitable acidic conditions to achieve higher than 55% contaminant removal rates.

46 **Key Words:** Fenton's reaction, citric acid, hydrogen peroxide, organic contaminant

47

48 **Introduction**

49 Contamination of soil and groundwater by chlorinated hydrocarbons imposes
50 significant threats to water resources and public health. One of the techniques used to
51 remediate chlorinated hydrocarbon contamination in soil and groundwater is *in situ*
52 chemical oxidation with Fenton's reagent. Ferrous iron and H₂O₂ are injected into an
53 acidic subsurface system to decompose contaminants in place. Normally, H₂O₂ is a
54 relatively low-activity oxidant. However, under acidic conditions (pH = 3 to 5), Fe²⁺
55 dissociates H₂O₂ to form unstable and highly reactive hydroxyl radicals (·OH), as shown
56 in Eq. 1, which actively mineralize organic contaminants (C_aH_bX_c) into CO₂, water, and
57 inorganic salts, (Eq. 2; Walling, 1975; Sun and Pignatello, 1992). The Fe²⁺ is then
58 catalytically regenerated by the Fe³⁺ reaction with H₂O₂ (Eq. 3).



59 Under less acidic conditions (pH > 6), the iron catalyst precipitates as Fe(OH)₃,
60 and instead of generating the hydroxyl radical, the H₂O₂ decomposes into oxygen, water,
61 and heat, which can create hazardous operation condition. Therefore, it is critical to
62 provide proper acidic conditions to achieve optimum and safe decontamination when
63 Fenton's reaction is employed (Walling 1975; Hickey et al., 1995).

64 Recent studies on Fenton's reaction are concentrated on improving the
65 remediation technique by minimizing the addition of extrinsic materials into subsurface
66 systems and by using environmentally benign chemicals. Deliverability of natural iron
67 catalyst as a means of minimizing the extrinsic chemical addition was examined
68 extensively by many researchers (Ravikumar and Gurol, 1994; Kong et al., 1998; Watts
69 et al., 1999; Teel et al., 2001; Kwan and Voelker, 2002; Teel and Watts, 2002), and
70 showed that H₂O₂ could initiate Fenton's reaction in the presence of naturally occurring
71 iron minerals, such as goethite and magnetite in soil. Those studies proved that an iron-
72 mineral-catalyzed H₂O₂ system could be successfully applied to field problems under
73 acidic conditions when soils contain 0.5 to 5 wt% of iron minerals.

74 The Fenton's reactions for degradation of organic compounds have also been
75 studied in the presence of naturally-occurring organic acids, such as humic and fulvic
76 acids (Voelker and Sulzberger, 1996; Paciolla et al., 1999). Organic acids contain a high
77 density of functional groups, which can conjugate metal ions to form ion complexes. The
78 acids can affect the effectiveness of Fenton's reaction by providing an iron source and by
79 creating proximity between the catalytic iron and organic contaminants for the reaction
80 (Lindsey et al., 2003). Paciolla et al. (1999) confirmed that iron-sorbed humic acid
81 produces ·OH through the reaction with H₂O₂. Complexes of Fe²⁺-fulvic acid increase the
82 Fenton's reaction rate at pH = 5, consuming more H₂O₂ than without fulvic acid (Voelker
83 and Sulzberger, 1996). Sun and Pignatello (1992) examined the oxidation of 2,4-
84 dichlorophenoxyacetic acid (2,4-D) with H₂O₂ and Fe³⁺ chelated to various organic acids
85 at pH = 6, and showed that when Fe³⁺ forms chelate with organic acid, the chelated Fe³⁺
86 was more active in generating ·OH and decomposing 2,4-D than the precipitated Fe³⁺.

87 This study investigates whether Fenton's reaction can be initiated by using an
88 organic acid such as citric acid, a food-grade substance, instead of sulfuric acid as an
89 acidifying agent. Citric acid is biodegradable and, when injected into subsurface
90 systems, it could be nutrients for microbes participating in biodegradation of
91 contaminants, as well as an acidifying agent for the chemical oxidation. Citric acid
92 makes a pH buffer at $\text{pH} = 3$ ($\text{pK}_a = 3.08$), at which Fenton's reaction actively occurs.
93 Citric acid has a strong ability to chelate metal ions and keep them in solution at those
94 values of pH where the metals would otherwise precipitate (Li et al., 2005). Citric acid,
95 however, can adversely affect the effectiveness of Fenton's reaction. Citric acid can
96 inhibit organic compound decomposition by scavenging the $\cdot\text{OH}$ (Voelker and
97 Sulzberger, 1996) and by separating the $\cdot\text{OH}$ formation sites from the pollutants (Lindsey
98 and Tarr, 2000).

99 The objectives of this study are to evaluate the applicability of citric acid as an
100 acidifying agent for Fenton's reagent and to ascertain optimum conditions for effective
101 citric-acid modified Fenton's reagent as an organic contaminant decomposing technique.

102

103 **Experimental Procedures**

104 **Chemicals and Analyses** Bench-scale experiments were performed to evaluate the
105 effectiveness of Fenton's oxidation for remediating soils contaminated with chlorinated
106 ethylenes, including trichloroethylene (TCE), tetrachloroethylene (PCE), and *cis* 1,2-
107 dichloroethylene (DCE) (98%, Aldrich, Milwaukee, WI.). The organic compound
108 concentrations in liquid and soil were measured using a GC-MS, using EPA Method

109 8260B, by an EPA certified laboratory. Various concentrations (3%, 15%, 30%, and
110 50%) of H₂O₂ solutions (EMD Chemicals, Gibbstown, NJ.) were used for a possible
111 range of H₂O₂ injection. Citric acid (2-Hydroxy-1,2,3-propanetricarboxylic acid) and
112 sulfuric acid stock solution were prepared at concentrations of 0.5 M and 1.0 N ,
113 respectively. Iron sulfate salt (FeSO₄·7H₂O) was used as a source of Fe²⁺. A silty clay soil
114 was collected for this study from the campus of Lawrence Berkeley National Laboratory
115 near Building 51L. The sample was air-dried and sieved through a 2-mm mesh before
116 use. Soil characteristics are listed in Table 1. Sorption coefficients in the table were
117 measured for the selected soil assuming linear sorption.

118 **Batch Experiments** Batch tests were conducted to examine whether or not Fenton's
119 oxidation decompose the organic compound in the aqueous solutions with 12
120 combinations of three acidifying agents (sulfuric acid, citric acid, and deionized water)
121 and four iron sources (FeSO₄, filtered soil solution, soil, and no iron). The 12 acidified
122 solutions were prepared by diluting two concentrated acid solutions (sulfuric acid and
123 citric acid) and deionized water as a control, with FeSO₄ solution (50 mg Fe²⁺ L⁻¹) for one
124 set and deionized water for three sets. While one set was further diluted by FeSO₄
125 solutions, the other three sets of the deionized water-diluted solutions were mixed with
126 (1) deionized water for a control (no iron), (2) acid solutions with the soil sample (2 g) as
127 an iron catalyst source, and (3) filtered soil solutions, respectively.

128 The filtered soil solutions were prepared by mixing 15 g of soil with 150 mL of
129 the diluted sulfuric acid solution, citric acid solutions, and deionized water separately on
130 a mechanical shaker overnight, and by filtering the supernatants of the soil solutions with
131 0.45 μm filters. In order to make consistent organic compound concentrations, a

132 concentrated organic compound aqueous solution (PCE, TCE, and DCE) was prepared
133 and spiked into the 12 acidified solution sets described above with different acids and
134 iron sources. Each 12-acidified solution batch had 5 subsets for varying H₂O₂
135 concentration (0 to 4% H₂O₂). The final volume of each acidified solution was about 25
136 mL including 2 mL of H₂O₂ solutions. There was no head space left in 25 mL reaction
137 bottles.

138 Final concentrations of acids in the acidified solutions were 24 mN for citric acid
139 and 16 mN for sulfuric acid. The pH values of the acidified solutions were near 3 while
140 the control solutions without acid had a pH value of about 7. Final organic compound
141 concentrations ranged from 800 to 1200 µg L⁻¹ for the three contaminants.

142 Reactions were allowed to continue for more than 24 h at 4 °C under dark
143 conditions. The sample bottles were visually observed to ascertain reactions occurring
144 and to identify reaction products before instrumental analysis.

145 **Column Experiments** The column experiments similarly involved the two different acid
146 solutions (sulfuric acid, and citric acid) and a control solution without acid. Soil samples
147 of 160 g were packed in three glass columns (2.5 cm diameter × 15 cm length). The soil
148 columns were treated in three steps: (1) wetting and contaminant emplacement with an
149 organic compound solution, (2) acidification with the three acid solutions (sulfuric acid,
150 citric acid, and control) spiked with organic compounds, (3) H₂O₂ injection for organic
151 compound decomposition. A 10-pore volume (10 × 25 mL) of an organic compound
152 stock solution (PCE, TCE, and DCE, 1300–5000 µg L⁻¹) was flushed through the
153 columns in a rate of 0.5 mL min⁻¹ to uniformly wet the columns and to emplace the

154 organic compounds thoroughly. The organic compound stock solution for the column
155 experiment was prepared with a CaCl_2 solution (0.005 M CaCl_2 with FeSO_4 , 50 mg Fe^{2+}
156 L^{-1}), instead of deionized water, in order to prevent soil dispersion. The volume of the
157 organic compound solutions injected for the contaminant emplacement was determined
158 by the retardation factors (≈ 3.0), which were calculated based on the sorption
159 coefficients estimated in preliminary measurements (Table 1) and an assumed soil
160 organic carbon content (0.5%), so that the organic compound concentrations in the
161 column would be uniform throughout the column.

162 In order to acidify the soil, each contaminated soil columns was additionally
163 injected with 1 pore volume (25 mL) of citric acid solution (CA; 0.5 M citric acid with
164 FeSO_4 , 50 mg $\text{Fe}^{2+} \text{L}^{-1}$), sulfuric acid solution (SA; 1 N sulfuric acid with FeSO_4 , 50 mg
165 $\text{Fe}^{2+} \text{L}^{-1}$), and CaCl_2 solution (0.005 M CaCO_3 with FeSO_4 , 50 mg $\text{Fe}^{2+} \text{L}^{-1}$) as a control,
166 respectively. Each of these three solutions had the same concentration of organic
167 compounds. The concentrations of the acid solutions were predetermined to have column
168 soil solutions of $\text{pH} = 3$, only for sulfuric acid and citric acid. The organic compound
169 concentrations in the injected acid solutions were the same as the concentration in the
170 initial organic compound stock solution.

171 As a final step, one pore volume of 3% H_2O_2 solution (30% stabilized H_2O_2
172 diluted with deionized water, FeSO_4 added) was injected into each acidified columns (CA
173 and SA), while the same volume of CaCl_2 solution was injected into the control column.
174 Liquid and gas effluent were collected separately with tedlar bags for the first one hour,
175 after which the columns were closed and kept in a refrigerator. Similar to batch tests,
176 H_2O_2 reactions inside the columns were allowed to proceed for 24 h before the columns

177 were opened for soil sampling and contaminant analysis. Liquid samples from the tedlar
178 bags and soil samples collected from the glass columns were directly analyzed for
179 organic compound concentrations, whereas, due to limited gas volume collected, the
180 organic compound concentrations in the gas samples were calculated using the measured
181 concentrations of liquid in the effluent bag based on Henry's constant. Mass balance of
182 organic compounds was calculated to demonstrate the removal efficiency of the organic
183 compounds with H₂O₂ injections.

184

185 **Results and Discussion**

186 **Batch Experiments** Batch samples were visually observed to examine the occurrence of
187 reaction products and gas accumulation resulting from the Fenton's reaction. H₂O₂ added
188 to sulfuric acid solutions with iron catalyst resulted in gas accumulation and solid
189 precipitation in the glass bottles. The pressurization and solid precipitation in a system
190 with H₂O₂ addition have been considered a potential hazard and a deliverability-
191 deteriorating factor of Fenton's technique for subsurface remediation. On the other hand,
192 no signs of gas accumulation or solid precipitation were observed in the citric acid
193 batches, suggesting that the citric acid addition alleviated the adverse impacts which
194 would have occurred with traditional sulfuric acid application.

195 Figure 1 shows the results of TCE removal with two acidified solutions (citric
196 acid and sulfuric acid), and deionized water at varying H₂O₂ additions (0 to 4%). Figure
197 1a depicts the case without iron catalysts in the system while Fig. 1b shows the result
198 with the application of FeSO₄. The comparison of Fig. 1a and 1b shows that the addition

199 of FeSO_4 as a catalyst significantly improved the H_2O_2 performance in removing TCE.
200 Even in the deionized water batch ($\text{pH} = 6$) with iron, the removal rate reached nearly
201 100% with less than 1% H_2O_2 . The results showed that in the pH range of 3 (citric acid
202 and sulfuric acid) to 6 (deionized water), the key component of TCE removal efficiency
203 with H_2O_2 oxidation was the iron catalyst, and citric acid acts as effectively as sulfuric
204 acid does, suggesting the scavenging of $\cdot\text{OH}$ by citric acid was not significant in the
205 given condition.

206 Figures 1c and 1d show difference in TCE removal rates with the two acid
207 solutions (citric acid and sulfuric acid), and deionized water when two filtered soil
208 solution (Fig. 1c) and soil (Fig. 1d) were utilized as naturally available iron sources. In
209 the filtered soil solutions (Fig. 1c) with TCE and acid solutions (citric acid and sulfuric),
210 nearly 100% of TCE were removed with less than 1% of H_2O_2 addition, while the
211 deionized (acid-free) water needed 4% H_2O_2 solution to completely remove TCE. This
212 result indicates that water-soluble iron for the H_2O_2 reaction was sufficiently available,
213 and that acidic conditions enhanced the dissolution of soil soluble iron, resulting in higher
214 efficiency in organic contaminant removals.

215 For Fig. 1d, two grams of soil samples was mixed with 25 mL organic compound
216 solutions to assess the role of the local soil as a source of the iron catalyst as well as a
217 scavenger for oxidants. Figure 1d shows the citric acid batches ($\text{pH} = 3$) had nearly 100%
218 TCE removal by less than 2% H_2O_2 solution, whereas the deionized water batches ($\text{pH} =$
219 7.6) had 64% organic compound removal by more than 3% H_2O_2 solution. The removal
220 rate was slower for the sulfuric acid solution than the citric acid, because the pH in the
221 sulfuric acid solution after soil mixing was higher ($\text{pH} = 6$) than with the citric acid ($\text{pH} =$

222 3.6). The removal rates with the actual soil were lower compared with other cases of
223 different iron sources (FeSO_4 or filtered soil solution), confirming the oxidant demand
224 from oxidizable components of the soil reduced the removal efficiencies.

225 Figures 2a and 2b show the results from repeated tests of citric acid added
226 Fenton's oxidation for *cis*-1,2-DCE (Fig. 2a) and PCE (Fig. 2b). In this study, the
227 chlorinated ethylenes generally showed decreasing susceptibility to H_2O_2 oxidation in an
228 order: DCE > TCE > PCE, which is consistent with the previous studies (e.g., Tang and
229 Huang, 1997). PCE removal rates with the filtered soil solution were higher than that
230 with FeSO_4 solution, suggesting that the concentration of iron mobilized by citric acid
231 from the soil would be higher than that supplied by FeSO_4 solution ($50 \text{ mg Fe}^{2+} \text{ L}^{-1}$).

232 Based on the results of the batch experiments, we found that (1) citric acid could
233 act as an effective agent for lowering pH in soil solution to provide appropriate
234 conditions for Fenton's reaction, (2) oxidant scavenging by citric acid was insignificant,
235 and (3) availability of soluble soil iron was enhanced by adding acids.

236 The removal efficiencies with citric acid in the batch tests consistently showed
237 that as the concentration of H_2O_2 increases beyond 1%, the efficiencies of the Fenton's
238 reaction in the organic contaminant removal decreased (see Figs. 1B, 1D, and 2), even
239 though increasing removal efficiency was expected to have higher H_2O_2 concentrations.
240 This pattern of decreasing removal efficiencies with increasing concentration of H_2O_2 (>
241 1%) was observed repeatedly in preliminary and subsequent duplicative tests with citric
242 acid, while this phenomenon was not observed in tests involving the sulfuric acid and
243 deionized water.

244 Possible explanations for this declining efficiency of organic contaminant
245 removals could be a reaction between $\cdot\text{OH}$ and H_2O_2 , and the formation of iron chelates
246 between citric acid and iron species in the solutions. Potential reactions occurring in the
247 citric acid-modified Fenton's system with excessive H_2O_2 are listed in the Table 2. As
248 shown in Eq. 1, Fenton's reaction initiates with reactions between Fe^{2+} and H_2O_2 with
249 second-order rate constant of $63.0 \text{ M}^{-1}\text{s}^{-1}$ (Gallard et al., 1998), which generates $\cdot\text{OH}$ and
250 Fe^{3+} . When the concentrations of H_2O_2 and iron species are stoichiometrically balanced,
251 iron species would play the role of catalyst. With excessive input of H_2O_2 ($> 1\%$),
252 however, H_2O_2 either competes for $\cdot\text{OH}$ with organic contaminants (Table 2, Eq. 4), or
253 reacts with Fe^{3+} (Eq. 5) to generate hydroperoxyl radicals ($\cdot\text{HO}_2$). As indicated by higher
254 reaction rates, H_2O_2 more actively reacts with $\cdot\text{OH}$ (Eq. 4), and the excessive H_2O_2 is
255 quickly consumed to generate $\cdot\text{HO}_2$. Furthermore, the $\cdot\text{HO}_2$ preferably reacts with Fe^{2+}
256 to oxidize it to Fe^{3+} (Eqs. 6 and 7) even though the reaction rate (Eq. 6) are slower than
257 for $\cdot\text{OH}$ oxidation of Fe^{2+} to Fe^{3+} (Eq. 8). Overall, the presence of excess H_2O_2 would
258 have Fe^{3+} to be a dominant species in the Fenton's system and fast consumption of H_2O_2 ,
259 as previously reported by (Barb et al., 1951; Yoon et al., 1998).

260 Citric acids form more stable iron chelates with Fe^{3+} as indicated by a stability
261 constant ($\log K$) of 11.85, compared to Fe^{2+} with $\log K = 3.2$ (Furia, 1972). When Fe^{3+}
262 forms complexes with chelators, the activity of Fe^{3+} to dissociate H_2O_2 usually becomes
263 low and it is inversely proportional to the stability of the chelations. The relations
264 between the stability of chelates and the activity of iron species was presented by Sun and
265 Pignatello (1992), which showed that the activity of iron chelates to transform 2,4-D
266 decreases in order of tartaric $>$ oxalic $>$ citric, and the decreasing activity corresponds to

267 increasing stability constants ($\log K$) of the three acids ($\log K = 7.49, 9.4,$ and $11.85,$
268 respectively) (Furia, 1972). Therefore, the strong chelates of citric acid- Fe^{3+} result in
269 low activity of Fe^{3+} , inhibiting the iron species from getting reduced back into Fe^{2+} , and
270 eventually Fe^{3+} will be sequestered from the Fenton's catalytic cycle.

271 Based on the batch system of this study, an optimum ratio of $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ at
272 1:330 (M:M) was estimated, and the ratio would become smaller with higher organic
273 contaminant concentrations.

274 **Column Experiments** During the column experiments, three mechanisms of organic
275 contaminant removal can occur: (1) volatile organic contaminant stripping with gas
276 (mainly O_2) generated from H_2O_2 decomposition, (2) liquid flushing of contaminants with
277 injected H_2O_2 solution, and (3) *in situ* chemical oxidation via Fenton's reaction. Mass
278 balances were calculated to find contributions from the different removing mechanisms.
279 Results are presented in Table 3 in terms of the relative contributions from the three
280 potential mechanisms. The percentages of contaminants removed by Fenton's reaction
281 were calculated by subtracting total mass of organic contaminants recovered by liquid
282 and soil analysis from initial organic contaminant mass, based on assumptions that there
283 were no other significant means of organic contaminant loss including biodegradation,
284 irreversible sorption, and volatilization.

285 Liquid flushing was the most efficient organic contaminant removal mechanism,
286 when CaCl_2 solution was injected without adding acidifying agents into the column (73%
287 for DCE, and 74% for TCE, and 50% for PCE). The higher flushing removals of DCE
288 and TCE result from the higher water solubility of those compounds. Calculated simply

289 by using Henry's constants based on assumption that the organic contaminants in gas
290 were in equilibrium with those in liquid, we found that the percentages of organic
291 contaminants removed by air stripping was negligibly small (< 1% of total organic
292 compounds), which is quite different from the results of Chen et al. (2001).

293 The total organic compound recovered by liquid and left in soil in the control
294 columns reached 81 to 100%, which indicated compound mass losses due to other than
295 H₂O₂ reaction (biodegradation, volatilization loss, and other experimental losses) were
296 less than 8% for TCE and PCE and less than 20% for DCE. The highest volatility of
297 DCE may result in the larger loss. The total recovered mass in the acid-treated columns
298 was less than 48%, meaning that more than 52% of mass were missing. This mass loss is
299 about 2.5 times of what was measured from the corresponding control columns. This
300 result suggested that the balance of contaminants masses were removed by the Fenton's
301 reaction with acids, and the Fenton's oxidation with citric acid is as effective as sulfuric
302 acid in destroying the organic contaminants. The citric acid columns showed 4– 6%
303 higher removal rates with the Fenton's reaction than the sulfuric acid columns. The
304 higher efficiency by the citric acid columns might be caused by lower pH. The pH values
305 in the liquid effluents were 3.5 for citric acid columns and 5.8 for sulfuric acid columns.

306 Overall, for 160 g of soil contaminated with organic compounds with a
307 concentration range of 1,300–5,000 µgL⁻¹ (480–870 µg kg⁻¹ soil), 25 mL of H₂O₂
308 solution (3% H₂O₂) was injected into acidified soil columns to achieve the organic
309 contaminant removal rates of 50 to 65%. However, note that the experiments specifically
310 address the efficiencies with respect to the reactants used and the chemistry of the soils
311 collected for this study, and the results do not address site-specific hydrogeological

312 characteristics (e.g. heterogeneities in composition and permeability, cracks and layering)
313 of this particular soil, which must be considered when applying any remediation
314 technology.

315

316 **Conclusions**

317 Citric acid has been examined for Fenton's reaction in terms of its possible role as
318 an acidifying agent and a scavenger of hydroxyl radicals. Batch and column experiments
319 performed with three types of organic contaminant demonstrate that the citric-acid-
320 modified Fenton's reaction shows the organic contaminant removal efficiencies similar to
321 the traditional sulfuric acid-aided Fenton's reaction. However, beyond a threshold
322 concentration of H_2O_2 with respect to the molar ratio with Fe^{2+} ($\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:330$), the
323 efficiency of H_2O_2 in removal organic contaminants decreases.

324 A citric-acid-modified Fenton's reaction does not show significant gas
325 accumulation and solid precipitations, which can cause flow path blockages, hamper
326 continuous reagent injection, and would result in hazardous operational conditions for
327 decontamination activity. Further studies on the reduction of gas accumulation and solid
328 precipitation need to be performed to understand the mechanisms. In addition,
329 subsequent to completion of Fenton's reaction, the residual citric acid could stimulate
330 microbial activities near the injected area initiating reductive dechlorination. Long-term
331 experiments need to be performed to verify the potential biological activities that could
332 lead to subsequent biodegradation of contaminants.

333

334 **Acknowledgment**

335 This article was developed at the Lawrence Berkeley National Laboratory, which
336 is operated by the University of California for the U.S. Department of Energy under
337 contract DE-AC02-05CH11231.

338

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401 Tables and Figures

402

403 Table 1. Soil Analysis

404 Table 2. Second-order rate constants for Fe^{3+} generation reactions with excessive H_2O_2

405 Table 3. Mass balance (%) of volatile organic compounds in column experiments

406

407 Figure 1. Batch test removal efficiencies (%) of TCE in three experiments (deionized,
408 two acidified) with the varying concentrations of H_2O_2 . No iron catalyst was added in
409 (a), and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in (b), filtered soil solution in (c), or two grams of soil in (d) was
410 added as an iron source for catalysts. 24 h reaction time at 4°C

411 Figure 2. Batch test removal efficiencies (%) of DCE (a) and PCE (b) in citric acid
412 solutions with the varying iron sources and concentrations of H_2O_2 . 24 h reaction time at
413 4°C

414

415 Table 1. Soil Analysis

Classification	Silty Clay
Soil pH	7.9
Alkalinity	1.56%
Total Fe Content	35000 mg kg ⁻¹
Sorption Coefficient (K_d , L kg ⁻¹)	<i>cis</i> -DCE: 0.48 TCE: 0.84 PCE: 1.66

416

417 Table 2. Second-order rate constants for Fe³⁺ generation reactions with excessive H₂O₂

$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O}$	¹ $k=3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	(4)
$\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2 \cdot$	² $k=2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	(5)
$\text{HO}_2 \cdot + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$	³ $k=1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	(6)
$\text{HO}_2 \cdot + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2$	⁴ $k=3.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	(7)
$\cdot\text{HO} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^-$	⁵ $k=3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	(8)

418 ¹Christensen et al. (1982), ²Pignatello (1992), ³Rush and Bielski (1985), ⁴Haber and Weiss (1934),419 ⁵Stuglik and Zagórski (1981)

420

421 Table 3. Mass balance (%) of volatile organic compounds in column experiments

Mass Balance (%)	DCE			TCE			PCE		
	CC	CA	SA	CC	CA	SA	CC	CA	SA
Removed with Liquid	73	38	44	74	28	36	50	15	22
Left in Soil	8	6	4	19	9	7	51	18	19
Removed with Gas	<1	<1	<1	<1	<1	<1	<1	<1	<1
Total VOC measured	81	44	48	93	36	43	101	33	38
¹ Unrecovered VOC	19	56	52	8	64	58	<1	67	62

422 ¹Calculated by subtracting the total VOC measured from 100%. VOC: volatile organic compound, DCE:423 *cis* 1,2-dichloroethylene, TCE: trichloroethylene, PCE: tetrachloroethylene, CC: CaCl₂ 0.005 M, CA: citric

424 acid 0.5 M, SA: sulfuric acid 1 N.

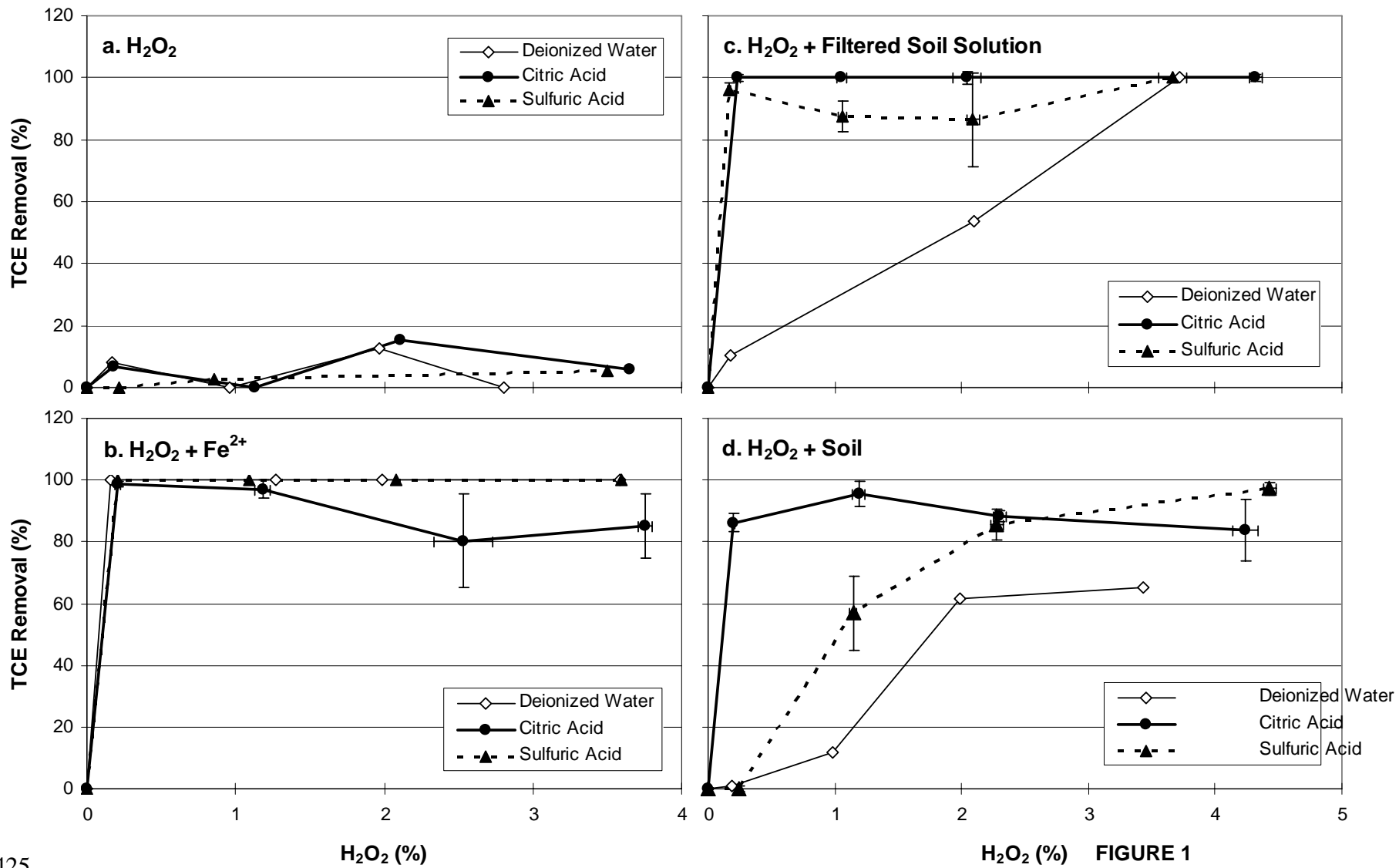
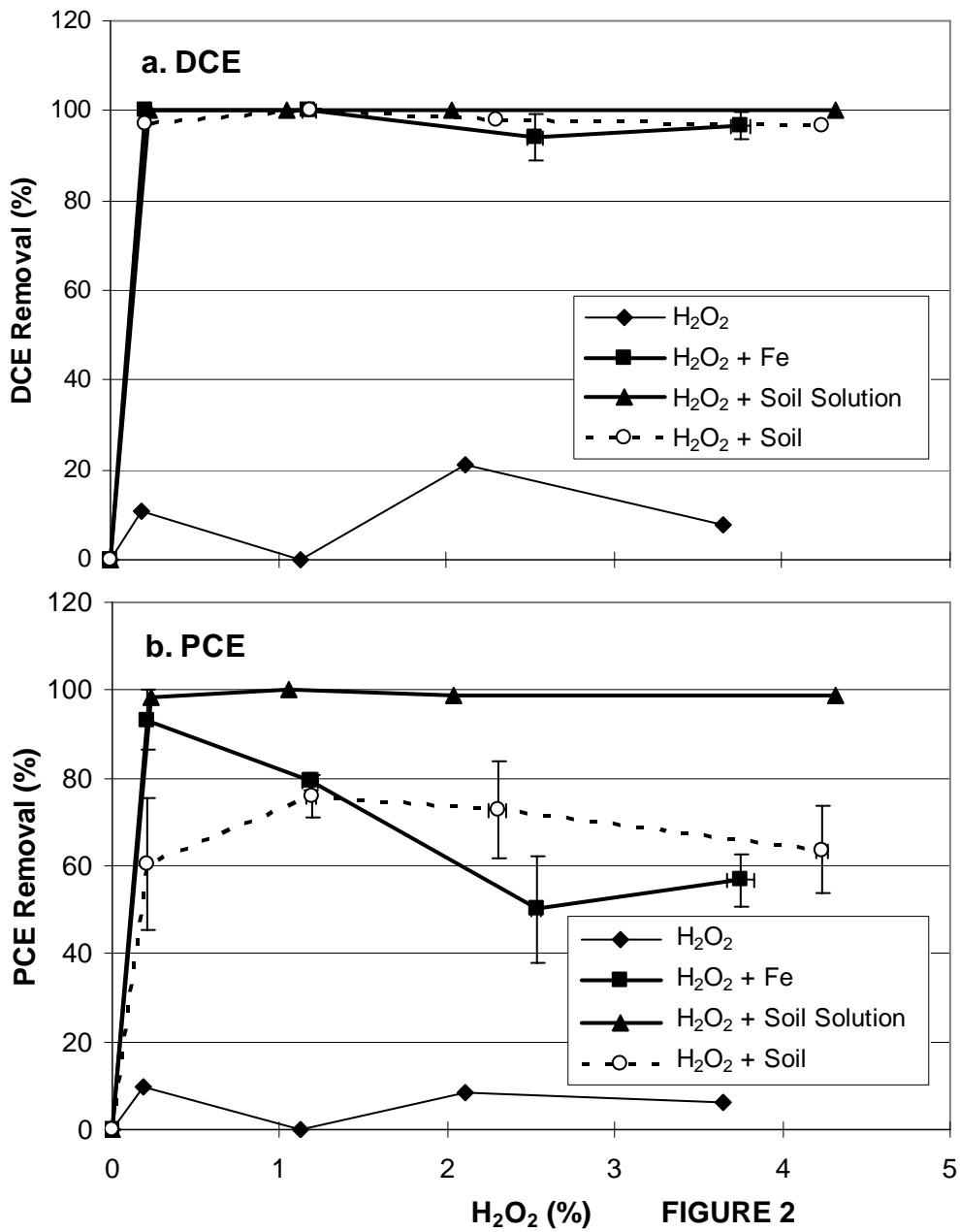


FIGURE 1



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