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Highlights

- Harmful chlorinated ethenes threaten the drinking water resource and its consumers
- Transformation of PCE in electrochemical flow-through reactors was studied
- Influence of various reactor design parameters was investigated, reaching 86% removal
- Normalization of data improved understanding of mechanisms across tests and studies
- Electrochemical reduction and oxidation can reduce mass flux of simulated PCE plumes

Transformation of tetrachloroethylene in a flow-through electrochemical reactor

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Abstract

Electrochemical transformation of harmful tetrachloroethylene (PCE) is evaluated as a method for management of groundwater plumes to protect the drinking water resource, its consumers and the environment. In contrast to previous work that reported transformation of trichloroethylene, a byproduct of PCE, this work focuses on transformation of PCE in a saturated porous matrix and the influence of design parameters on the removal performance. Design parameters investigated were electrode configuration, catalyst load, electrode spacing, current intensity, orientation of reactor and flow through a porous matrix. A removal of 86% was reached in the fully liquid-filled, horizontally oriented reactor at a current of 120 mA across a cathode → bipolar electrode → anode arrangement with a Darcy velocity of 0.03 cm/min (150 m/yr). The palladium load on the cathode significantly

23 influenced the removal. Enhanced removal was observed with increased electrode spacing.
24 Presence of an inert porous matrix improved PCE removal by 9%-point compared to a completely
25 liquid-filled reactor. Normalization of the data indicated, that a higher charge transfer per
26 contaminant mass is required for removal of low PCE concentrations. No chlorinated intermediates
27 were formed. The results suggest, that PCE can be electrochemically transformed in reactor designs
28 replicating that of a potential field-implementation. Further work is required to better understand the
29 reduction and oxidation processes established and the parameters influencing such. This knowledge
30 is essential for optimization towards testing in complex conditions and variations of contaminated
31 sites.

33 **Keywords**

35 Chlorinated ethenes, removal, groundwater, electrochemistry, design screening

37 **1. Introduction**

39 Chlorinated ethenes have been unintentionally introduced to the environment causing extensive
40 and harmful contamination of the subsurface, potentially impacting the groundwater and indoor air
41 quality [1,2]. Effort has been put into remediation of low-permeable zones, where use of
42 electrokinetics has shown to overcome some of the challenges faced [3–7]. However, the dense
43 chlorinated ethenes slowly leak into aquifers, causing an increase in detection above regulatory
44 maximum contaminant levels [8]. Current remedies used for chlorinated ethene plumes include
45 pump-and-treat [9,10], enhanced reductive dechlorination [1,10], in-situ chemical oxidation [11,12],
46 permeable reactive barriers [13,14] and air-sparging [15,16]. These technologies can be challenged

by inadequate delivery of reactants [12,17,18], short longevity of reactants [12,19,20] or varying contaminant phase transfer affinities with generation of contaminated waste [16,21]. Challenges, which may be overcome by adaptation of the mechanisms of electrokinetics towards mass flux reduction in these high-permeable zones by establishment of electrochemical zones. This is gaining increasing focus, since reducing and oxidizing zones sufficient for degradation of the chlorinated ethenes can be established [22–25]. The reducing zone is generated from electrolysis at the cathode (Eq. 1) [26,27], which can directly and indirectly reduce the parent components tetrachloroethylene (PCE) and trichloroethylene (TCE) and stimulate microbial degradation [28–31]. In addition, hydrogen peroxide (H₂O₂), which is a strong oxidant that can break down the chlorinated ethenes [32,33], can be effectively formed (Eq. 2) at a sufficiently high dissolved oxygen concentration, or if a catalyst like palladium (Pd) is applied to the cathode. Furthermore, Pd can catalyze formation of $\bullet$ OH radicals (Eq. 3), which also oxidize the chlorinated ethenes [34].

60

The anode generates oxidizing conditions (Eq. 4) [26], specifically by Ti/IrO₂-Ta₂O₅ mixed metal oxide (MMO) anodes (Eq. 5) [35], which can oxidize e.g. TCE and the chlorinated intermediates dichloroethylene (DCE) and vinyl chloride (VC). However, the oxygen evolution competes with oxidation of the chlorinated ethenes.

65

66

67 Research on electrochemical removal of chlorinated ethenes has focused on TCE [22,23,39–
68 44,24,28,32,34–38]. Since TCE is more volatile than PCE, mass balances of TCE can be
69 particularly poor. Also, the reported optimal design parameters are dependent on the specific system
70 studied, and little knowledge is available on the specific mechanisms responsible for degradation of
71 PCE and TCE in flow-through electrochemical reactors. This makes it complex to adapt the current
72 level of knowledge on electrochemical removal of TCE towards complete removal of PCE. The
73 reduction mechanisms have been investigated on iron metal (Fe(0)) surfaces, showing higher
74 dechlorination rates with increased halogenation [45–47], but also the opposite trend [48–50].
75 Arnold and Roberts [49] found, that 87% of PCE and 97% of TCE follow direct reduction on Fe(0),
76 i.e. contact between the surface of Fe(0) and the chlorinated ethene is essential. During direct
77 reduction on Fe(0) surfaces, the reaction rate constant for PCE is higher than that for TCE [51].
78 While during indirect reduction via atomic hydrogen formed from electrolysis (Eq. 1) [51], the
79 reaction rate constant for PCE is lower than that for TCE. Thus, a smaller fraction of PCE than TCE
80 follows the direct reduction pathway, but reaction kinetics is faster during direct reduction of PCE
81 than TCE. The rate limiting steps for direct and indirect reduction are chemisorption onto the
82 electrode, electron transfer, bond-breaking or molecular rearrangement [52].

83 Competing reactions, due to presence of ionic species in the electrolyte, can interfere with the
84 chemical mechanisms responsible for removal of the chlorinated ethenes, which may be non-
85 linearly distributed, and time and space dependent. This may explain observed variations over time,
86 the course of reactors and between batch and column set-ups [51,53]. In addition, electrode

compositions and impurities influence the reduction processes [49,54,55]. For development of flexible full-scale remediation designs that can overcome the complexity and variations of contaminated sites, improved understanding of the transformation mechanisms and parameters controlling those is essential.

The objective of this study is to examine the influence of reactor design on the electrochemical removal of PCE in a flow-through reactor using palladized Fe foam cathodes and MMO anodes. The study is a screening of the significance of parameters relevant to a field design on the electrochemical PCE removal performance, e.g. a porous matrix and horizontal orientation. Such knowledge is required for development of a more robust test design for enhanced applicability and feasibility testing at conditions simulating that of potential in-situ applications. Previous work has studied electrochemical removal of mainly TCE in static reactors [37,56], stirred reactors [22,57], recirculated reactors [23,35,40], vertical flow-through reactors [24,34,41–44,56,58], applied constant voltage [39,59,60] or studied electrochemistry in combination with other remediation strategies, e.g. bioremediation [29,61–64]. Assessment of the potential of flow-through electrochemical transformation of PCE is important to cover the full range of chlorinated ethene species detected at contaminated sites. This study differs from previous work by studying the electrochemical removal of PCE in horizontally oriented undivided reactors with flow through a porous matrix and operated at constant current. Studying such a reactor design is a necessary step towards upscaling of electrochemical remediation for treatment of contaminated groundwater. In the field, the primary groundwater flow direction is horizontal, flow is through a porous matrix, and the charge transfer is best controlled with application of constant current.

2. Materials and methods

111 2.1 Chemicals and materials

112

113 Chemicals used were of analytical grade: PCE (99%, Sigma-Aldrich), TCE (99.5%, Sigma-
114 Aldrich), cis-DCE (97%, Sigma-Aldrich), calcium sulfate (JT Baker), hydrochloric acid (HCl)
115 (37%, Carolina) and palladium(II) chloride (PdCl_2 , 99.9%, Alfa Aesar). MMO meshes (1.8 mm in
116 width, 3N International), composed of IrO_2 and Ta_2O_5 coating on titanium were used as bipolar
117 electrodes (BPE) and anodes. Cathodes of Fe foam (3 mm in width, 45 pores per inch, 98% Fe, 2%
118 Ni, Aibixi Ltd.) and/or 316 stainless steel discs (SS, 0.7 mm in width, 0.4 mm wire diameter, 20 x
119 20 mesh size, 0.86 mm opening size, 12% Ni, McMaster-Carr) were used. The diameter of
120 electrodes used was 77 mm. The 316 SS cathode was assembled using four discs to increase the
121 width. Fe foam cathodes were perforated with 4 mm holes for every 10 mm and coated with Pd.
122 Prior to electroless plating with Pd, the Fe foam was rinsed in 1 M HCl for 10 minutes, thoroughly
123 washed in deionized water, submerged in a solution of 0.1 M HCl and PdCl_2 , rotated until the
124 orange solution turned colorless and washed with deionized water [41,42]. Solid glass beads (5 mm,
125 2.23 g/cm^3) were purchased from Propper Manufacturing Co. Inc. Nylon meshes (0.1 mm in width,
126 0.12 mm wire diameter, 61 x 61 mesh size, 0.3 mm opening size, McMaster-Carr) were mounted on
127 each side of the electrodes to prevent glass beads in blocking openings of the electrode meshes.
128 Feedstock solutions were stored in Tedlar® bags (Sigma-Aldrich) and prepared using $18.2 \text{ M}\Omega\text{cm}$
129 high-purity water from a Millipore Milli-Q system. Tygon® tubing (2.06 mm ID, 3.79 mm OD,
130 Cole-Parmer) and a peristaltic pump (0.4-85 ml/min, Cole-Parmer), were used to control the flow of
131 liquid. Constant current was applied using one Agilent E3612A 0-120V, 0-0.25 A power supply.

132

133 2.2 Analytical methods

134

Concentrations of PCE, TCE and cis-DCE were measured in 2 ml samples by an Agilent 1200 Infinity Series HPLC with a 1260 DAD detector and a Thermo ODS Hypersil C18 column (4.6 x 50 mm) as described in Rajic et al. [41]. Release of Pd ions was analyzed using a Varian ICP-EOS 720-ES. Samples were filtrated prior to analysis using 0.2 µm PVDF syringe filters from Jin Teng. Conductivity of the feedstock solutions was measured using a Thermo Orion 5 Star meter with corresponding probe. pH of the feedstock solutions was measured using a Mettler Toledo Seven Compact meter with corresponding probe. pH of samples collected from sampling ports was assessed using EMD MilliporeTM MColorpHastTM pH test strips.

2.3 Electrochemical flow-through reactor

Synthetic groundwater simulating the conductivity of a sandy aquifer was prepared by dissolving 1600 mg/l calcium sulfate in deionized water. Calcium sulfate was used instead of calcium carbonate to limit the influence of the carbonate system on the electrochemical mechanisms and pH gradients established [65]. The resulting conductivity was 700-890 µS/cm with a pH of 5.7 ± 0.4 and a constant temperature of 20°C. The synthetic groundwater was spiked with PCE to a concentration of 2.7 mg/l. A saturated stock solution of free-phase PCE in deionized water was used. The feedstock solution was stored in Tedlar® bags with minimal headspace to limit mass loss by volatilization. Flow through the reactor was kept constant at velocities reported in Table 1.

Table 1. Experimental conditions for the electrochemical treatment of initially 2.7 mg/l PCE.

Electrode configuration ^a	Electrode material	Electrode spacing [cm]	Column orientation	Current [mA]	Pd catalyst loading ^b [mg/cm ²]	Darcy velocity [cm/min]	Porosity, water- filled ^c [%]
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0 ^d	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	0	0.76	0.09	31.1 ± 0.3
1	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	60	0.76	0.09	30.8
2	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	0.76	0.09	30.8
3 ^d	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	1.14	0.08	34.8 ± 0.5
4	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	180	1.14	0.08	35.3
5	C → BPE → A	Fe foam → MMO → MMO	2.5	Horizontal	120	1.14	0.08	34.1
6	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	1.14	0.03	100
7	C → BPE → A	Fe foam → MMO → MMO	4	Vertical	120	1.14	0.03	100
8	C → C → A	SS → Fe foam → MMO	4	Horizontal	120	1.14	0.08	34.2
9	C → C → A	Fe foam → Fe foam → MMO	4	Horizontal	120	1.14	0.08	35.0
10	C → A	Fe foam → MMO	8	Horizontal	120	1.14	0.08	34.3
11	C → A	Fe foam → MMO	2.5	Horizontal	120	1.14	0.25	100
12	C → A	Fe foam → MMO	2.5	Vertical	120	1.14	0.25	100

^a A: Anode, C: Cathode, BPE: Bipolar electrode

^b Catalyst applied on Fe foam only. Load is given as mass per geometric electrode surface area

^c Porosities of 100 % indicate a fully liquid-filled reactor, while tests with porosities < 100 % incorporate the porous matrix

^d Duplicate testing

An acrylic column was used as the flow-through electrochemical reactor (L 16.8 cm and D 7.8 cm in inner dimensions). The influence of reactor design on electrochemical removal of PCE was investigated in a sequence of a) electrode configurations and spacings. For three-electrode configurations, the constant current was split equally between the two cathodes by a rheostat, b) current intensities and Pd catalyst loadings, c) porous matrices and reactor orientations. The inert porous matrix was incorporated to replicate field-conditions and to reduce amount of contaminated waste generated, and d) groundwater flow and test duration (Table 1).

The position of electrodes and sampling ports (P0-P5) in the electrochemical reactor is shown in Figure 1. In horizontally orientated reactors, electrolytically generated gases were extracted manually from sampling ports above the electrodes using syringes with needles. To limit mass loss

172 by volatilization, the gas extraction occurred whenever a gas phase was observed. The frequency of
 173 this manual venting depended on current intensity, electrode configuration and electrode material
 174 with a range of once every 30-90 seconds. In vertically oriented reactors, released gases moved up
 175 through the reactor and out with the effluent.
 176

177
 178
 179 **Figure 1.** The baseline flow-through electrochemical set-up composed of a feedstock solution, peristaltic pump, a
 180 cathode, bipolar electrode and an anode connected to a power supply. P0-P5 are sampling ports. Sampling ports above
 181 the electrodes served for manual extraction of gases generated. Measures are of inner dimensions.

182
 183 Prior to the electrochemical application, the reactor was saturated with the feedstock solution at
 184 elevated flow to limit volatilization, followed by flow-through for one pore volume (PV) at the flow
 185 velocities given in Table 1 to ensure a uniform contaminant distribution. Direct current was applied
 186 for 3.5 PV and 1.2 PV for flow through the porous matrix (Table 1, test 1-5, 8-10) and completely
 187 liquid-filled reactor (Table 1, test 6-7, 11-12), respectively.

188

189 **3. Results and discussion**

190

191 Different designs of the electrochemical reactor were tested. To evaluate the influence of a
192 design parameters on the PCE removal, each experiment conducted is compared to similar ones of
193 which one parameter varied only. Accordingly, the significance of electrode spacing, electrode
194 configuration, current intensity, Pd loading on the cathode, duration of electrochemical treatment,
195 orientation of reactor and porosity on PCE removal, potential difference over the electrodes and pH
196 downstream of the electrochemical zone is assessable (Figure 2). The design parameter category,
197 e.g. electrode spacing, is indicated above comparable experiments, whereas the specific dimension
198 of that design parameter, e.g. 2.5 cm and 4 cm, is given on the horizontal axis. Figures written on
199 the bars refer to the experimental numbers given in Table 1.

200

201 *3.1 Impact of electrode configuration and spacing on PCE removal*

202

203 Influence of electrode configuration and spacing on electrochemical removal of PCE was
204 investigated in the flow-through reactor with Fe and MMO electrodes at 120 mA and a Darcy
205 velocity of 0.08 cm/min (experiments 3,5,8-10, Figure 2a, Table 1).

206 A three-electrode configuration of two Pd coated Fe foam cathodes and an MMO anode
207 performed similar to the corresponding two-electrode configuration, reaching removals of 42% and
208 39%, respectively (exp. 9-10, Figure 2a). Rajic et al. [41] also observed comparable removals of
209 TCE in two- and three-electrode configured reactors using Fe and MMO electrodes, while the
210 reaction rate nearly doubled in the three-electrode arrangement. By replacing the first Pd/Fe foam
211 cathode with 316 SS, the removal increased to 51% (exp. 8, Figure 2a). The high content of Ni in

212 this type of stainless steel can catalyze reduction, since Ni like Pd lowers the cathodic hydrogen
213 overpotential [55,66], enhancing the hydrodechlorination. Use of Ni-containing stainless steels for
214 electrochemical removal of chlorinated ethenes has shown to be cost-efficient [55]. The best
215 performing electrode configuration was $C \rightarrow BPE \rightarrow A$ with a removal of $54 \pm 3\%$ (exp. 3, Figure
216 2a). By introducing a BPE, a supplementary oxidizing-reducing zone is established, enhancing the
217 hydrodechlorination and oxidation by increased formation of H_2O_2 (Eq. 2) [34]. Of the electrode
218 configurations and materials tested, the lowest potential difference of 17V was obtained in the
219 $SS \rightarrow Pd/Fe \rightarrow MMO$ arrangement, and the highest potential difference of 36V in the $Pd/Fe \rightarrow$
220 MMO reactor (exp. 8 and 10, Figure 2b). The BPE lowered the potential difference from 36V to
221 32V (exp. 3 and 10, Figure 2b); a simple measure to potentially reduce the costs of power
222 consumption in upscaling activities.

223 Increasing the electrode spacing from 2.5 cm to 4 cm in the $C \rightarrow BPE \rightarrow A$ arrangement
224 improved the PCE removal from 41% to $54 \pm 3\%$ (exp. 3 and 5, Figure 2a). This is opposite to
225 previous findings in completely liquid-filled reactors, where the observed decrease in removal with
226 an increase in electrode spacing was explained by a resulting increase in potential difference over
227 the reactor [41]. In this study, the potential difference also increased, from 22V to $31.6 \pm 0.4V$ (exp.
228 3 and 5, Figure 2b), and thereby the resistivity of the system [67], but the increase did not inhibit the
229 removal as previously shown for TCE [41,68]. By increasing the electrode spacing, the redox zone
230 is prolonged, which possibly accounts for the increased PCE removal. Considering upscaling, this
231 can reduce the direct costs for the plant due to a cutback in the network of electrodes.

232 pH measured in the porewater downgradient the electrochemical zone (sampling port P5) was
233 4.5-5 in the $C \rightarrow C \rightarrow A$ and $C \rightarrow A$ configurations tested (exp. 8-10, Figure 2c). For $C \rightarrow BPE \rightarrow$
234 A , pH was 8.5 ± 1.5 (exp. 3, Figure 2c). The elevated pH in the latter configuration could be due to
235 enhanced H_2O_2 formation when introducing a BPE: free oxygen and hydrogen ions generated at

236 anodic sites (Eq. 4) are consumed at adjacent cathodic sites (Eq. 2), i.e. the acidic gradient is
237 weakened and incapable of neutralizing the alkaline gradient established at cathodic sites. BPEs
238 have shown to significantly assist in H_2O_2 formation in electrochemical flow-through reactors [34].
239 For comparison, pH in the control experiment without applied current was 7 (exp. 0, Figure 2c).

241 3.2 Significance of current intensity and catalyst loading on PCE removal

243 Currents of 0 mA, 60 mA, 120 mA and 180 mA were tested in the $\text{C} \rightarrow \text{BPE} \rightarrow \text{A}$ arrangement
244 for electrochemical removal of PCE with Pd catalyst loadings on the Fe foam cathode of 0.76
245 mg/cm^2 and/or 1.14 mg/cm^2 (exp. 0-4, Figure 2a).

246 For catalyst loadings of 0.76 mg/cm^2 , PCE removals were 0%, 14% and 18% at currents of 0
247 mA, 60 mA and 120 mA, respectively (exp. 0-2, Figure 2a). For catalyst loadings of 1.14 mg/cm^2 ,
248 PCE removals were $54 \pm 3\%$ and 39% at 120 mA and 180 mA, respectively (exp. 3-4, Figure 2a).
249 Thus, the current intensity and PCE removal are parabolic correlated. The decline in removal at 180
250 mA is explained by increased competition of oxygen evolution at the anode. In addition, the oxygen
251 generated physically covered the anode and thereby occupied active sites for oxidation [41,42].

252 Catalysts are important for the transformation of PCE, since a 50% increase in Pd load enhanced
253 PCE removal by 36%-point at 120 mA (exp. 2-3, Figure 2a). The significance of Pd on chlorinated
254 ethene removal has been studied previously, where an optimal concentration of 0.76 mg/cm^2 was
255 found [42]. The inconsistency in findings of optimal load of Pd on Fe foam cathodes possibly is
256 associated with the geometry of the Fe foam cathodes used; the electrode surface areas tend to be
257 estimated based on geometrical shape, since the actual surface area of the foams is unknown. Thus,
258 the electrode surface area ratio between experimental set-ups cannot be applied directly in the
259 dimensioning of Pd load.

260 In the set-up studied, a further increase in Pd load could optimize the removal performance, since
261 the $C \rightarrow C \rightarrow A$ arrangement with 316 SS and Pd/Fe foam cathodes was superior to two Pd/Fe
262 foam cathodes (Section 3.1., exp. 8-9, Figure 2a), with higher catalytic content in the 316 SS than
263 the resulting palladization. However, replacing the Pd/Fe foam cathode with 316 SS in a $C \rightarrow A$
264 set-up is insufficient [55]. In the remainder of tests, a Pd load of 1.14 mg/cm^2 was applied. The
265 voltage stabilized at 32V at 120 mA independent of Pd load (exp. 2-3, Figure 2b). Whereas the
266 potential difference increased from 20V to 32V to 38V at 60 mA, 120 mA and 180 mA,
267 respectively (exp. 1-4, Figure 2b), a linear correlation with R^2 of 0.93. According to Ohms Law, the
268 electrical resistivity should remain constant when the experimental conditions, besides current
269 intensity, are unaltered. In this study, the resistivity increased with increasing current, which
270 possibly can be ascribed to increased oxygen and hydrogen generation at the anode ((Eq. 4)-(Eq. 5)
271 and cathode (Eq. 1) with increased current. The additional gases formed extended the gas coverage
272 of the electrode surfaces. Evolving gas layers on the electrode surfaces reduce connectivity between
273 electrodes and the conductive liquid phase, wherefore the electrical resistivity increases.

274 MMO anodes are known to maintain pH of the water treated [41]. However, in the studied $C \rightarrow$
275 BPE $\rightarrow A$ arrangement, pH of the porewater downgradient of the electrochemical zone (sampling
276 port P5) was elevated to 8.5 ± 1.5 at 120 mA and 180 mA (exp. 0 and 3-4, Figure 2c). The elevated
277 pH post electrochemical treatment indicates formation of H_2O_2 (Eq. 2) instead of neutralization of
278 the alkaline front established at cathodic sites.

279 A concern of using catalysts like Pd and Ni for treatment of water, whether it is for drinking
280 purposes or discharge into the nature, is the release of ions, which may inhibit living organisms
281 [69,70]. If the catalyst is applied on the cathode and polarity is not reversed, release is of little
282 concern. Whether Pd is released when no current is applied, is not reported. Therefore, effluent
283 samples extracted throughout the 360 min of control testing (exp. 0) were analyzed for Pd.

284 Concentration of Pd was below 0.002 mg/l. Tests on *Daphnia magna* indicate long-term effects of
285 concentrations >1 mg/l [71].

Figure 2. Comparison of the experimental conditions tested on a) PCE removal obtained in sampling port P5, b)

potential difference over the reactor measured after app. 1 PV (was rather constant), and c) pH measured in sampling

port P5. Error bars are included for duplicate testing. * denotes direct reuse of the experimental set-up. Figures on the bars refer to experiment no. in Table 1.

3.3 Influence of a porous matrix and orientation of reactor on PCE removal

Electrochemical performance in porous matrices was assessed for flow through a porous matrix of glass beads with a porosity of 34.3% at a Darcy velocity of 0.08 cm/min in the C → A electrochemical reactor at 120 mA. Presence of the porous matrix enhanced PCE removal to 39% compared to 30% in the completely liquid-filled reactor (exp. 10 and 11, Figure 2a). The experimental parameters electrode spacing and flow are varied in this comparison (Table 1, test 10-11). Sorption of PCE onto glass beads is neglectable [32,43], verified by the insignificant mass loss in control experiments (exp. 0, Figure 2a). The more complex flow pattern through a porous matrix than a completely liquid-filled reactor may improve the contact between generated reactants and the PCE and explain the enhanced removal in porous matrices. In the porewater downgradient of the electrochemical zone (sampling port P5), pH 5 was measured with and without presence of the porous matrix (exp. 10 and 11, Figure 2c). The potential difference increased from 7V to 36V when including the porous matrix (exp. 10 and 11, Figure 2b). Hence, resistivity was 5 times higher in the porous matrix. An increase in potential difference as the alkaline front progresses towards the anode in a porous matrix has been observed [72].

Vertical oriented reactors are applied in most studies on flow-through electrochemical removal of chlorinated ethenes [24,32,58,33,34,40–44,55]. One major advantage is automatic venting of gases generated, since gases released from the electrodes will bubble up through the reactor and leave the reactor with the effluent. For horizontally oriented reactors, the gases will accumulate in a vapor phase above the electrodes, pressurize the system and eventually drain out the fluid, if no

314 means of venting are installed. However, a horizontally oriented reactor may be desirable for
315 feasibility studies of field-implementations of electrochemical contaminant transformation in
316 saturated porous matrices. Whether orientation of the reactor influenced the treatment performance
317 was assessed in the $C \rightarrow BPE \rightarrow A$ and $C \rightarrow A$ arrangement at 120 mA. At the two flow velocities
318 tested, the horizontally oriented reactor was superior to the vertically oriented with 9-16%-point
319 (exp. 6 vs. 7 and 11 vs. 12, Figure 2a). pH in the porewater downgradient the electrochemical zone
320 (sampling port P5) was similar in the horizontal and vertical orientations of 4.5 and 5 for the low
321 and high flow velocity studied, respectively (exp. 6-7, 11-12, Figure 2c). For the potential
322 difference over the electrodes, no clear trend is observed (exp. 6-7, 11-12, Figure 2b).

323 Based on observations, the differences in performance of horizontal and vertical oriented
324 reactors probably were related to the system's ability to release gases generated at the electrodes. In
325 the vertically oriented reactors, the gases accumulated on the upgradient side (lower) of the
326 electrodes until a certain gas volume was reached. The bubbles then pushed through the perforated
327 mesh electrodes and escaped the reactor with the effluent. During the buildup of gases, the potential
328 difference increased followed by a sudden drop once the bubbles had migrated through the mesh
329 electrodes. Accumulation of gases was most prevalent during the high flow tested. Significance of
330 stripping of the volatile contaminant into those gas phases is unknown. In the horizontally oriented
331 reactors, gas phases were immediately extracted above the electrodes using syringes. The gases
332 appeared to be more readily and steadily released and extracted in the horizontal reactors, thus
333 disturbing the system less: the potential difference remained steadier, less pressure build up and the
334 vapor phases were less extensive. Mass loss through volatilization is considered less in the
335 horizontally oriented reactors. Several means of automatic venting in the horizontally oriented
336 reactors were tested; automatic vents, gas-liquid separation membranes, gravity and water-locks.
337 Transient changes in the electrochemical system challenged these venting mechanisms, i.e. the

338 manual extraction of gases was most suitable. Venting mechanisms are lab challenges only, because
339 the test set-ups must be closed systems to hinder mass loss through volatilization. In the field, the
340 test area is an open system from which gases can escape through the electrode wells, in which they
341 are generated, or migrate through the soil matrix. If stripping of chlorinated ethenes is an issue,
342 granular activated carbon above the electrodes can capture the volatilized fraction of the
343 contamination.

344

345 *3.4 Effect of flow and test duration on PCE removal*

346

347 Flow rate is inverse proportional to residence time of PCE within the electrochemical reactor, i.e.
348 lowering the flow rate prolongs the residence time. Effect of flow was studied in the completely
349 liquid-filled reactor with a high flow in the C → A arrangement (exp. 11-12) and compared to a low
350 flow in the C → BPE → A configuration (exp. 6-7). The experimental parameters electrode
351 spacing, electrode configuration and flow are varied in this comparison (Table 1, test 6-7 vs.11-12),
352 wherefore changes cannot solely be ascribed to altered flow. However, the effect of flow rate on the
353 PCE removal is significant in comparison to the effect from electrode spacing and configuration
354 alone (exp. 6-7,11-12 vs. 3,5,8-10, Figure 2a).

355 Reducing the Darcy velocity from 0.25 cm/min (1314 m/yr) to 0.03 cm/min (150 m/yr) increased
356 PCE removal with 56-63%-point reaching a removal of 86%. For electrochemical treatment of TCE
357 at 60 mA, a reduction in Darcy velocity from 2628 m/yr to 1314 m/yr resulted in a 31%-point
358 improvement in TCE removal to 87% [41]. The low flow in the present investigation is
359 representative of common aquifer flows at contaminated sites.

360 pH of the porewater downgradient the electrochemical zone (sampling port P5) was similar of
361 4.5-5 (exp. 6-7 vs. 11-12, Figure 2c). The potential difference decreased by 6.5-13V at elevated

362 flow (exp. 6-7 vs. 11-12, Figure 2b), i.e. the resistivity of the high-flow system was lower,
363 indicating a higher mass-transfer of ionic species.

364 Electrochemical treatment during 120 min and 290 min insignificantly influenced the PCE
365 removal, pH in porewater downgradient the electrochemical zone (sampling port P5) and the
366 potential difference over the electric field in the C → BPE → A configuration at 120 mA and a
367 Darcy velocity of 0.08 cm/min (exp. 3, Figure 2). The electrochemical processes appeared to
368 rapidly establish and stabilize in this system having a simple hydrogeochemistry.

369

370 *3.5 Charge transfer in the electrochemical set-up*

371

372 Experimental specifications vary between studies, e.g. cross-sectional areas, flow velocities,
373 current intensities etc. For comparison of data across studies, normalization of the experimental data
374 is necessary. Many procedures exist for normalization. In the present study, normalization for
375 current intensity (I), flow rate (Q) and contaminant concentration (C) was chosen. Flow rate was
376 chosen instead of flow velocity to account for differences in cross-sectional areas of reactors. The
377 output is charge transfer per contaminant mass and the lower the number, the better in terms of
378 power consumption and thereby cost. The normalized data are plotted against PCE removal
379 percentage (Figure 3) and compared to data reported on electrochemical removal of TCE in a
380 similar set-up [41] (Figure 3, squares). The ratio of electrode surface area to liquid volume was
381 different in the two experimental set-ups applied (lower in the present work) and was not optimized
382 for in the experimental series carried out. Therefore, a deviation in levels of normalized data for a
383 specific removal percentage obtained was expected. Figure 3 allows to compare the overall level of
384 the normalized data obtained for electrochemical removal of PCE and TCE and the shape of the
385 resulting curves. Note, if sequential degradation via e.g. hydrogenolysis was in progress, a fraction

386 of the current supplied would be directed towards concurrent transformation of the degradation
 387 products formed. In this case, however, TCE nor DCE was detected (VC analysis was not possible),
 388 neither in Rajic et al. [41].

389

390

391

392 **Figure 3.** Normalization of experimental data for PCE based on samples extracted in the final sampling port (solid
 393 dots) and data for TCE in Rajic et al. [41] (squares) for current intensity (I), flow (Q) and contaminant concentration (C)
 394 plotted against the removal of PCE and TCE. Numbers next to markers refer to experiment number (Table 1).

395

396 For PCE removals beyond 30%, the charge input required increased, while for TCE a similar
 397 increase appeared for removals beyond 77% (Figure 3). Thus, a higher charge transfer was required
 398 to remove PCE than TCE. The difference in electrode surface area to liquid volume ratio between
 399 the two experimental set-ups possibly contributed to the observed deviation, where the contact
 400 between contaminant, Pd catalyst on the cathode and the energy source itself is improved at a
 401 higher such ratio, enhancing the conditions for contaminant transformation at a specific charge
 402 input. A low ratio of electrode surface area to liquid volume can be compensated for by increasing
 403 the current and/or Pd load. The similar levels of normalized data for PCE and TCE at a removal of
 404 30% support this: MMO anodes and an electrode spacing of 2.5 cm were used in both set-ups.

405 However, in the study on TCE, a Pd load of 0.76 mg/cm^2 and a current of 60 mA was applied [41].
406 In the study on PCE, having a lower electrode surface area to liquid volume, a Pd load of 1.14
407 mg/cm^2 and a current of 120 mA was applied (exp. 11). I.e. the lower electrode surface area to
408 liquid volume was counterbalanced by a 50% increase in Pd load and a 100% increase in current. A
409 further increase in current would possibly not be beneficial (exp. 4 vs. 11, Figure 2a). Instead, a
410 reduction in flow (exp. 6 vs. 11, Figure 2a) and an increase in Pd load is suggested for optimization
411 of electrochemical removal of PCE in the experimental set-up studied.

412 If comparing the normalized data obtained from all sampling ports, sampling rounds and test
413 designs (data not shown), and neglecting the associated removal levels, a generally best fit with
414 those of Rajic et al. [41] is seen when set-ups are most alike. I.e., for vertically oriented reactors
415 excluding a porous matrix (exp. 7 and 12), which illustrates the sensitivity towards the experimental
416 design. The concept of electrochemical treatment of chlorinated ethenes must be strengthened to
417 overcome the complex conditions of contaminated sites [65,73]. Finally, removals beyond app. 60%
418 and 90% for PCE and TCE, respectively, required a significant additional charge transfer, as
419 indicated by the steep slope of curves in Figure 3. Thus, treating the low levels of contaminant
420 concentrations, which is required to comply with the regulatory contaminant level for PCE and TCE
421 in drinking water, are the most expensive.

422 423 *3.6 PCE transformation pathways in the electrochemical reactor*

425 Mass loss is a concern when working with volatile contaminants like PCE, because it can give
426 false positive test results and thereby incorrect foundations for decision making. Two control
427 experiments were carried out in a set-up similar to that of experiment 1-4, except that no current
428 was applied (exp. 0, Table 1). No mass loss was observed throughout the 360 min of testing,

429 measured downgradient the electrochemical zone (sampling port P5, exp. 0, Figure 2a). An
430 observed drop in PCE concentration during experiments with applied current therefore is stimulated
431 by the electrochemistry. Stripping of the contaminants due to the gas generating electrode processes
432 (Eq. 1 and 4) rather than transformation is another concern when applying electrochemistry for
433 removal of chlorinated ethenes. A risk especially at stable anodes like MMO, since these produce
434 more oxygen (Eq. 5 vs. 4) [41] and PCE may be more prone to volatilization than oxidation at the
435 anode, as opposite to the higher affinity of reduction near the cathode. The specific electrode's
436 contribution to removal of PCE was found in the order of cathode > BPE > anode, indicating that
437 electrochemically induced transformation was occurring rather than stripping. Furthermore,
438 increasing the Pd load on the cathode from 0.76 mg/cm² to 1.14 mg/cm² improved the removal at
439 120 mA from 19% to 54±3% (exp. 2 vs. 3, Figure 2a), suggesting that the cathode induced
440 processes removed PCE.

441 Transformation mechanisms at the cathode possibly were related to the catalytic properties of Pd
442 through enhanced adsorption of atomic hydrogen, and thereby reductive hydrodechlorination of
443 PCE, and/or formation of the strong oxidative species H₂O₂ and •OH (Eq. 2-3). Formation of H₂O₂
444 and •OH appeared to contribute to the transformation of PCE, since 12% more PCE was removed
445 in the C → BPE → A arrangement than C → C → A (exp. 3 vs. 9, Figure 2a). Rajic et al. [34]
446 showed that using a BPE in between the cathode and anode strengthened the H₂O₂ formation. This
447 could be due to i) oxygen and dihydrogen being formed concurrently on each side of the BPE,
448 improving the contact necessary for conversion into H₂O₂, and ii) the anodic side of the BPE facing
449 the cathode, i.e. in closer contact and thus, if the oxygen diffused towards the cathode, it could
450 combine with the dihydrogen generated, forming H₂O₂ at the Pd surface [32]. Elevated pH
451 measured downstream the C → BPE → A electrochemical zone (sampling port P5) indicated
452 formation of H₂O₂ (Section 3.1).

453 The sequential hydrogenolysis products TCE and DCEs were not detected in any sampling point
454 of the experiments conducted. This suggests fast concurrent hydrogenolysis of TCE and DCEs or
455 another transformation pathway for PCE in the electrochemical reactor, e.g. oxidation by H_2O_2 and
456 $\cdot\text{OH}$, and/or β -elimination [73]. In parallel to the Fe cathodes applied in this study, degradation of
457 PCE on Fe(0) has shown to follow β -elimination for 87% of the contaminant mass [49]. The
458 electrochemical mechanisms responsible for PCE transformation along with the parameters
459 controlling those should be studied in detail for design of a robust electrochemical methodology for
460 removal of chlorinated ethenes.

461

462 **4. Conclusion**

463

464 Protection of the groundwater resource from harmful chlorinated ethenes is crucial and
465 challenging. Electrochemically induced reduction and oxidation may overcome some of the
466 difficulties experienced. In the development of the method, PCE must be included in the assessment
467 of electrochemical transformation of chlorinated ethenes, but is mostly overlooked. This study
468 screened the significance of parameters influencing electrochemical removal of PCE in a flow-
469 through reactor using a palladized Fe foam cathode and an MMO mesh anode. The major findings
470 are:

- 471 • Of the electrode configurations tested, presence of a BPE between the cathode and anode
472 improved removal of PCE to $54\pm 3\%$. The BPE added an oxidizing-reducing zone and
473 lowered the electrical resistivity.
- 474 • Pd played a major role in the transformation of PCE with a 50% increase in Pd load on
475 the cathode improving the removal by 36%-point.

- Increasing the electrode spacing from 2.5 cm to 4 cm enhanced the removal from 41% to 54±3%, due to extension of redox zones, which is a promising trend when considering the installation and cost of field-implementation.

PCE removal in liquid flowing through an inert porous matrix was investigated to simulate in-situ conditions. Presence of the porous matrix enhanced PCE removal by 9%-point compared to a completely liquid-filled reactor due to a more complex flow pattern within the porous matrix. A horizontally orientated reactor improved PCE removal by 9-16%-point compared to vertically oriented reactors. Release of oxygen and hydrogen gas from the electrode surfaces in the horizontal reactor was enhanced, wherefore a higher number of active electrode surface sites were available for PCE transformation. The highest removal of 86% was obtained using a horizontally oriented reactor at a current of 120 mA applied to an electrode configuration of C → BPE → A with a Pd load on the cathode of 1.14 mg/cm² and a Darcy velocity of 0.03 cm/min (150 m/yr) through a fully liquid-filled reactor. No chlorinated ethene degradation products were detected in any of the test designs studied.

Normalization of the data revealed, that the low contaminant concentrations were the most difficult to treat in that a significant charge transfer was required for removal beyond 60%. The removal performance was found sensitive to dimensional changes in experimental reactors. The transformation mechanisms and the parameters controlling those need to be better understood to control and adjust the relevant parameters for a flexible remediation design, that can overcome the variations occurring between lab set-ups and not least at contaminated sites. Thus, this study identified some weaknesses in the current stage of development of electrochemical removal of chlorinated ethenes, but also some promising trends in conceptual designs that better simulate that of a potential field-implementation.

500

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502

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509

510 **References**

511

- 512 [1] J.F. Pankow, S. Feenstra, J.A. Cherry, C.M. Ryan (Eds.), Dense chlorinated solvents and
513 other DNAPLs in groundwater: History, behavior, and remediation, Waterloo Press,
514 Portland, Oregon, 1996: pp. 1-522.
- 515 [2] A.M. Ruder, Potential health effects of occupational chlorinated solvent exposure, Ann. N.
516 Y. Acad. Sci. 1076 (2006) 207–227. doi:10.1196/annals.1371.050.
- 517 [3] A.N. Alshawabkeh, Electrokinetic soil remediation: Challenges and opportunities, Sep. Sci.
518 Technol. 44 (2009) 2171–2187. doi:10.1080/01496390902976681.
- 519 [4] A.T. Lima, A. Hofmann, D. Reynolds, C.J. Ptacek, P. Van Cappellen, L.M. Ottosen, S.
520 Pamukcu, A.N. Alshawabkeh, D.M. O’Carroll, C. Riis, E. Cox, D.B. Gent, R. Landis, J.
521 Wang, A.I.A. Chowdhury, E.L. Secord, A. Sanchez-Hachair, Environmental electrokinetics
522 for a sustainable subsurface, Chemosphere. 181 (2017) 122–133.
523 doi:10.1016/j.chemosphere.2017.03.143.

- 524 [5] K.R. Reddy, C. Cameselle (Eds.), *Electrochemical remediation technologies for polluted*
 525 *soils, sediments and groundwater*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2009: pp.
 526 1-732.
- 527 [6] A.B. Ribeiro, E.P. Mateus, N. Couto (Eds.), *Electrokinetics across disciplines and continents,*
 528 *new strategies for sustainable development*, Springer International Publishing, London, 2016:
 529 pp. 1-469. doi:10.1007/978-3-319-20179-5.
- 530 [7] H.F. Stroo, C.H. Ward (Eds.), *In situ remediation of chlorinated solvent plumes*, Springer,
 531 New York, NY, 2010: pp. 1-786. doi:10.1007/978-1-4419-1401-9.
- 532 [8] M.J. Moran, J.S. Zogorski, P.J. Squillace, *Chlorinated solvents in groundwater of the United*
 533 *States*, *Environ. Sci. Technol.* 41 (2007) 74–81. doi:10.1021/es061553y.
- 534 [9] D.M. Mackay, J.A. Cherry, *Groundwater contamination: Pump-and-treat remediation*,
 535 *Environ. Sci. Technol.* 23 (1989) 630–636. doi:10.1021/es00064a001.
- 536 [10] Interstate Technology & Regulatory Council, *Integrated DNAPL site strategy*, Washington,
 537 DC, USA, 2011: pp. 1-209. <http://www.itrcweb.org>.
- 538 [11] B.H. Kueper, H.F. Stroo, C.M. Vogel, C.H. Ward (Eds.), *Chlorinated solvent source zone*
 539 *remediation*, Springer, New York, USA, 2014: pp. 1-759. doi:10.1007/978-1-4614-6922-3.
- 540 [12] R.L. Siegrist, M. Crimi, M.M. Broholm, J.E. McCray, T.H. Illangasekare, P.L. Bjerg,
 541 *Advances in groundwater remediation: Achieving effective in situ delivery of chemical*
 542 *oxidants and amendments*, in: F.F. Quercia, D. Vidojevic (Eds.), *Clean Soil Safe Water*,
 543 Springer, Dordrecht, The Netherlands, 2012: pp. 197–212. doi:10.1007/978-94-007-2240-
 544 8_22.
- 545 [13] Interstate Technology & Regulatory Council, *Permeable reactive barriers: Lessons*
 546 *learned/new directions*. PRB-4, Washington, DC, USA, 2005: pp. 1-202.
- 547 [14] Y.T. He, J.T. Wilson, C. Su, R.T. Wilkin, *Review of abiotic degradation of chlorinated*

548 solvents by reactive iron minerals in aquifers, *Groundw. Monit. Remediat.* 35 (2015) 57–75.
549 doi:10.1111/gwmr.12111.

550 [15] D.H. Bass, N.A. Hastings, R.A. Brown, Performance of air sparging systems: a review of
551 case studies, *J. Hazard. Mater.* 72 (2000) 101–119. doi:10.1016/S0304-3894(99)00136-3.

552 [16] M.H. Stenzel, U. Sen Gupta, Treatment of contaminated groundwaters with granular
553 activated carbon and air stripping, *J. Air Pollut. Control Assoc.* 35 (1985) 1304–1309.
554 doi:10.1080/00022470.1985.10466035.

555 [17] H.F. Stroo, A. Leeson, J.A. Marqusee, P.C. Johnson, C.H. Ward, M.C. Kavanaugh, T.C.
556 Sale, C.J. Newell, K.D. Pennell, C.A. Lebrón, M. Unger, Chlorinated ethene source
557 remediation: Lessons learned, *Environ. Sci. Technol.* 46 (2012) 6438–6447.
558 doi:10.1021/es204714w.

559 [18] C. Scheutz, M.M. Broholm, N.D. Durant, E.B. Weeth, T.H. Jørgensen, P. Dennis, C.S.
560 Jacobsen, E.E. Cox, J.C. Chambon, P.L. Bjerg, Field evaluation of biological enhanced
561 reductive dechlorination of chloroethenes in clayey till, *Environ. Sci. Technol.* 44 (2010)
562 5134–5141. doi:10.1021/es1003044.

563 [19] F. Aulenta, A. Pera, S. Rossetti, M. Petrangeli Papini, M. Majone, Relevance of side
564 reactions in anaerobic reductive dechlorination microcosms amended with different electron
565 donors, *Water Res.* 41 (2007) 27–38. doi:10.1016/j.watres.2006.09.019.

566 [20] D. O'Connor, D. Hou, Y.S. Ok, Y. Song, A.K. Sarmah, X. Li, F.M.G. Tack, Sustainable in
567 situ remediation of recalcitrant organic pollutants in groundwater with controlled release
568 materials: A review, *J. Control. Release.* 283 (2018) 200–213.
569 doi:10.1016/j.jconrel.2018.06.007.

570 [21] K. Urano, E. Yamamoto, M. Tonegawa, K. Fujie, Adsorption of chlorinated organic
571 compounds on activated carbon from water, *Water Res.* 25 (1991) 1459–1464.

- doi:10.1016/j.arabjc.2015.04.013.
- [22] X. Mao, A. Ciblak, M. Amiri, A.N. Alshawabkeh, Redox control for electrochemical dechlorination of trichloroethylene in bicarbonate aqueous media, *Environ. Sci. Technol.* 45 (2011) 6517–6523. doi:10.1021/es200943z.
- [23] X. Mao, A. Ciblak, K. Baek, M. Amiri, R. Loch-Caruso, A.N. Alshawabkeh, Optimization of electrochemical dechlorination of trichloroethylene in reducing electrolytes, *Water Res.* 46 (2012) 1847–1857. doi:10.1016/j.watres.2012.01.002.
- [24] X. Mao, S. Yuan, N. Fallahpour, A. Ciblak, J. Howard, I. Padilla, R. Loch-Caruso, A.N. Alshawabkeh, Electrochemically induced dual reactive barriers for transformation of TCE and mixture of contaminants in groundwater, *Environ. Sci. Technol.* 46 (2012) 12003–12011. doi:10.1021/es301711a.
- [25] P.H. Fallgren, J.J. Eisenbeis, S. Jin, In situ electrochemical manipulation of oxidation-reduction potential in saturated subsurface matrices, *J. Environ. Sci. Heal. Part A.* 53 (2018) 517–523. doi:10.1080/10934529.2017.1422951.
- [26] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediation, *Environ. Sci. Technol.* 27 (1993) 2638–2647. doi:10.1021/es00049a002.
- [27] M. Zheng, J. Bao, P. Liao, K. Wang, S. Yuan, M. Tong, H. Long, Electrogenation of H₂ for Pd-catalytic hydrodechlorination of 2,4-dichlorophenol in groundwater, *Chemosphere.* 87 (2012) 1097–1104. doi:10.1016/j.chemosphere.2012.01.058.
- [28] F. Aulenta, L. Tocca, R. Verdini, P. Reale, M. Majone, Dechlorination of trichloroethene in a continuous-flow bioelectrochemical reactor: Effect of cathode potential on rate, selectivity, and electron transfer mechanisms, *Environ. Sci. Technol.* 45 (2011) 8444–8451. doi:10.1021/es202262y.
- [29] R. Verdini, F. Aulenta, F. de Tora, A. Lai, M. Majone, Relative contribution of set cathode

- 596 potential and external mass transport on TCE dechlorination in a continuous-flow
 597 bioelectrochemical reactor, *Chemosphere*. 136 (2015) 72–78.
 598 doi:10.1016/j.chemosphere.2015.03.092.
- 599 [30] S.T. Lohner, D. Becker, K.M. Mangold, A. Tiehm, Sequential reductive and oxidative
 600 biodegradation of chloroethenes stimulated in a coupled bioelectro-process, *Environ. Sci.*
 601 *Technol.* 45 (2011) 6491–6497. doi:10.1021/es200801r.
- 602 [31] F. Aulenta, R. Verdini, M. Zeppilli, G. Zanaroli, F. Fava, S. Rossetti, M. Majone,
 603 Electrochemical stimulation of microbial cis-dichloroethene (cis-DCE) oxidation by an
 604 ethene-assimilating culture, *N. Biotechnol.* 30 (2013) 749–755.
 605 doi:10.1016/j.nbt.2013.04.003.
- 606 [32] S. Yuan, M. Chen, X. Mao, A.N. Alshawabkeh, A three-electrode column for Pd-catalytic
 607 oxidation of TCE in groundwater with automatic pH-regulation and resistance to reduced
 608 sulfur compound foiling, *Water Res.* 47 (2013) 269–278. doi:10.1016/j.watres.2012.10.009.
- 609 [33] W. Zhou, L. Rajic, Y. Zhao, J. Gao, Y. Qin, A.N. Alshawabkeh, Rates of H₂O₂
 610 electrogeneration by reduction of anodic O₂ at RVC foam cathodes in batch and flow-
 611 through cells, *Electrochim. Acta*. 277 (2018) 185–196. doi:10.1016/j.electacta.2018.04.174.
- 612 [34] L. Rajic, R. Nazari, N. Fallahpour, A.N. Alshawabkeh, Electrochemical degradation of
 613 trichloroethylene in aqueous solution by bipolar graphite electrodes, *J. Environ. Chem. Eng.*
 614 4 (2016) 197–202. doi:10.1016/j.jece.2015.10.030.
- 615 [35] P. Lakshmipathiraj, G. Bhaskar Raju, Y. Sakai, Y. Takuma, A. Yamasaki, S. Kato, T.
 616 Kojima, Studies on electrochemical detoxification of trichloroethene (TCE) on Ti/IrO₂-
 617 Ta₂O₅ electrode from aqueous solution, *Chem. Eng. J.* 198–199 (2012) 211–218.
 618 doi:10.1016/j.cej.2012.05.092.
- 619 [36] B. Liu, H. Zhang, Q. Lu, G. Li, F. Zhang, A Cu Ni bimetallic cathode with nanostructured

620 copper array for enhanced hydrodechlorination of trichloroethylene (TCE), *Sci. Total*
621 *Environ.* 635 (2018) 1417–1425. doi:10.1016/j.scitotenv.2018.04.238.

622 [37] S. Yuan, X. Mao, A.N. Alshawabkeh, Efficient degradation of TCE in groundwater using Pd
623 and electro-generated H₂ and O₂: A shift in pathway from hydrodechlorination to oxidation
624 in the presence of ferrous ions, *Environ. Sci. Technol.* 46 (2012) 3398–3405.
625 doi:10.1021/es204546u.

626 [38] W. Xie, S. Yuan, X. Mao, W. Hu, P. Liao, M. Tong, A.N. Alshawabkeh, Electrocatalytic
627 activity of Pd-loaded Ti/TiO₂ nanotubes cathode for TCE reduction in groundwater, *Water*
628 *Res.* 47 (2013) 3573–3582. doi:10.1016/j.watres.2013.04.004.

629 [39] M.A. Petersen, T.C. Sale, K.F. Reardon, Electrolytic trichloroethene degradation using
630 mixed metal oxide coated titanium mesh electrodes, *Chemosphere.* 67 (2007) 1573–1581.
631 doi:10.1016/j.chemosphere.2006.11.056.

632 [40] N. Fallahpour, S. Yuan, L. Rajic, A.N. Alshawabkeh, Hydrodechlorination of TCE in a
633 circulated electrolytic column at high flow rate, *Chemosphere.* 144 (2016) 59–64.
634 doi:10.1016/j.chemosphere.2015.08.037.

635 [41] L. Rajic, N. Fallahpour, A.N. Alshawabkeh, Impact of electrode sequence on electrochemical
636 removal of trichloroethylene from aqueous solution, *Appl. Catal. B Environ.* 174–175 (2015)
637 427–434. doi:10.1016/j.apcatb.2015.03.018.

638 [42] L. Rajic, N. Fallahpour, E. Podlaha, A.N. Alshawabkeh, The influence of cathode material on
639 electrochemical degradation of trichloroethylene in aqueous solution, *Chemosphere.* 147
640 (2016) 98–104. doi:10.1016/j.chemosphere.2015.12.095.

641 [43] L. Rajic, N. Fallahpour, R. Nazari, A.N. Alshawabkeh, Influence of humic substances on
642 electrochemical degradation of trichloroethylene in limestone aquifers, *Electrochim. Acta.*
643 181 (2015) 123–129. doi:10.1016/j.electacta.2015.03.121.

- [44] L. Rajic, N. Fallahpour, S. Yuan, A.N. Alshawabkeh, Electrochemical transformation of trichloroethylene in aqueous solution by electrode polarity reversal, *Water Res.* 67 (2014) 267–275. doi:10.1016/j.watres.2014.09.017.
- [45] R.W. Gillham, S.F. O’Hannesin, Enhanced degradation of halogenated aliphatics by zero-valent iron, *Ground Water*. 32 (1994) 958–967. doi:10.1111/j.1745-6584.1994.tb00935.x.
- [46] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Kinetics of halogenated organic compound degradation by iron metal, *Environ. Sci. Technol.* 30 (1996) 2634–2640. doi:10.1021/es9600901.
- [47] M.M. Scherer, B.A. Balko, D.A. Gallagher, P.G. Tratnyek, Correlation analysis of rate constants for dechlorination by zero-valent iron, *Environ. Sci. Technol.* 32 (1998) 3026–3033. doi:10.1021/es9802551.
- [48] E.C. Butler, K.F. Hayes, Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide, *Environ. Sci. Technol.* 33 (1999) 2021–2027. doi:10.1021/es9809455.
- [49] W.A. Arnold, A.L. Roberts, Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles, *Environ. Sci. Technol.* 34 (2000) 1794–1805. doi:10.1021/es980252o.
- [50] Y.H. Kim, E.R. Carraway, Dechlorination of chlorinated ethenes and acetylenes by palladized iron, *Environ. Technol.* 24 (2003) 809–819. doi:10.1080/09593330309385618.
- [51] J. Farrell, N. Melitas, M. Kason, T. Li, Electrochemical and column investigation of iron-mediated reductive dechlorination of trichloroethylene and perchloroethylene, *Environ. Sci. Technol.* 34 (2000) 2549–2556. doi:10.1021/es991135b.
- [52] T. Li, J. Farrell, Electrochemical investigation of the rate-limiting mechanisms for trichloroethylene and carbon tetrachloride reduction at iron surfaces, *Environ. Sci. Technol.*

668 35 (2001) 3560–3565. doi:10.1021/es0019878.

669 [53] W.F. Wüst, R. Köber, O. Schlicker, A. Dahmke, Combined zero- and first-order kinetic
670 model of the degradation of tce and cis-DCE with commercial iron, *Environ. Sci. Technol.*
671 33 (1999) 4304–4309. doi:10.1021/es980439f.

672 [54] C. Su, R.W. Puls, Kinetics of trichloroethene reduction by zerovalent iron and tin:
673 Pretreatment effect, apparent activation energy, and intermediate products, *Environ. Sci.*
674 *Technol.* 33 (1999) 163–168. doi:10.1021/es980481a.

675 [55] L. Rajic, N. Fallahpour, E. Oguzie, A.N. Alshawabkeh, Electrochemical transformation of
676 trichloroethylene in groundwater by Ni-containing cathodes, *Electrochim. Acta.* 181 (2015)
677 118–122. doi:10.1016/j.electacta.2015.03.112.

678 [56] S. Yuan, M. Chen, X. Mao, A.N. Alshawabkeh, Effects of reduced sulfur compounds on Pd-
679 catalytic hydrodechlorination of trichloroethylene in groundwater by cathodic H₂ under
680 electrochemically induced oxidizing conditions, *Environ. Sci. Technol.* 47 (2013) 10502–
681 10509. doi:10.1021/es402169d.

682 [57] V. Sáez, M.D. Esclapez Vicente, Á.J. Frías-Ferrer, P. Bonete, J. González-García,
683 Electrochemical degradation of perchloroethylene in aqueous media: An approach to
684 different strategies, *Water Res.* 43 (2009) 2169–2178. doi:10.1016/j.watres.2009.02.019.

685 [58] N. Fallahpour, X. Mao, L. Rajic, S. Yuan, A.N. Alshawabkeh, Electrochemical
686 dechlorination of trichloroethylene in the presence of natural organic matter, metal ions and
687 nitrates in a simulated karst media, *J. Environ. Chem. Eng.* 5 (2017) 240–245.
688 doi:10.1016/j.jece.2016.11.046.

689 [59] O. Scialdone, C. Guarisco, A. Galia, R. Herbois, Electroreduction of aliphatic chlorides at
690 silver cathodes in water, *J. Electroanal. Chem.* 641 (2010) 14–22.
691 doi:10.1016/j.jelechem.2010.01.018.

- 692 [60] T. Li, J. Farrell, Reductive dechlorination of trichloroethene and carbon tetrachloride using
693 iron and palladize-iron cathodes, *Environ. Sci. Technol.* 34 (2000) 173–179.
- 694 [61] A. Tiehm, S.T. Lohner, T. Augenstein, Effects of direct electric current and electrode
695 reactions on vinyl chloride degrading microorganisms, *Electrochim. Acta.* 54 (2009) 3453–
696 3459. doi:10.1016/j.electacta.2009.01.002.
- 697 [62] F. Aulenta, A. Canosa, P. Reale, S. Rossetti, S. Panero, M. Majone, Microbial reductive
698 dechlorination of trichloroethene to ethene with electrodes serving as electron donors without
699 the external addition of redox mediators, *Biotechnol. Bioeng.* 103 (2009) 85–91.
700 doi:10.1002/bit.22234.
- 701 [63] F. Aulenta, P. Reale, A. Canosa, S. Rossetti, S. Panero, M. Majone, Characterization of an
702 electro-active biocathode capable of dechlorinating trichloroethene and cis-dichloroethene to
703 ethene, *Biosens. Bioelectron.* 25 (2010) 1796–1802. doi:10.1016/j.bios.2009.12.033.
- 704 [64] A. Lai, R. Verdini, F. Aulenta, M. Majone, Influence of nitrate and sulfate reduction in the
705 bioelectrochemically assisted dechlorination of cis-DCE, *Chemosphere.* 125 (2015) 147–154.
706 doi:10.1016/j.chemosphere.2014.12.023.
- 707 [65] B.H. Hyldegaard, R. Jakobsen, E.B. Weeth, N.D. Overheu, D.B. Gent, L.M. Ottosen,
708 Challenges in electrochemical remediation of chlorinated solvents in natural groundwater
709 aquifer settings, *J. Hazard. Mater.* 368 (2019) 680–688. doi:10.1016/j.jhazmat.2018.12.064.
- 710 [66] J.H. Brewster, Mechanisms of reductions at metal surfaces. I. A general working hypothesis,
711 *J. Am. Chem. Soc.* 76 (1954) 6361–6363. doi:10.1021/ja01653a034.
- 712 [67] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38
713 (2004) 11–41. doi:10.1016/j.seppur.2003.10.006.
- 714 [68] D. Ghosh, C.R. Medhi, H. Solanki, M.K. Purkait, Decolorization of crystal violet solution by
715 electrocoagulation, *J. Environ. Prot. Sci.* 2 (2008) 25–35.

- 716 [69] T. Umemura, K. Sato, Y. Kusaka, H. Satoh, Palladium, in: G. Nordber, B. Fowler, M.
 717 Nordberg (Eds.), Handbook on the toxicology of metals 4E, Academic Press, 2015: pp.
 718 1113–1123. doi:10.1016/B978-0-444-59453-2.00049-4.
- 719 [70] A. Okamoto, M. Yamamuro, N. Tatarazako, Acute toxicity of 50 metals to *Daphnia magna*,
 720 J. Appl. Toxicol. 35 (2015) 824–830. doi:10.1002/jat.3078.
- 721 [71] S. Lüderwald, F. Seitz, G.. Seisenbaeva, V.. Kessler, R. Schulz, M. Bundschuh, Palladium
 722 nanoparticles: Is there a risk for aquatic ecosystems?, Bull. Environ. Contam. Toxicol. 97
 723 (2016) 153–158. doi:10.1007/s00128-016-1803-x.
- 724 [72] L. Gabrieli, A.N. Alshawabkeh, Influence of boundary conditions on transient excess pore
 725 pressure during electrokinetic applications in soils, J. Appl. Electrochem. 40 (2010) 1113–
 726 1121. doi:10.1007/s10800-010-0075-0.
- 727 [73] L.M. Ottosen, T.H. Larsen, P.E. Jensen, G.M. Kirkelund, H. Kern-Jespersen, N. Tuxen,
 728 B.H. Hyldegaard, Electrokinetics applied in remediation of subsurface soil contaminated
 729 with chlorinated ethenes – A review, Chemosphere. 235 (2019) 113–125.
 730 doi:10.1016/j.chemosphere.2019.06.075.
 731

Table 1. Experimental conditions for the electrochemical treatment of initially 2.7 mg/l PCE.

	Electrode configuration ^a	Electrode material	Electrode spacing [cm]	Column orientation	Current [mA]	Pd catalyst loading ^b [mg/cm ²]	Darcy velocity [cm/min]	Porosity, water-filled ^c [%]
0 ^d	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	0	0.76	0.09	31.1 ± 0.3
1	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	60	0.76	0.09	30.8
2	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	0.76	0.09	30.8
3 ^d	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	1.14	0.08	34.8 ± 0.5
4	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	180	1.14	0.08	35.3
5	C → BPE → A	Fe foam → MMO → MMO	2.5	Horizontal	120	1.14	0.08	34.1
6	C → BPE → A	Fe foam → MMO → MMO	4	Horizontal	120	1.14	0.03	100
7	C → BPE → A	Fe foam → MMO → MMO	4	Vertical	120	1.14	0.03	100
8	C → C → A	SS → Fe foam → MMO	4	Horizontal	120	1.14	0.08	34.2
9	C → C → A	Fe foam → Fe foam → MMO	4	Horizontal	120	1.14	0.08	35.0
10	C → A	Fe foam → MMO	8	Horizontal	120	1.14	0.08	34.3
11	C → A	Fe foam → MMO	2.5	Horizontal	120	1.14	0.25	100
12	C → A	Fe foam → MMO	2.5	Vertical	120	1.14	0.25	100

^a A: Anode, C: Cathode, BPE: Bipolar electrode
^b Catalyst applied on Fe foam only. Load is given as mass per geometric electrode surface area
^c Porosities of 100 % indicate a fully liquid-filled reactor, while tests with porosities < 100 % incorporate the porous matrix
^d Duplicate testing

Figure 1. The baseline flow-through electrochemical set-up composed of a feedstock solution, peristaltic pump, a cathode, bipolar electrode and an anode connected to a DC source. P0-P5 are sampling ports. Sampling ports above the electrodes served for manual extraction of gases generated. Measures are of inner dimensions.

Figure 2
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Figure 3
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Figure 3. Normalization of experimental data for PCE based on samples extracted in the final sampling port (solid dots) and data for TCE in Rajic et al. [25] (squares) for current intensity (I), flow (Q) and contaminant concentration (C) plotted against the removal of PCE and TCE. Numbers next to markers refer to experiment number (Table 1).