

1 **Ferrate(VI) oxidation of pentachlorophenol in water and soil**

2 Olivier Monfort^{a,b,*}, Muhammad Usman^{c,d,*}, Khalil Hanna^{a,e}

3 ^a Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR (Institut des
4 Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

5 ^b Comenius University in Bratislava, Faculty of Natural Sciences, Department of Inorganic
6 Chemistry, Ilkovicova 6, Mlynska Dolina, 84215 Bratislava, Slovakia

7 ^c Environmental Mineralogy, Center for Applied Geosciences, University of Tübingen, 72074
8 Tübingen, Germany

9 ^d PEIE Research Chair for the Development of Industrial Estates and Free Zones, Center for
10 Environmental Studies and Research, Sultan Qaboos University, Al-Khoud 123, Muscat,
11 Oman

12 ^e Institut Universitaire de France (IUF), MESRI, 1 rue Descartes, 75231 Paris, France.

13 * These authors contributed equally to this work.

14 * corresponding authors: monfort1@uniba.sk (O. Monfort); muhammad.usman@squ.edu.om
15 (M. Usman)

16

Credit Author Statement for the manuscript “Ferrate(VI) oxidation of pentachlorophenol in water and soil” by O. Monfort, M. Usman and K. Hanna.

Olivier Monfort: Conceptualization, Investigation, Writing – Original Draft, Writing – Review & Editing

Muhammad Usman: Conceptualization, Investigation, Writing – Original Draft, Writing – Review & Editing

Khalil Hanna: Conceptualization, Funding acquisition, Supervision, Writing – Review & Editing

Journal Pre-proof

17 **Abstract**

18 Although the use of ferrate(VI), an emerging green oxidant, has been widely investigated to
19 remove organic pollutants in water, its ability to remediate contaminated soils has been
20 scarcely evaluated. Here, we explore the use of ferrate(VI) to degrade a polychlorinated
21 persistent compound, the pentachlorophenol (PCP), in aqueous solution and in an aged
22 contaminated soil under batch, water-saturated and water-unsaturated flow conditions. The
23 first results showed the prominent efficiency of ferrate(VI) over conventional oxidants (e.g.
24 H₂O₂ and persulfate) in both matrices and at different oxidant doses. In aqueous solution,
25 more than 80% of PCP was degraded by ferrate(VI) while complete removal was observed in
26 soil under batch conditions. In column experiments, PCP removal by ferrate(VI) remained
27 efficient but dependent on the flow rate and water saturation. Maximum PCP removal (95%)
28 in columns was observed under water saturated conditions when ferrate(VI) (0.2 g g⁻¹ of soil)
29 was injected at a low flow rate (i.e. 0.025 mL min⁻¹). This study has strong implications in the
30 development of new sustainable processes based on ferrate(VI) for the remediation of
31 different environmental compartments.

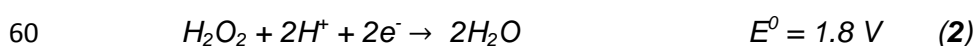
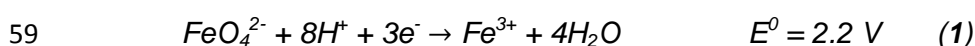
32

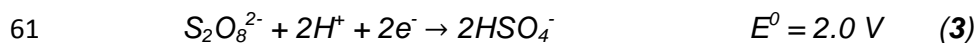
33 **Keywords:** PCP Remediation; Soil; Water; Chemical Oxidation; Ferrate(VI)

34

35 1 Introduction

36 Ferrate(VI) (Fe(VI)) is amongst the most powerful oxidants with oxidation potential of
37 2.2 V, which is higher than conventional oxidants like H₂O₂ (1.8 V), persulfate (2.0 V) or
38 permanganate (1.7 V) (eqs. 1-4) (Jiang, 2007; Sharma et al., 2001; Sharma, 2002). Use of
39 ferrate(VI) is advantageous mainly because it can be applied without any catalytic activation
40 unlike traditional oxidants which require activation to produce stronger radicals. Moreover,
41 decomposition of ferrate(VI) mainly yields Fe(III) minerals which are non-toxic (Jiang, 2007;
42 Rai et al., 2018; Sharma, 2002; Talaiekhosani et al., 2017; Zajicek et al., 2015).
43 Ferrate(VI) has shown promising efficiency to degrade a wide range of pollutants in aqueous
44 solutions such as pharmaceuticals, persistent organic pollutants, heavy metals, etc. (Han et
45 al., 2015; Yang et al., 2016; Zhou and Jiang, 2015a, 2015b). However, very limited data is
46 available about its application in the remediation of contaminated soils and sediments
47 (Hrabak et al., 2016; Johansson et al., 2019; Talaiekhosani et al., 2017). Our very recent
48 study (Monfort et al., 2019) was the first attempt to explore the ability of ferrate(VI) to
49 remove polychlorinated biphenyls (PCBs) in an aged contaminated soil. The ferrate(VI)
50 oxidation efficiency has been found to be mainly limited by the strong persistence and low
51 solubility of target compounds in addition to the soil matrix effect (Monfort et al., 2019).
52 Furthermore, polychlorinated compounds with stable C-Cl bonds exhibit strong refractory
53 behavior against remediation processes (Monfort et al., 2019; Rybnikova et al., 2016;
54 Tang et al., 2015). Therefore, there is still much to learn about the ability of ferrate(VI) in the
55 oxidative degradation of polychlorinated compounds and remediation of contaminated soils.
56 For this purpose, an aged PCP contaminated soil sampled from a timber mill in Waipa district
57 of Waikato Region, New Zealand, was used to evaluate the performance of ferrate(VI)
58 oxidation.





63 PCP appears to be an ideal candidate due to its classification among persistent
64 organic pollutants (Stockholm Convention), and its widespread contamination in soil and
65 water (Rybnikova et al., 2017). PCP can be efficiently degraded in aqueous solution through
66 biological, physical and chemical treatments (Chen et al., 2018; Guemiza et al., 2017;
67 Rybnikova et al., 2017; Xue et al., 2017; Zimbron and Reardon, 2009). To our knowledge,
68 there exists only two studies which focused on the use of ferrate(VI) to remove PCP in water
69 (Homolkova et al., 2016, 2017) but no work has been reported in soil matrix. Present study
70 is intended to assess the efficiency of ferrate(VI) to remove PCP in aqueous solution and in
71 historically contaminated soil. For this purpose, preliminary experiments were performed in
72 aqueous solution at various ferrate(VI) dose and PCP concentration. The stability of ferrate in
73 aqueous solution was also assessed. Further experiments were performed in an aged PCP
74 contaminated soil in batch mode as well as in dynamic columns under water -saturated and -
75 unsaturated conditions. Continuous flow-through experiments allow evaluating the effect of
76 kinetic limitations and water saturation on the oxidation performance and provide more
77 accurate operational parameters for future field applications. The oxidation efficiency of
78 ferrate(VI) was also compared with that of conventional chemical oxidants (persulfate, H₂O₂
79 alone or H₂O₂ catalyzed by magnetite). This work on the use of ferrate(VI) as an innovative
80 oxidant for PCP removal would open doors for further developments in this research field
81 leading to its scale-up application.

82

83 2 Experimental section

84 2.1 Materials and soil characteristics

85 Potassium ferrate (K_2FeO_4 , 20%) was provided by *Nanolron* (Czech Republic). It
86 contained impurities (e.g. K_3FeO_4 , $KFeO_2$ and KOH salts) which improve its stability and
87 allow relatively long-term storage. Pentachlorophenol (PCP, 97%), hydrogen peroxide (H_2O_2 ,
88 50 wt%) and diammonium 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were
89 supplied by *Sigma-Aldrich*. Potassium persulfate extra pure grade was purchased from
90 *Merck*. Magnetite powder (97%) was supplied by *Alfa Aesar*. Solutions were prepared using
91 deionized water produced by *Milli-Q* system from *Millipore*. The pH of solutions was adjusted
92 by using NaOH and HCl solutions.

93 Tested soil was obtained from a timber mill located in Waikato Region, New Zealand
94 and was characterized by *French Institute for Agro-environmental Health* (ISAE, France).
95 The soil was dried, ground and sieved through 1 mm mesh. A summary of major soil
96 characteristics is provided in the **Table S1** and is discussed in the **section 3.2**.

97

98 **2.2 Oxidation experiments**

99 A summary of the different experiments carried out in this study is presented in **Table**
100 **1**. Experiments were first performed in aqueous solution. For this purpose, different
101 concentrations of ferrate(VI) and PCP were used as described in **Table 1**. Stock solutions of
102 20 mg L^{-1} of PCP and $800\text{ }\mu\text{M}$ of ferrate(VI) were prepared at pH 12 and 9, respectively, to
103 increase PCP solubility and ferrate(VI) stability. Typical batch experiment was carried in 100
104 mL solution in *Nalgene* bottle at pH 7.2 (i.e. similar conditions as in soil) for 5 hours at room
105 temperature ($20 \pm 2\text{ }^\circ\text{C}$). In order to assess ferrate(VI) oxidation efficiency regarding to
106 conventional oxidants, experiments with persulfate, H_2O_2 , magnetite-activated H_2O_2 were
107 also performed. Similar conditions as ferrate(VI) oxidation were used (**Table 1**). Magnetite
108 (Fe_3O_4) is a mixed-valent mineral (**Usman et al., 2018a**) which has shown strong ability to
109 catalyze chemical oxidation for the remediation of contaminated soils (**Usman et al., 2012,**
110 **2013**) and sediments (**Usman et al., 2018b**). In addition, the decomposition of ferrate(VI)

111 was determined in both deionized water and PCP solutions in order to evaluate the influence
 112 of the chlorinated pollutant on the stability of ferrate(VI). The decomposition of ferrate(VI)
 113 was assessed using UV-vis spectrophotometry as described elsewhere (Lee et al., 2015).
 114 Briefly, aliquots containing ferrate(VI) were added to an ABTS solution, giving rise to an iron-
 115 ABTS complex detectable at 415 nm (Lee et al., 2015).

116 **Table 1.** Summary of experiments performed in aqueous solution and soil.

117

Purpose of experiment	Tested oxidant	Oxidant dose	PCP concentration	Other conditions
<i>Experiments in aqueous solution</i>				
Comparison of Fe(VI) with other oxidants	Fe(VI)	800 μM	20 mg L^{-1}	pH = 7.2 / 5 h
	$\text{S}_2\text{O}_8^{2-}$	4 mM		
	H_2O_2	4 mM		
	H_2O_2 + magnetite	4 mM + magnetite 0.5 g L^{-1}		
Effect of Fe(VI) dose on PCP degradation	Fe(VI)	15 μM	20 mg L^{-1}	pH = 7.2 / 5 h
		75 μM		
		150 μM		
		800 μM		
		8 mM (excess)		
Effect of PCP dose	Fe(VI)	150 μM	5 mg L^{-1}	pH = 7.2 / 5

on PCP degradation and Fe(VI) decomposition			10 mg L ⁻¹	h
			20 mg L ⁻¹	
Experiments in contaminated soil				
Batch experiments to compare different oxidants	Blank	No oxidant	6 mg kg ⁻¹ (real soil)	24 h, no pH adjustment, 7.2
	Fe(VI)	0.1 g g ⁻¹ of soil		
		0.25 g g ⁻¹ of soil		
		0.5 g g ⁻¹ of soil		
	H ₂ O ₂	200 mM		
H ₂ O ₂ + magnetite	200 mM + 25 mg magnetite g ⁻¹ soil			
Dynamic column conditions at different oxidant doses and flow rates	Fe(VI)	0.1 g g ⁻¹ of soil	6 mg kg ⁻¹ (real soil)	Saturated conditions with three different flow rates: 0.025, 0.25 and 2.5 mL min ⁻¹
		0.25 g g ⁻¹ of soil		
Dynamic column conditions at different oxidant doses and flow rates	Fe(VI)	0.1 g g ⁻¹ of soil	6 mg kg ⁻¹ (real soil)	Unsaturated conditions with three different flow rates: 0.025,
		0.25 g g ⁻¹ of soil		

				0.25 and 2.5 mL min ⁻¹
--	--	--	--	--------------------------------------

118

119 Oxidation study in soil involved batch and column experiments. Batch experiments
120 were performed at liquid-to-solid ratios (L/S) of 1 chosen on the basis of our previous study
121 **(Monfort et al., 2019)** which reported that L/S ratio had no impact on oxidation efficiency of
122 ferrate(VI). Moreover, L/S ratio of 1 is highly relevant for column experiments and ultimate
123 field application. These batch experiments are preliminary tests to compare ferrate(VI) to the
124 other oxidants and to chose the optimal conditions for removing PCP in the historically
125 contaminated soil. Firstly, contaminated soil was subjected to chemical oxidation by applying
126 three different doses of ferrate(VI) salt including 0.1, 0.25 and 0.5 g g⁻¹ soil. For that, 2 g of
127 soil was homogenized with suitable amount of solid potassium ferrate followed by adding 2
128 mL of water to obtain L/S ratio of 1. These samples were stirred for 24 h. Oxidation efficiency
129 of ferrate(VI) was also compared with that of H₂O₂ and magnetite-activated H₂O₂. For H₂O₂
130 based experiments, 200 mM of H₂O₂ was used alone or with magnetite (25 mg g⁻¹) in case of
131 magnetite-activated H₂O₂. Subsequently, column experiments were conducted under water
132 saturated and unsaturated conditions to perform experiments closer to field conditions.
133 Experimental setup for these column experiments is presented in a previous work
134 **(Rybnikova et al., 2017)**. Briefly, glass columns were packed with 5 g of PCP-contaminated
135 soil and 50 mL ferrate(VI) oxidant solution was injected either downward or upward to satisfy
136 saturated and unsaturated conditions, respectively. Different doses of oxidant (0.1 and 0.2 g
137 g⁻¹ soil) and flow rates (0.025, 0.25 and 2.5 mL min⁻¹) were used as summarized in **Table 1**.
138 Column effluents were collected to analyze PCP. All experiments were performed in
139 triplicates (n = 3) and without pH adjustment. The error bars in the figures represent relative
140 standard deviation calculated on the basis of 3 replicates and blank experiments were
141 carried out without any oxidant.

142

143 **2.3 Extraction and analysis**

144 PCP extraction from soil slurries was performed as reported earlier (**Rybnikova et al.,**
145 **2017**). For this, methanol/water solution (50/50, v/v) was mixed with soil slurries (L/S ratio:
146 2/1) in ultrasonic bath for 1 h followed by centrifugation at 4000 rpm for 10 min. Then,
147 supernatant solution (2 mL) filtered (0.2 μm filter) for further analyses. The pH was adjusted
148 before extraction (if needed) to 7.2 ± 0.2 with NaOH (1 M) solution. It has been reported by
149 **Rybnikova et al. (2017)** that pH of 7 – 7.5 leads to an extraction efficiency of >95% of PCP.
150 For column experiments, effluents were also filtered and analyzed.

151 To quantify PCP concentrations in solution and soil extracts, HPLC was performed on
152 *Alliance Waters 2487* device equipped with *XBridge C18* column fixed at 30 °C and UV
153 detector at 254 nm. A mixture of acetonitrile/ultra pure water (ACN/UPW), both acidified with
154 formic acid 0.1 vol%, was used as mobile phase. Isocratic mode ACN/UPW 70:30 was
155 realized for 9 min with injection volume of 50 μL at 1 mL min^{-1} flow rate.

156

157 **3 Results and discussion**

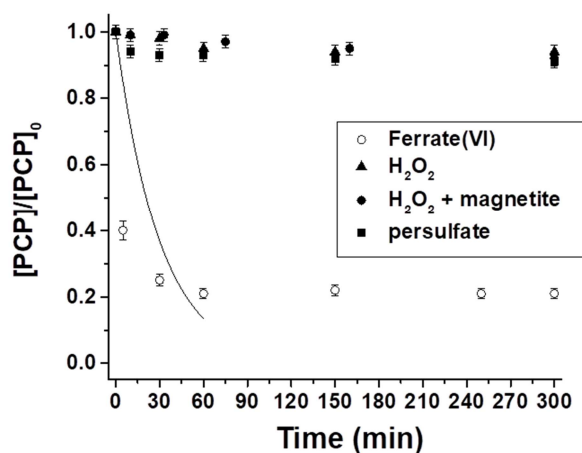
158 **3.1 Use of ferrate(VI) for PCP removal in water**

159 Preliminary experiments were conducted in aqueous solutions to determine the
160 feasibility of ferrate(VI) oxidation for PCP removal. These experiments offer simplicity and
161 better control on reaction conditions, prior for assessing the performance of ferrate(VI)
162 oxidation in a more complex system, the soil matrix.

163 First, ferrate(VI) oxidation was compared with other oxidants including persulfate,
164 H_2O_2 and $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ (**Figure 1**) under similar conditions. Magnetite (Fe_3O_4) was chosen as
165 a catalyst because of its proven catalytic ability to produce hydroxyl radicals at circumneutral
166 pH (**Usman et al., 2018a**). The initial pH of the solution was adjusted at 7.2 which is also the

167 pH of tested soil (**section 2**). It appears that conventional oxidants (including persulfate,
 168 H_2O_2 and magnetite-activated H_2O_2) are inefficient as compared to ferrate(VI) (**Figure 1**).
 169 Only 10% of PCP was removed with these traditional oxidants whereas 80% of PCP removal
 170 was obtained by ferrate(VI) oxidation. This strong degradation efficiency can be ascribed to
 171 the high reactivity of ferrate(VI) toward electron rich moieties (ERM) (**Rai et al., 2018**;
 172 **Sharma et al., 2016**; **Talaiekhosani et al., 2017**). Indeed, molecules containing phenols,
 173 amines, chlorine, olefins, etc. are degraded efficiently by ferrate(VI) (**Feng et al., 2018**;
 174 **Homolkova et al., 2017**; **Rai et al., 2018**). In addition, the circumneutral pH (7.2 in the
 175 present study) favors the ferrate(VI) oxidation while it could limit the formation of radicals
 176 from conventional oxidants (**Sharma, 2002**; **Sharma et al., 2015, 2016**), thus explaining the
 177 superiority of ferrate(VI) in PCP removal. This latter observation also highlights the better
 178 adaptability of ferrate(VI) among a wide range of experimental conditions (compared to the
 179 conventional oxidants) (**Monfort et al., 2019**).

180



181

182 **Figure 1:** Removal kinetics of PCP (20 mg L^{-1}) using $800 \mu\text{M}$ of ferrate(VI), 4 mM of H_2O_2
 183 and $\text{S}_2\text{O}_8^{2-}$, and magnetite-activated H_2O_2 system ($0.5 \text{ g/L Fe}_3\text{O}_4$ with $4 \text{ mM H}_2\text{O}_2$) and $n=3$.
 184 The solid line represents the pseudo-first order kinetic model.

185

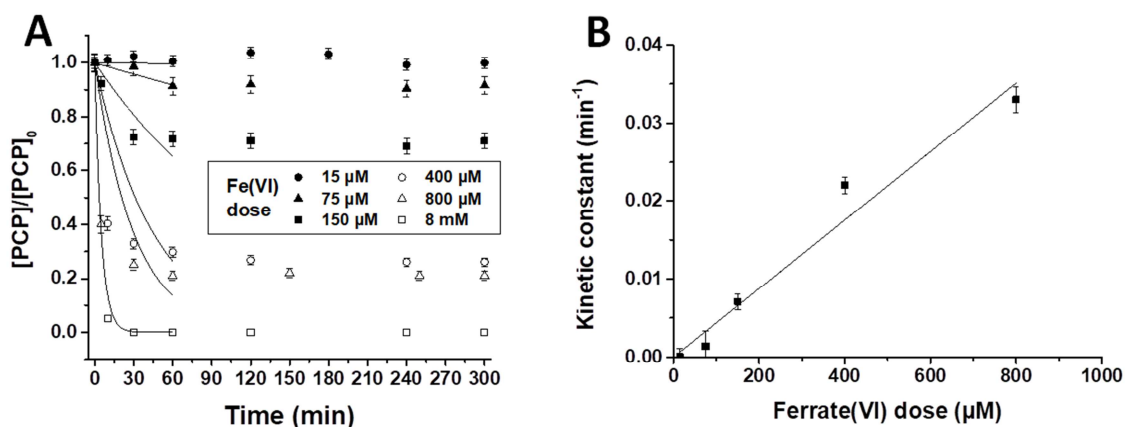
186 The removal extent of PCP increases with the dose of ferrate(VI) (**Figure 2A**). Around 80%
 187 of PCP is degraded using 0.8 M ferrate(VI) while 100% removal is achieved with higher dose
 188 of ferrate(VI) (8 mM). In addition, most of PCP was degraded within few minutes due to the
 189 fast reactivity of ferrate(VI) and a plateau is then observed since ferrate(VI) has been
 190 decomposed into iron oxides (**Goodwill et al., 2015; Jiang et al., 2015; Sharma, 2002**). The
 191 degradation kinetics of PCP over the first stage (i.e. 60 min) can be described by the pseudo-
 192 first-order equation:

$$[PCP]_t = [PCP]_0 \exp^{-k_a t} \quad (5)$$

194 where k_a is obtained by linear regression of $\ln([PCP]_t/[PCP]_0)$ versus time t .

195 The kinetic rate constant as well as the degradation efficiency strongly depend on the ferrate
 196 dose and PCP concentration. At a fixed PCP concentration (20 mg L^{-1}), the kinetic rate
 197 constants increased linearly with ferrate(VI) concentration increasing (**Figure 2B**).

198



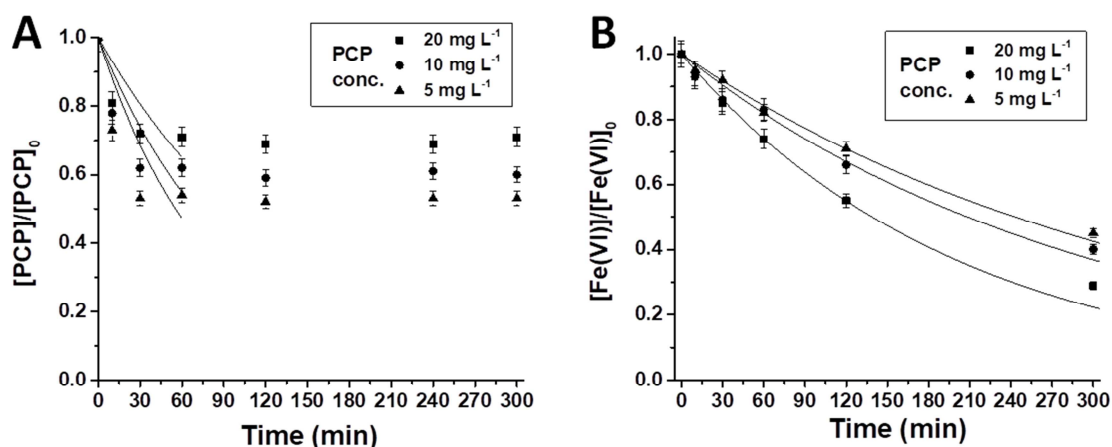
199

200 **Figure 2:** (A) Removal kinetics of PCP (20 mg L^{-1}) using ferrate(VI) at different
 201 concentrations at pH 7.2 ($n = 3$). The solid lines represent the pseudo first order kinetic. (B)
 202 Evolution of kinetic constant value of PCP degradation as a function of ferrate(VI) dose. The
 203 kinetic constant is calculated from pseudo first order kinetic applied to the first 60 minutes of
 204 reaction.

205

206 At a fixed dose of ferrate(VI) ($150 \mu\text{M}$), oxidation efficiency decreased with an
 207 increase in PCP concentration (**Figure 3A**). Indeed, when PCP concentration increased from
 208 5 to 20 mg L^{-1} , the kinetic rate constant decreased from $1.2 \cdot 10^{-2}$ to $7.1 \cdot 10^{-3} \text{ min}^{-1}$, thereby
 209 suggesting the significant impact of oxidant/PCP ratio. Furthermore, the decomposition of
 210 ferrate(VI) increases with PCP concentration increasing (**Figure 3B**). The pseudo first order
 211 kinetic constant of ferrate decomposition ranges from $2.9 \cdot 10^{-3}$ to $5.0 \cdot 10^{-3} \text{ min}^{-1}$, when PCP
 212 concentration increases from 5 to 20 mg L^{-1} respectively. Reaction between the organic
 213 compound and the oxidant leads to more decomposition of ferrate(VI) (**Han et al., 2015;**
 214 **Jiang et al., 2015; Homolkova et al., 2017**).

215

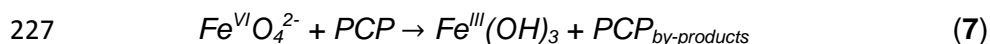
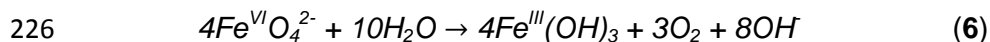


216

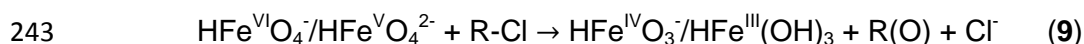
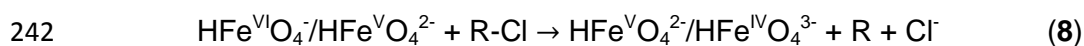
217 **Figure 3:** (A) Removal kinetics of PCP at different concentrations ($5, 10, 20 \text{ mg L}^{-1}$) using
 218 $150 \mu\text{M}$ ferrate(VI) at pH 7.2. Experiments were performed in triplicates ($n = 3$). The solid
 219 lines represent the pseudo-first order of PCP degradation for the first 60 minutes. (B)
 220 Decomposition kinetics of $150 \mu\text{M}$ ferrate(VI) in different PCP solutions ($5, 10, 20 \text{ mg L}^{-1}$).
 221 The solid lines are the pseudo-first order models of ferrate(VI) decomposition..

222

223 It is known that ferrate(VI) decomposition in water leads to iron(III) species (**eq. 6**) (**Goodwill**
 224 **et al., 2015; Jiang et al., 2015; Sharma, 2002**). In presence of PCP which is rich in
 225 electrons, the decomposition of ferrate (**eq. 7**) occurs faster as shown in **Figure 3**:



228 The oxidation of PCP by ferrate(VI) is a process similar to that involving permanganate,
 229 isostructural to ferrate(VI), where PCP is oxidized by electron transfer resulting in
 230 dechlorination (**Matta and Chiron, 2018**). The ferrate(VI) oxidation mechanism probably
 231 involved a dechlorination step of PCP releasing chloride anion (**Homolkova et al., 2017**)
 232 followed by further oxidation by high valent iron through electron transfer (**Monfort et al.,**
 233 **2019**). Regarding the existence of several high oxidation states of ferrate (+VI, +V and +IV)
 234 and the possibility to transfer O-atom to the PCP, several reactions are plausible (**eqs. 8 and**
 235 **9**). For instance, 1-electron transfer (**eq. 8**) or 2-electron transfer followed by O-atom transfer
 236 (**eq. 9**) are plausible mechanisms for the PCP (R-Cl in **eqs. 8 and 9**) removal. The pollutant
 237 oxidation process is effectively improved by increasing in the amount of electron transfer
 238 acceptor (i.e. ferrate) (**Feng et al., 2016; Ma et al., 2012; Rai et al., 2018**). In addition, at pH
 239 = 7.2, the predominant ferrate species is the monoprotonated form (HFeO_4^- for ferrate(VI)
 240 and HFeO_4^{2-} for ferrate(V)) which is the most reactive one (**Sharma, 2002; Sharma et al.,**
 241 **2015, 2016**).



244

245

246

247 **3.2 Use of ferrate(VI) to degrade PCP in contaminated soil**

248 Efficiency of ferrate(VI) was, then, tested in PCP contaminated soil. Tested soil is
249 characterized as “loamy sand” with pH 7.2. It contains 0.3 wt% carbonate contents (CaCO_3),
250 1.5% soil organic matter and high iron contents (9.8 g kg^{-1}). Concentration of PCP in soil is 6
251 mg kg^{-1} which is above the threshold guideline values for agricultural soils and is, therefore,
252 categorized as a soil with serious threats in New Zealand as well as in Europe (**Rybnikova**
253 **et al., 2017**).

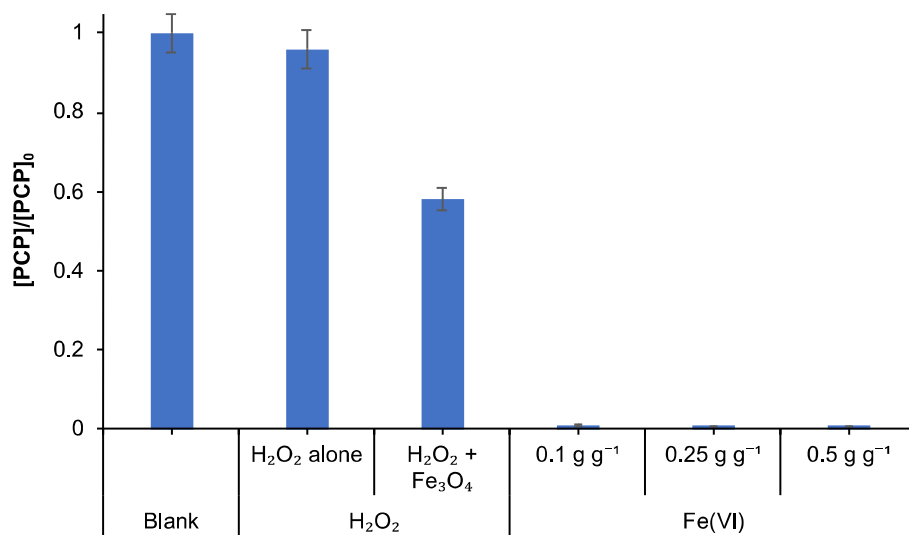
254

255 **3.2.1. Soil remediation under batch conditions**

256 To evaluate the treatment efficiency in contaminated soil, we employed different doses of
257 ferrate(VI) (w/w) including 0.1, 0.25 and 0.5 g g^{-1} soil without pH adjustment (i.e. $\text{pH } 7.2 \pm$
258 0.2) in batch mode. Oxidation efficiency of ferrate(VI) was compared with that of H_2O_2 alone
259 (200 mM) or in combination with magnetite ($200 \text{ mM H}_2\text{O}_2 + 25 \text{ mg Fe}_3\text{O}_4 \text{ g}^{-1}$ soil) under
260 similar experimental conditions. Obtained results (**Figure 4**) revealed that PCP degradation
261 was negligible with H_2O_2 alone. Application of H_2O_2 alone often leads to weak oxidation
262 because of the inability of H_2O_2 to generate hydroxyl radicals without activation (**Usman et**
263 **al., 2012**). In the presence of a catalyst ($\text{H}_2\text{O}_2 + \text{Fe}_3\text{O}_4$), almost 45% of PCP degradation was
264 observed. It should be noted that **Rybnikova et al. (2017)** reported negligible PCP
265 degradation by $\text{H}_2\text{O}_2 + \text{Fe}_3\text{O}_4$ in the same soil (under similar experimental conditions) that
266 could be linked to the lower reagent dose in their study ($0.2 - 4 \text{ mM H}_2\text{O}_2$ and $5 \text{ mg Fe}_3\text{O}_4 \text{ g}^{-1}$
267 soil). On the other hand, application of ferrate(VI) resulted in complete removal of PCP at all
268 tested doses ($0.1, 0.25$ and 0.5 g g^{-1} soil). These results clearly illustrate the strong efficiency
269 of ferrate(VI) to remove PCP in contaminated soils as compared to the traditional oxidant
270 (H_2O_2) even in the presence of an efficient catalyst (Fe_3O_4). Our previous study using
271 ferrate(VI) to remove PCBs in an aged contaminated soil (**Monfort et al., 2019**) reported only
272 40% of PCB degradation despite efforts to address the soil matrix-associated effects.

273 Complete degradation of PCP in present study reveals that incomplete removal of PCBs was
 274 mainly associated to the refractory nature of PCB. Thus, ferrate(VI) can be an effective
 275 oxidant to treat contaminated soils but pollutant nature should be considered. Compared to
 276 the aqueous system, ferrate(VI) could be stabilized in soil by natural organic matter which
 277 would act as a complexing agent (Jiang et al., 2015), thus ferrate(VI) could sustain its
 278 efficiency for long duration and at low dose. This would ultimately improve the durability of
 279 the ferrate(VI)-based treatment.

280



281

282 **Figure 4:** Degradation extents of PCP in contaminated soil in the presence of various
 283 treatments such as (i) H₂O₂ alone (200 mM), (ii) 200 mM H₂O₂ + 25 mg Fe₃O₄ g⁻¹ soil and
 284 different doses of ferrate(VI) (0.1, 0.25 and 0.5 g g⁻¹ soil). Experiments were performed
 285 without pH adjustment (i.e. pH 7.2 ± 0.2) for 24 h and n=3. Blank experiments were
 286 conducted without any oxidant under similar experimental conditions.

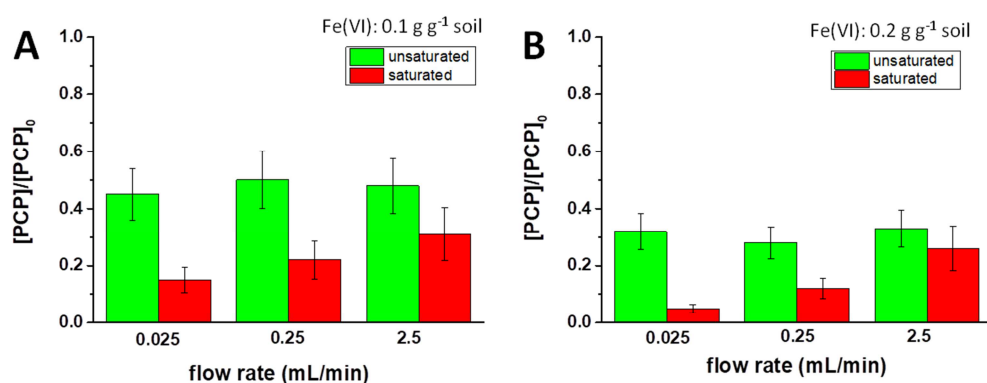
287

288 3.2.2. Soil remediation under flow-through conditions

289 Batch experiments are characterized by an improved contact between oxidant/pollutant/soil
 290 matrix. However, such conditions are not prevalent in field conditions and therefore, we

291 performed the column experiments under water saturated and unsaturated conditions.
 292 Different doses of ferrate(VI) (0.1 and 0.2 g g⁻¹ soil) and flow rates (0.025, 0.25 and 2.5 mL
 293 min⁻¹) were chosen in order to emulate the field conditions (**Figure 5**).

294



295

296 **Figure 5.** Degradation of PCP using columns of contaminated soil. A quantity of (A) 0.1 and
 297 (B) 0.2 g g⁻¹ soil of ferrate(VI) was used under both saturated and unsaturated conditions (n =
 298 3). Different flow rates (0.025, 0.25 and 2.5 mL min⁻¹) of ferrate(VI) oxidant solution was
 299 used. Experiments were performed without pH adjustment (i.e. pH 7.2 ± 0.2).

300

301 The blank experiment was performed by flushing deionized water which neither cause any
 302 PCP degradation nor its loss in the column effluent (data not shown). The degradation extent
 303 of PCP increased with an increase in the quantity of ferrate under both saturated and
 304 unsaturated conditions. Ferrate(VI) at 0.1 g g⁻¹ removed PCP up to 55% (unsaturated
 305 conditions) and 85% (saturated conditions). On the other hand, increase in dose of ferrate
 306 (0.2 g g⁻¹) improved the degradation extent to 72% (unsaturated conditions) and 95%
 307 (saturated conditions). In any case, degradation efficiency of ferrate(VI) is higher than that of
 308 traditional oxidants (<60%) reported by **Rybnikova et al. (2017)** in the same soil under
 309 similar experimental setup. It was also observed that PCP removal is higher under saturated
 310 conditions as compared to that in unsaturated columns at all tested doses of ferrate(VI)

311 **(Figure 5)**. This might be correlated to the presence of gas phase and/or preferential
312 pathways in the unsaturated columns, which did not permit an optimum contact between
313 contaminated area and the oxidant **(Rybnikova et al., 2017)**. Saturated conditions, on the
314 other hand, offer better contact between oxidant and contaminant, which led to higher PCP
315 removal. This can also explain the decrease in oxidation efficiency under column conditions
316 as compared to that in batch **(Rybnikova et al., 2017; Usman et al., 2013)**. It is worth noting
317 that the PCP concentration in column effluents was negligible (i.e. under detection limit).

318 Experiments were also performed under different flow rates (0.025, 0.25 and 2.5 mL min⁻¹) of
319 ferrate(VI) to evaluate the impact of oxidant residence time on the treatment efficiency
320 **(Figure 5)**. Degradation extent was almost similar at all flow rates (0.025 to 2.5 mL min⁻¹)
321 under unsaturated conditions, which can once again be correlated to preferential pathways of
322 the oxidant. On the other hand, under saturated conditions, the degradation extent
323 decreased (from 85% to 69% at lower oxidant dose and from 95% to 74% at higher dose of
324 ferrate(VI)) with increasing flow rate (from 0.025 to 2.5 mL min⁻¹), which can be correlated to
325 kinetic limitations in the column **(Rybnikova et al., 2017)**. It is worth mentioning that effect of
326 kinetic limitations in columns are determined by evaluating the Damköhler number (Da), a
327 ratio of hydrodynamic residence time to reaction time in the column. Estimated Da values in
328 present study are relatively low, suggesting the lack of local equilibrium **(Hanna and Boily,**
329 **2010; Homolkova et al., 2016)**. Consequently, decrease in flow rate increases the oxidant
330 residence time, overcomes kinetic limitations and ultimately enhances the treatment
331 efficiency **(Rybnikova et al., 2017)**.

332 Taken together, these results show that ferrate(VI) is a viable oxidant to remove PCP
333 in aqueous solution and contaminated soils. These results also enlighten us that incomplete
334 removal of PCBs by ferrate(VI) application in our previous study **(Monfort et al., 2019)** was
335 mainly related to the nature of the pollutant and not to the inability of ferrate(VI) to perform in
336 complex soil medium. Owing to the strong persistence and lower water solubility, PCBs were
337 not removed by ferrate(VI) despite multiple efforts to improve pollutant availability or soil

338 matrix effects (Monfort et al., 2019). On the other hand, effective PCP removal was
339 observed in multiple environmental compartments (aqueous solution or soil) or experimental
340 setup (batch and column).

341

342 **4 Conclusion**

343 Ferrate(VI) oxidation has exhibited promising results in the degradation of chlorinated
344 persistent organic pollutants in both water and soil systems. Indeed, compared to
345 conventional oxidants, especially H_2O_2 , and at similar experimental conditions, ferrate(VI)
346 exhibited about 8-fold increase in the removal extent of PCP in solution (from 10 to 80 %
347 approximatively). In soil, in batch mode, ferrate(VI) completely removed the PCP which is
348 much higher than H_2O_2 (5 %) or magnetite-activated H_2O_2 (45 %). In column experiments,
349 ferrate(VI) efficiently degraded the PCP especially under saturated conditions. Moreover,
350 oxidation efficiency increased with increasing in column residence time under saturated
351 conditions. We have notably demonstrated that ferrate(VI) oxidation efficiency is controlled
352 not only by soil matrix effects but also by the nature of target pollutant. Owing to the proven
353 efficiency of ferrate(VI) for the remediation of different environmental compartments, present
354 study open the doors in the research of innovative sustainable processes based on this
355 green oxidant.

356

357 **Acknowledgement**

358 We gratefully acknowledge the financial support of this work by ADEME "Agence de
359 l'Environnement et de la Maîtrise de l'Energie". Muhammad Usman also acknowledges the
360 support of Alexander von Humboldt Foundation of Germany. We thank Prof. Singhal from the
361 University of Auckland (New Zealand) for providing the contaminated soil. Authors declare
362 that there is no conflict of interest.

363

364 **References**

365 Chen, M., Tong, H., Li, F., Liu, C., Lan, Q., Liu, C., 2018. The effect of electron donors on the
366 dechlorination of pentachlorophenol (PCP) and prokaryotic diversity in paddy soil. *Eur. J. Soil*
367 *Biolog.* 86, 8-15.

368 Feng, M., Wang, X., Chen, J., Qu, R., Sui, Y., Cizmas, L., Wang, Z., Sharma, V.K., 2016.
369 Degradation of fluoroquinolone antibiotics by ferrate(VI): Effects of water constituents and
370 oxidized products. *Water Res.* 103, 48-57.

371 Feng, M., Jinadatha, C., McDonald, T.J., Sharma, V.K., 2018. Accelerated oxidation of
372 organic contaminants by ferrate(VI): the overlooked role of reducing additives. *Environ. Sci.*
373 *Technol.* 52(19), 11319-11327.

374 Goodwill, J.E., Jiang, Y., Reckhow, D.A., Gikonyo, J., Tobiason, J.E., 2015. Characterization
375 of particles from ferrate preoxidation. *Environ. Sci. Technol.* 49, 4955-4962.

376 Guemiza, K., Coudert, L., Metahni, S., Mercier, G., Besner, S., Blais, J.F., 2017. Treatment
377 technologies used for the removal of As, Cr, Cu, PCP and/or PCDD/F from contaminated
378 soil : A review. *J. Hazard. Mater.* 333, 194-214.

379 Han, Q., Wang, H., Dong, W., Liu, T., Yin, Y., Fan, H., 2015. Degradation of bisphenol A by
380 ferrate(VI) oxidation: Kinetics, products and toxicity assessment. *Chem. Eng. J.* 262, 34–40.

381 Hanna, K., Boily, J.F., 2010. Sorption of two naphthoic acids to goethite surface under flow
382 through conditions. *Environ. Sci. Technol.* 44, 8863-8869.

383 Homolkova, M., Hrabak, P., Kolar, M., Cernik, M., 2016. Degradability of chlorophenols using
384 ferrate(VI) in contaminated groundwater. *Environ. Sci. Pollut. Res.* 23, 1408-1413.

385 Homolkova, M., Hrabak, P., Graham, N., Cernik, M., 2017. A study of the reaction of ferrate
386 with pentachlorophenol – kinetics and degradation products. *Water Sci. Technol.* 75(1-2),
387 189-195.

- 388 Hrabak, P., Homolkova, M., Wacławek, S., Cernik, M., 2016. Chemical Degradation of
389 PCDD/F in contaminated sediment. *Ecol. Chem. Eng. S.* 23(3), 473-482.
- 390 Jiang, J.Q., 2007. Research progress in the use of ferrate(VI) for the environmental
391 remediation. *J. Hazard. Mater.* 146, 617-623.
- 392 Jiang, Y., Goodwill, J.E., Tobiasson, J.E., Reckhow, D.A., 2015. Effect of different solutes,
393 natural organic matter, and particulate Fe(III) on ferrate(VI) decomposition in aqueous
394 solution. *Environ. Sci. Technol.* 49, 2841-2848.
- 395 Johansson, C., Bataillard, P., Biache, C., Lorgeoux, C., Colombano, S., Joubert, A., Pigot, T.,
396 Faure, P., 2019. Ferrate VI oxidation of polycyclic aromatic compounds (PAHs and polar
397 PACs) on DNAPL-spiked sand: degradation efficiency and oxygenated by-products formation
398 compared to conventional oxidants. *Environ. Sci. Pollut. Res.* 27(1), 704-706.
- 399 Lee, Y., Yoon, J., von Gunten, U., 2005. Spectrophotometric determination of ferrate (Fe(VI))
400 in water by ABTS. *Water Res.* 39, 1946-1953.
- 401 Lewis, J., Sjostrom, J., 2010. Optimizing the experimental design of soil columns in saturated
402 and unsaturated transport experiments. *J. Contam. Hydrol.* 115, 1-13.
- 403 Ma, Y., Gao, N., Li, C., 2012. Degradation and pathway of tetracycline hydrochloride in
404 aqueous solution by potassium ferrate. *Environ. Eng. Sci.* 26(5), 357-362.
- 405 Matta, R., Chiron, S., 2018. Oxidative degradation of pentachlorophenol by permanganate
406 for ISCO application. *Environ. Technol.* 39(5), 651-657.
- 407 Monfort, O., Usman, M., Soutrel, I., Hanna, K., 2019. Ferrate(VI) based chemical oxidation
408 for the remediation of aged PCB contaminated soil: Comparison with conventional oxidants
409 and study of limiting factors. *Chem. Eng. J.* 355, 109-117.
- 410 Rai, P.K., Lee, J., Kailasa, S.K., Kwon, E.E., Tsang, Y.F., Ok, Y.S., Kim, K.H., 2018. A critical
411 review of ferrate(VI)-based remediation of soil and groundwater. *Environ. Res.* 160, 420-448.

- 412 Rybnikova, V., Usman, M., Hanna, K., 2016. Removal of PCBs in contaminated soils by
413 means of chemical reduction and advanced oxidation processes. *Environ. Sci. Pollut. Res.*
414 23(17), 17035-17048.
- 415 Rybnikova, V., Singhal, N., Hanna, K., 2017. Remediation of an aged PCP-contaminated soil
416 by chemical oxidation under flow-through conditions. *Chem. Eng. J.* 314, 202-211.
- 417 Sharma, V.K., Burnett, C.R., Millero, F.J., 2001. Dissociation constants of the monoprotic
418 ferrate(VI) ion in NaCl media. *Phys. Chem. Chem. Phys.* 3, 2059-2062.
- 419 Sharma, V.K., 2002. Potassium ferrate(VI): an environmentally friendly oxidant. *Adv. Environ.*
420 *Res.* 6,143-156.
- 421 Sharma, V.K., Zboril, R., Varma, R.S., 2015. Ferrates: Greener Oxidants with Multimodal
422 Action in Water Treatment Technologies. *Acc. Chem. Res.* 48, 182-191.
- 423 Sharma, V.K., Chen, L., Zboril, R., 2016. Review on High Valent FeVI (Ferrate): A
424 Sustainable Green Oxidant in Organic Chemistry and Transformation of Pharmaceuticals.
425 *ACS Sust. Chem. Eng.* 4, 18-34.
- 426 Talaiekhosani, A., Talaei, M.R., Rezaia, S., 2017. An overview on production and
427 application of ferrate (VI) for chemical oxidation, coagulation and disinfection of water and
428 wastewater. *J. Environ. Chem. Eng.* 5, 1828-1842.
- 429 Tang, X., Hashmi, M.Z., Zeng, B., Yang, J., Shen, C., 2015. Application of iron-activated
430 persulfate oxidation for the degradation of PCBs in soil. *Chem. Eng. J.* 279, 673-680.
- 431 Usman, M., Faure, P., Ruby, C., Hanna, K., 2012. Remediation of PAH-contaminated soils
432 by magnetite catalyzed Fenton-like oxidation. *Appl. Catal. B* 117–118, 10-17.
- 433

- 434 Usman, M., Faure, P., Lorgeoux, C., Ruby, C., Hanna, K., 2013. Treatment of hydrocarbon
435 contamination under flow through conditions by using magnetite catalyzed chemical
436 oxidation. *Environ. Sci. Pollut. Res.* 20(1), 22-30.
- 437 Usman, M., Byrne, J.M., Chaudhary, A., Orsetti, S., Hanna, K., Ruby, C., Kappler, A.,
438 Haderlein, S.B., 2018a. Magnetite and Green Rust: Synthesis, Properties, and
439 Environmental Applications of Mixed-Valent Iron Minerals. *Chem. Rev.* 118(7), 3251-3304.
- 440 Usman, M., Hanna, K., Faure, P., 2018b. Remediation of oil-contaminated harbor sediments
441 by chemical oxidation. *Sci. Total. Environ.* 634, 1100-1107.
- 442 Xue, L., Feng, X., Xu, Y., Li, X., Zhu, M., Xu, J., He, Y., 2017. The dechlorination of
443 pentachlorophenol under a sulfate and iron reduction co-occurring anaerobic environment.
444 *Chemosphere* 182, 166-173.
- 445 Yang, B., Kookana, R.S., Williams, M., Ying, G.G., Du, J., Doan, H., Kumar, A., 2016.
446 Oxidation of ciprofloxacin and enrofloxacin by ferrate(VI): Products identification, and toxicity
447 evaluation. *J. Hazard. Mater.* 320, 296-303.
- 448 Zajicek, P., Kolar, M., Pucek, R., Ranc, V., Bednar, P., Varma, R.S., Sharma, V.K., Zboril,
449 R., 2015. Oxidative degradation of triazine- and sulfonyleurea-based herbicides using Fe(VI):
450 The case study of atrazine and iodosulfuron with kinetics and degradation products. *Sep.*
451 *Purif. Technol.* 156(3), 1041-1046.
- 452 Zhou, Z., Jiang, J.Q., 2015a. Reaction kinetics and oxidation products formation in the
453 degradation of ciprofloxacin and ibuprofen by ferrate(VI). *Chemosphere* 119, S95-S100.
- 454 Zhou, Z., Jiang, J.Q., 2015b. Treatment of selected pharmaceuticals by ferrate(VI):
455 Performance, kinetic studies and identification of oxidation products. *J. Pharm. Biomed. Anal.*
456 106, 37-45.
- 457 Zimbron, J.A., Reardon, K.F., 2009. Fenton's oxidation of pentachlorophenol. *Water Res.* 43,
458 1831-1840.

Highlights

- **Oxidation of PCP by ferrate(VI) is studied under on dynamic soil columns**
- **Maximum PCP removal is observed under water saturated conditions**
- **PCP is completely removed by ferrate(VI) in batch mode**
- **Ferrate(VI) is more efficient than conventional oxidants for PCP removal**

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof