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

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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

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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 H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup> of soil)  
29 was injected at a low flow rate (i.e. 0.025 mL min<sup>-1</sup>). 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.

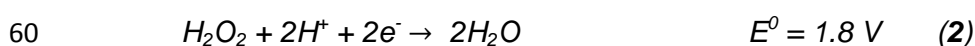
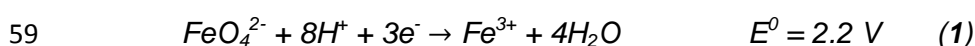
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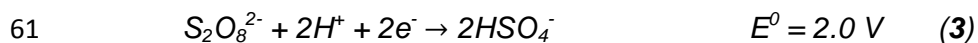
33 **Keywords:** PCP Remediation; Soil; Water; Chemical Oxidation; Ferrate(VI)

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 H<sub>2</sub>O<sub>2</sub> (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, H<sub>2</sub>O<sub>2</sub>  
79 alone or H<sub>2</sub>O<sub>2</sub> 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  $20\text{ mg L}^{-1}$  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 $\mu\text{M}$	20 $\text{mg L}^{-1}$	pH = 7.2 / 5 h
	$\text{S}_2\text{O}_8^{2-}$	4 mM		
	$\text{H}_2\text{O}_2$	4 mM		
	$\text{H}_2\text{O}_2$ + magnetite	4 mM + magnetite 0.5 $\text{g L}^{-1}$		
Effect of Fe(VI) dose on PCP degradation	Fe(VI)	15 $\mu\text{M}$	20 $\text{mg L}^{-1}$	pH = 7.2 / 5 h
		75 $\mu\text{M}$		
		150 $\mu\text{M}$		
		800 $\mu\text{M}$		
		8 mM (excess)		
Effect of PCP dose	Fe(VI)	150 $\mu\text{M}$	5 $\text{mg L}^{-1}$	pH = 7.2 / 5



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

				0.25 and 2.5 mL min <sup>-1</sup>
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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<sup>-1</sup> 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 H<sub>2</sub>O<sub>2</sub> and magnetite-activated H<sub>2</sub>O<sub>2</sub>. For H<sub>2</sub>O<sub>2</sub>  
130 based experiments, 200 mM of H<sub>2</sub>O<sub>2</sub> was used alone or with magnetite (25 mg g<sup>-1</sup>) in case of  
131 magnetite-activated H<sub>2</sub>O<sub>2</sub>. 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<sup>-1</sup> soil) and flow rates (0.025, 0.25 and 2.5 mL min<sup>-1</sup>) 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  $\mu\text{m}$  filter) for further analyses. The pH was adjusted  
148 before extraction (if needed) to  $7.2 \pm 0.2$  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  $\mu\text{L}$  at 1  $\text{mL min}^{-1}$  flow rate.

156

## 157 **3 Results and discussion**

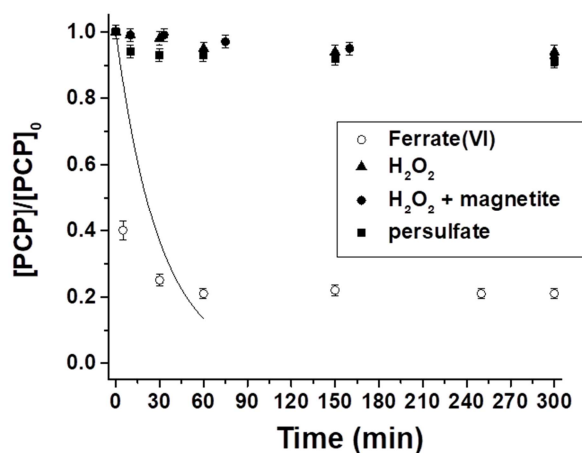
### 158 **3.1 Use of ferrate(VI) for PCP removal in water**

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  $\text{H}_2\text{O}_2$  and  $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$  (**Figure 1**) under similar conditions. Magnetite ( $\text{Fe}_3\text{O}_4$ ) 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  $\text{H}_2\text{O}_2$  and magnetite-activated  $\text{H}_2\text{O}_2$ ) 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 ( $20 \text{ mg L}^{-1}$ ) using  $800 \mu\text{M}$  of ferrate(VI),  $4 \text{ mM}$  of  $\text{H}_2\text{O}_2$   
 183 and  $\text{S}_2\text{O}_8^{2-}$ , and magnetite-activated  $\text{H}_2\text{O}_2$  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.

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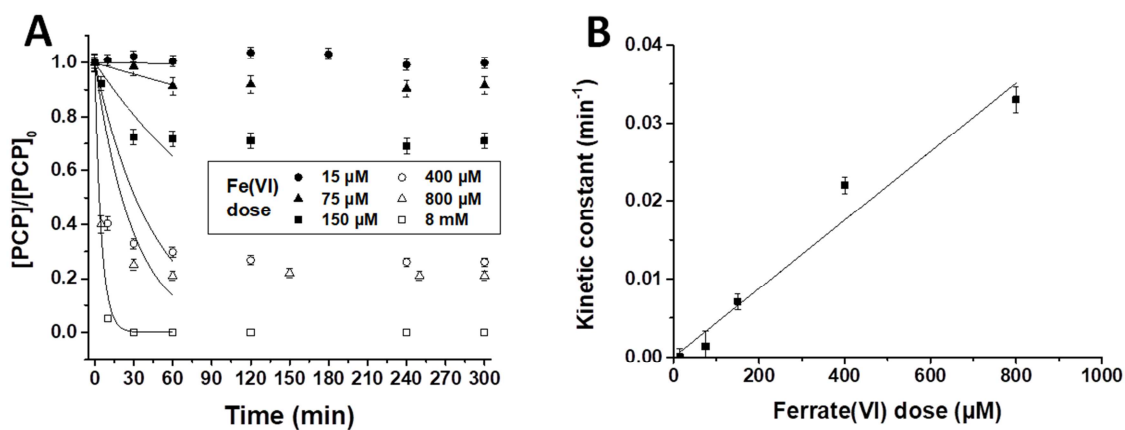
186 The removal extent of PCP increases with the dose of ferrate(VI) (**Figure 2A**). Around 80%  
 187 of PCP is degraded using 0.8 M ferrate(VI) while 100% removal is achieved with higher dose  
 188 of ferrate(VI) (8 mM). In addition, most of PCP was degraded within few minutes due to the  
 189 fast 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 ( $20 \text{ mg L}^{-1}$ ), the kinetic rate  
 197 constants increased linearly with ferrate(VI) concentration increasing (**Figure 2B**).

198



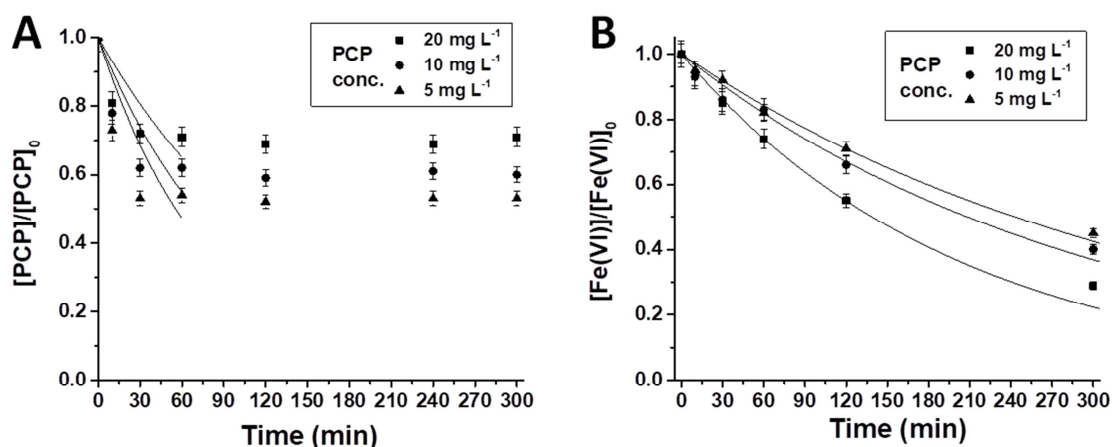
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200 **Figure 2:** (A) Removal kinetics of PCP ( $20 \text{ mg L}^{-1}$ ) using ferrate(VI) at different  
 201 concentrations at pH 7.2 ( $n = 3$ ). The solid lines represent the pseudo first order kinetic. (B)  
 202 Evolution of kinetic constant 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  $20 \text{ mg L}^{-1}$ , 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  $20 \text{ mg L}^{-1}$  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**).

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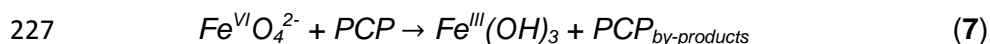
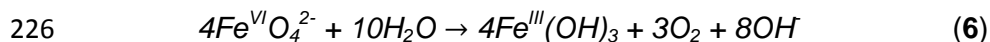


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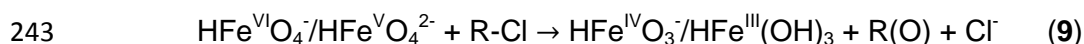
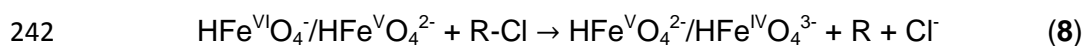
217 **Figure 3:** (A) Removal kinetics of PCP at different concentrations ( $5, 10, 20 \text{ mg L}^{-1}$ ) using  
 218  $150 \mu\text{M}$  ferrate(VI) at pH 7.2. Experiments were performed in triplicates ( $n = 3$ ). The solid  
 219 lines represent the pseudo-first order of PCP degradation for the 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 ( $\text{HFeO}_4^-$  for ferrate(VI)  
 240 and  $\text{HFeO}_4^{2-}$  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 ( $\text{CaCO}_3$ ),  
250 1.5% soil organic matter and high iron contents ( $9.8 \text{ g kg}^{-1}$ ). Concentration of PCP in soil is 6  
251  $\text{mg kg}^{-1}$  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

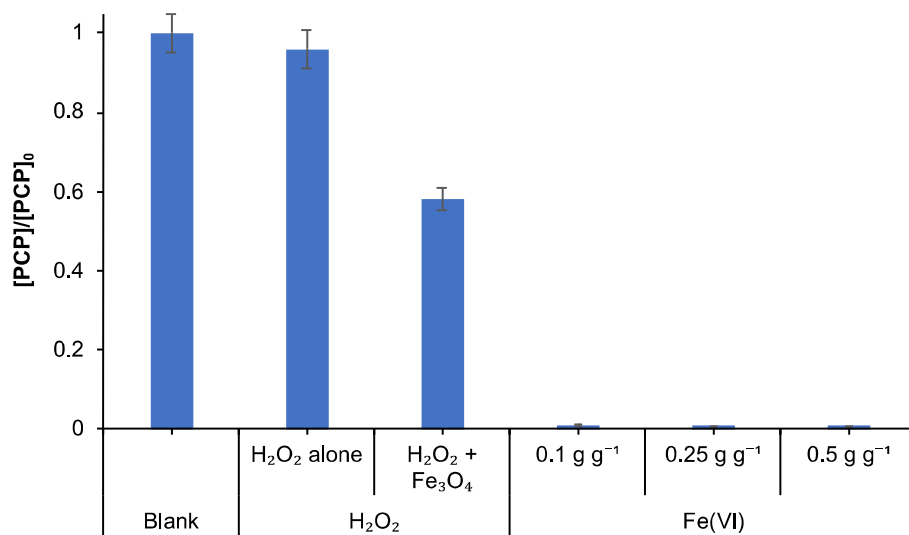
#### 255 **3.2.1. Soil remediation under batch conditions**

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  $0.5 \text{ g g}^{-1}$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  alone. Application of  $\text{H}_2\text{O}_2$  alone often leads to weak oxidation  
262 because of the inability of  $\text{H}_2\text{O}_2$  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  $0.5 \text{ g g}^{-1}$  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 ( $\text{H}_2\text{O}_2$ ) even in the presence of an efficient catalyst ( $\text{Fe}_3\text{O}_4$ ). 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) H<sub>2</sub>O<sub>2</sub> alone (200 mM), (ii) 200 mM H<sub>2</sub>O<sub>2</sub> + 25 mg Fe<sub>3</sub>O<sub>4</sub> g<sup>-1</sup> soil and  
 284 different doses of ferrate(VI) (0.1, 0.25 and 0.5 g g<sup>-1</sup> 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.

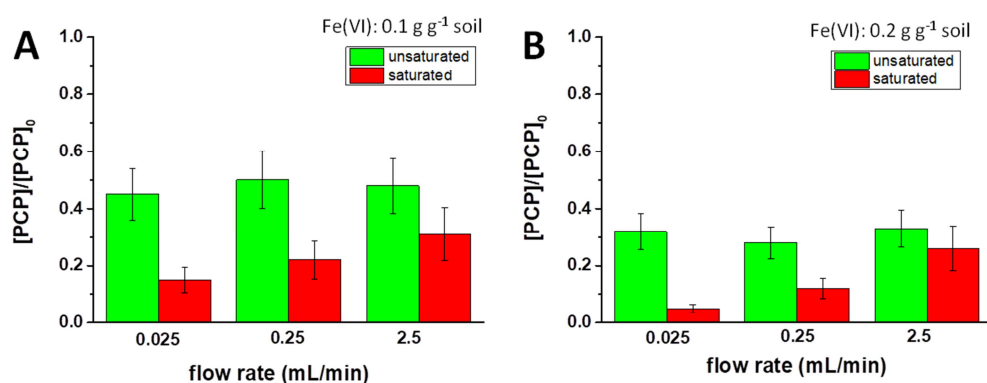
287

### 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  $0.2 \text{ g g}^{-1}$  soil) and flow rates ( $0.025$ ,  $0.25$  and  $2.5 \text{ mL}$   
 293  $\text{min}^{-1}$ ) 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)  $0.2 \text{ g g}^{-1}$  soil of ferrate(VI) was used under both saturated and unsaturated conditions ( $n =$   
 298  $3$ ). Different flow rates ( $0.025$ ,  $0.25$  and  $2.5 \text{ mL min}^{-1}$ ) of ferrate(VI) oxidant solution was  
 299 used. Experiments were performed without pH adjustment (i.e.  $\text{pH } 7.2 \pm 0.2$ ).

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  $0.1 \text{ g g}^{-1}$  removed PCP up to 55% (unsaturated  
 305 conditions) and 85% (saturated conditions). On the other hand, increase in dose of ferrate  
 306 ( $0.2 \text{ g g}^{-1}$ ) 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<sup>-1</sup>) 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<sup>-1</sup>)  
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<sup>-1</sup>), 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

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363

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## 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: