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1 Electrokinetic delivery of persulfate to remediate PCBs polluted 2 soils: effect of different activation methods

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8 **ABSTRACT:** Persulfate-based in-situ chemical oxidation (ISCO) for the remediation of
9 organic polluted soils has gained much interest in last decade. However, the transportation of
10 persulfate in low-permeability soil is very low, which limits its efficiency in degrading
11 soil pollutants. Additionally, the oxidation-reduction process of persulfate with organic
12 contaminants takes place slowly, while, the reaction will be greatly accelerated by the production
13 of more powerful radicals once it is activated. Electrokinetic remediation (EK) is a good way
14 for transporting persulfate in low-permeability soil. In this study, different activation methods,
15 using zero-valent iron, citric acid chelated Fe²⁺, iron electrode, alkaline pH and peroxide, were
16 evaluated to enhance the activity of persulfate delivered by EK. All the activators and the
17 persulfate were added in the anolyte. The results indicated that zero-valent iron, alkaline,
18 and peroxide enhanced the transportation of persulfate at the first stage of EK test, and the
19 longest delivery distance reached sections S4 or S5 (near the cathode) on the 6th day. The
20 addition of activators accelerated decomposition of persulfate, which resulted in the
21 decreasing soil pH. The mass of persulfate delivered into the soil declined with the continuous
22 decomposition of persulfate by activation. The removal efficiency of PCBs in soil followed the
23 order of alkaline activation > peroxide activation > citric acid chelated Fe²⁺ activation > zero-
24 valent iron activation > without activation > iron electrode activation, and the values were
25 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation effect was
26 highly dependent on the ratio of activator and persulfate.

27 **Key words:** Polychlorinated biphenyls (PCBs), soil remediation, electrokinetics,
28 persulfate activation.

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30

31 **Introduction**

32 Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that strongly adsorb in
33 soils and sediments. Developing cost-effective and sustainable solutions for the remediation of
34 PCB-contaminated soils is imperative (Gomes et al., 2014). The present technologies include
35 capping, solvent extraction, thermal desorption, Fe-promoted dechlorination, chemical oxidation,
36 biological remediation and many others still in development phase (Gomes et al., 2013).
37 Among these technologies, in-situ chemical oxidation (ISCO) is an emerging technology for soil
38 and groundwater remediation due to its wide applicability, relatively fast treatment, simplicity of
39 operation and cost effectiveness (ITRC, 2005; Watts and Teel, 2006; Rastogi et al., 2009b;
40 Tsitonaki et al., 2010). ISCO involves the introduction of chemical oxidant into the subsurface to
41 transform organic contaminants into less harmful chemical species. Hydrogen peroxide,
42 permanganate and ozone are widely used oxidants, but their practical applications are hindered
43 due to their low stability (hydrogen peroxide and ozone) or high soil affinity for natural soil
44 organics (permanganate) (Gates-Anderson et al., 2001; Li and Schwartz, 2004; Tsai et al., 2008;
45 Navalon et al., 2010). Persulfate is a strong oxidant with a redox potential (E_0) of 2.01 V and a
46 relatively long life in the subsurface due to its slow reaction kinetics with organics, which can
47 promote more favorable contact time (Tsitonaki et al., 2010). Also, upon activation, persulfate can
48 produce sulfate radicals ($SO_4^{\bullet-}$, $E_0=2.6$ V) and hydroxyl radicals ($\bullet OH$, $E_0=2.7$ V) which are more
49 powerful and kinetically faster than persulfate anions (Liang et al., 2004a). There are many
50 methods available for persulfate activation including the use of heat, chelated or unchelated
51 transition metals, hydrogen peroxide, or strong alkaline pH (Eqs. (1)-(4)) (Petri et al., 2011). But
52 the site conditions such as lithology (clay, sand, etc.), hydrogeology and the structure of the target
53 contamination will affect the oxidation effectiveness. Thus, the activation method selected must be
54 dependent on the contaminants to be treated and the subsurface environment (Block et al., 2004).



59 Fe(II) was used initially to activate persulfate. However, the activation by Fe^{2+} is not practical
60 because the reaction is almost instantaneously stopped due to the $SO_4^{\bullet-}$ scavenging by excess Fe^{2+}

61 or to the rapid conversion of Fe^{2+} to Fe^{3+} . As an alternative activator, zero-valent iron (an insoluble
 62 form of iron) has been employed to activate persulfate with promising results by directly reacting
 63 with persulfate to release Fe^{2+} , or releasing Fe^{2+} through the corrosion of zero-valent iron
 64 activation (Eqs. (5)-(7)) (Oh et al., 2009; Liang and Guo, 2010; Oh et al., 2010). On the other hand,
 65 aqueous Fe(II) is relatively insoluble at the ambient $\text{pH} \geq 5$ of most aquifer systems and Fe(II)
 66 chelated by chelating agents (e.g. ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic
 67 acid and citric acid) is effective in activating persulfate by maintaining iron in solution at neutral
 68 pH (Liang et al., 2004b; Crimi and Taylor, 2007; Rastogi et al., 2009a).



72 A significant difficulty in ISCO is promoting the contact between the oxidant and the contaminant,
 73 particularly in low-permeability subsurface. When ISCO is combined with EK, EK has the
 74 potential to increase the delivery of oxidant in soil and improve the remediation efficiency (Reddy
 75 and Cameselle, 2009). Also, in-situ electrolysis by iron electrodes allows to manipulate the
 76 reactivity of persulfate in EK + ISCO system. According to Yuan et al. (2013), Fe^{2+} can be
 77 continuously produced in situ by electrochemical corrosion (Eqs. (8) and (6)) and chemical
 78 corrosion (Eqs. (9) and (7)) when applying a positive current on an iron anode, and the electrolytic
 79 supply of Fe^{2+} will improve the utilization of both Fe^{2+} and persulfate (Yuan et al., 2013).



84 The effect of different activators on persulfate oxidation has been studied extensively. However,
 85 the persulfate activation in EK was rarely referred. Recently, Yukselen-Aksoy et al. (2012)
 86 investigated the effect of heat and alkaline activation on the electrokinetically enhanced persulfate
 87 oxidation of PCB44 in kaolin and glacial till soils. Persulfate (30%) was injected from a position 3
 88 cm away from the anode and the result showed that both activation methods (heat or heat and high
 89 pH) improved the degradation of PCB44 in kaolin, but not in glacial till soil due to its high
 90 buffering capacity, nonhomogeneous mineral contents and high organic content (Yukselen-Aksoy

91 and Reddy, 2012). Furthermore, we investigated the **transport** behaviors of inactivated persulfate
92 under electric field, and found that electroosmotic flow (**EOF**) was more effective for persulfate
93 delivery than electromigration and the anode was the best injection spot for high dosage of
94 persulfate (Fan et al., 2014a). However, the activity of persulfate in soil is relatively low without
95 activation, so choosing appropriate activators to accelerate the reaction kinetics of persulfate is a
96 key process for the application of EK + persulfate technology.
97 In this study, different activation methods, using zero-valent iron, **citric acid** chelated Fe^{2+} , iron
98 electrode, alkaline pH, and peroxide, were evaluated to enhance the activity of persulfate delivered
99 by EK. The **transport** behavior of activated persulfate under electric field and the remediation
100 efficiency of PCBs contaminated soil **were** also investigated.

101 **2. Experimental**

102 *2.1 Chemicals and materials*

103 PCBs standard solution containing 20 PCBs congeners ($> 99.4\%$) were obtained from
104 AccuStandard (New Haven, CT, USA). Sodium persulfate (99.0%) was purchased from Chengdu
105 Kelon Chemical Reagent Factory. Zero-valent iron powder (98.0%) was provided by Shanghai
106 Miura Chemical Co. Ltd., China. Sodium hydroxide ($>96\%$), citric acid ($>99.6\%$), acetone
107 (analytical reagent) and hexane (analytical reagent) were obtained from Nanjing Chemical Reagent
108 Co. Ltd., China. Hydrogen peroxide (30% solution, 99.0%) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99.0%) were
109 supplied by Sinopharm Chemical Reagent Co. Ltd., China. Deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$)
110 obtained from a Millipore Milli-Q system was used in all experiments.

111 The PCBs polluted soil was sampled from a place near a capacitor storage site in Zhejiang
112 province, which was diluted with a clean soil sampled from a farmland in Nanjing. The properties
113 of the two soils are shown in **Table 1**. Both soils belong to yellow brown soil and have similar
114 properties. The soils were air-dried, ground and passed through 20 mesh and 60 mesh sieves,
115 respectively. Approximately 100 g of PCBs polluted soil was mixed with 2200 g of clean soil
116 thoroughly, **after that, the mixed soil was stored in the fume hood one week for equilibrium. Also,**
117 **the properties of the mixed soil were analyzed and shown in Table 1.** The initial values of PCBs in
118 the final soil were determined before starting the experiments.

119 2.2 EK tests

120 The experimental setup used in this study was reported in our previous studies (Fan et al., 2014a).
121 The setup consisted of a direct-current power supply, a four-channel peristaltic pump, a cylindrical
122 soil column (12 cm L × 6.6 cm D), anode and cathode compartments with two titanium electrodes,
123 *in situ* soil solution samplers and a pH auto-control system. About 570 g of the dry soil was loaded
124 into the EK cell in layers and compacted manually using a rammer. During this process, five
125 *in-situ* soil solution samplers were also vertically embedded at target locations through the soil
126 column. According to our previous results, the anode was selected as the persulfate injection
127 location and 200 g L⁻¹ (20%) of persulfate was chosen as the optimum oxidation dosage injection
128 in the anode (Fan et al., 2014a; Fan et al., 2014b). A total of six tests were conducted under
129 different conditions as shown in Table 2. The initial PCBs concentration was 46 mg kg⁻¹. In the
130 control test (Exp-01), only 20% of persulfate was added in the anode to evaluate the performance
131 of transported persulfate by EK without activation. Exp-02 was performed with zero-valent iron
132 activation by adding 1 g of zero-valent iron powder in the anode compartment on 3rd, 6th, 9th and
133 12th day, and the molar ratio of persulfate and the total zero-valent iron we added was 5.88:1. The
134 discontinuous input of zero-valent iron aimed to avoid the over-consumption of persulfate by the
135 activator. In Exp-03, citric acid was selected as the Fe²⁺ chelator, injecting citric acid chelated Fe²⁺
136 in the anode at one time under the Na₂S₂O₈/ citric acid /Fe²⁺ molar ratio of 20/5/5 (Liang et al.,
137 2004b). In Exp-04, a 14# galvanized iron wire (2.03 mm D × 8 cm L) was used as the iron anode
138 to keep the current continuity. The iron anode was occasionally replaced by a new one after its
139 complete corrosion. Exp-05 was performed with alkaline activation using a pH controller to keep
140 the anode pH at 12.0. In Exp-06, 6 mL of 30% H₂O₂ was injected into the anolyte per day to keep
141 a molar ratio of the total H₂O₂ and Na₂S₂O₈ nearly 1:1 (Block et al., 2004). For all the treatments,
142 0.01 M NaNO₃ was used as the supporting electrolyte. Before application of electrical field, the
143 soil was saturated with 0.01 M NaNO₃ solution for 24 h. A voltage gradient of 1.0 V cm⁻¹ was
144 applied to the EK system by a DC power supply for a period of 15 d (14 d for Exp-03). During EK
145 tests, the electric current and the EOF were recorded and the soil solution and electrolytes were
146 sampled on 3rd, 6th, 9th, 12th and 15th day for persulfate concentration and pH analysis. At the
147 end of the tests, the soil was extruded from the column and divided into five sections, labeled as

148 S1 to S5 from anode to cathode. For each soil section, pH, EC (electrical conductivity) and
149 residual PCBs concentration were determined.

150 *2.3 Analytical methods*

151 The soil pH and EC were determined with a solid:water ratio of 1:2.5 (Lu, 2000). The soil
152 particle-size distribution was analyzed by laser particle analyzer (LS13320, Beckman Coulter Inc.
153 USA). The TOC (total organic carbon) of soil was measured by potassium dichromate oxidation
154 method at 100 °C for 90 min and determined by the UV-Vis spectrophotometer at 590 nm
155 (721-100, Jinghua Science and Technology Instrument Co., Ltd, China). Moreover, the OM
156 (organic matter) of soil was calculated after the soil TOC with a factor of 1.724 (Lu, 2000). The
157 CEC (cationic interchange capacity) of soil was measured by the ammonium acetate extraction
158 method (Lu, 2000). The metal concentration of soil was determined by ICP (Inductively Coupled
159 Plasma, Optima 8000, PerkinElme Inc., USA) after HF-HClO₄-HNO₃ digestion. After extracting
160 the soil solution, persulfate concentration was determined in the UV-Vis spectrophotometer
161 according to Liang et al. (Liang et al., 2008). This method was detailed in our previous study (Fan
162 et al., 2014a). For PCBs concentration measurement, the air-dried soil samples were ground and
163 passed through 20-mesh sieve, and then extracted by sonication using hexane:acetone (V/V, 1:1)
164 for three times. Three replicate samples were tested for each analysis to ensure accuracy. PCBs in
165 the supernatant was quantified by gas chromatography (GC-×ECD, Agilent 7890A, USA) coupled
166 with a micro-electron capture detector and a HP-5 (30 m × 0.25 mm × 0.25 μm) fused silica
167 capillary column. The oven temperature was programmed starting at 150 °C for 2 min, and then
168 increased to 280 °C at a rate of 5 °C min⁻¹ where it was hold for 2 min. The temperature of the
169 injector and detector was 250 °C and 300 °C, respectively. High pure nitrogen was used as the
170 carrier gas and the ECD makeup gas with a constant of 1.0 mL min⁻¹ and 30 mL min⁻¹,
171 respectively.

172 **3. Results and discussion**

173 *3.1 Electrical current and EOF*

174 The evolution of electric current and EOF is presented in Fig. 1. In the control test (Exp-01), the
175 current started increasing, reached a peak value of 66 mA at 121 h, and then decreased rapidly and

176 stabilized at around 8 mA at the end of the test (Fig. 1a). In Exp-02, the addition of zero-valent
177 iron activator every three days in the anolyte increased the current drastically with a peak value of
178 330 mA at 197 h. The **periodic** addition of zero-valent iron caused the decomposition of persulfate
179 into more ions (e.g. Fe^{2+} and SO_4^{2-}), and the increased ionic strength enhanced the current intensity.
180 When **citric acid** chelated Fe^{2+} was introduced into the persulfate solution in the anode chamber
181 (Exp-03), the current was relatively low with a small fluctuation (ranged from 10 to 34 mA). The
182 sharp contrast of the ionic concentration in the anodic and the counter compartment increased the
183 electric resistance that resulted in the low current (Yuan et al., 2013). In the presence of Fe^{2+}
184 chelator, once the activator is injected into the persulfate solution, a large amount of chelated Fe^{2+}
185 reacted and exhausted most of the persulfate in the anolyte before it could be transported in the
186 soil by EK. The treatment using an iron anode (Exp-04) yielded the lowest current, with a highest
187 current value about 20 mA at the initial and last stages. This was attributed to the small surface
188 area of the iron electrode as the current intensity is proportional to the electrode surface area. The
189 iron wire anode ($d = 2.03$ mm) used in Exp-04 had a much small surface area comparing to the
190 other electrodes ($4 \text{ cm} \times 4 \text{ cm}$) and needed to be replaced with a new one after it was completely
191 corroded within several hours. The highest current value was obtained in Exp-05 using alkaline
192 activate persulfate, **and the current reached its peak value of 700 mA at 164 h**. In order to maintain
193 the high pH value (12.0) of the anolyte, large amount of NaOH solution was applied in the anode,
194 which increased the ionic density and current of the system. In Exp-06, the current reached the
195 maximum value of 194 mA due to the addition of H_2O_2 in the anode every day, which can activate
196 persulfate and accelerate its decomposition to produce more acidity. The decreased soil pH may
197 cause more salts dissolving into the soil solution and also enhance the current.

198 Fig. 1b presents the variation of cumulative EOF during the experiments. EOF was required to
199 deliver persulfate and its derivatives into the soil from the anode to the cathode to interact with
200 PCBs in soil (Yukselen-Aksoy and Reddy, 2012; Fan et al., 2014a). In all treatments, the EOF was
201 directed and followed the order of alkaline activation > zero-valent iron activation > without
202 activation > **citric acid** chelated Fe^{2+} activation > peroxide activation > iron electrode activation. In
203 the treatment without activation (Exp-01), a EOF of 299 mL was obtained. Persulfate activated by
204 alkaline (Exp-05) yielded the highest EOF of 370 mL due to its high pH (Saichek and Reddy,
205 2005). Persulfate activated by zero-valent iron (Exp-02) has the second highest EOF of 327 mL

206 after Exp-05. The EOF was related to its current, and it was proportional to the current strength. In
207 the treatment of citric acid chelated Fe^{2+} activation and peroxide activation (Exp-03 and Exp-06),
208 the EOF was lower than that without activation. This was probably attributed to the exhaustion of
209 persulfate. The activator accelerated the decomposition of persulfate and the acidic by-product
210 (such as H^+ or HSO_4^-) enter into the soil solution, resulting in the decrease of soil pH (Liang and
211 Lai, 2008). As a result of lower pH, the zeta potential of the soil surface will also be reduced and
212 the EOF hampered. The Exp-04, using an iron electrode to activate persulfate obtained the lowest
213 EOF, only 164 mL. The relatively lower electric current was responsible for this weak EOF.

214 3.2 Soil pH and EC

215 Fig. 2 shows the pH and EC distribution of soil sections after EK tests. The initial soil pH was 5.7.
216 In the control test without activation (Exp-01), the soil pH ranged from 1.4 to 4.0 in S1-S3 with
217 the transport of persulfate from anode to cathode by electroosmosis, whereas in the pH jumping
218 location, the soil pH drastically increased to above 11.0 in S4 and S5 due to water electrolysis on
219 the cathode. Compared to Exp-01, the addition of zero-valent iron (Exp-02) decreased the soil pH
220 near the anode (S1-S3) to some extent, with pH in the range of 1.3 to 2.2 due to the persulfate
221 decomposition after activation. The pH reduction was also observed in the treatment with citric
222 acid chelated Fe^{2+} (Exp-04) and peroxide (Exp-06), and the pH in the pH jumping location
223 dropped to 2.6 and 3.6, respectively. This result indicated that the acidic by-products after
224 persulfate decomposition were transported to this section by electroosmosis and electromigration
225 and promoted the pH decrease. When persulfate was activated by pH control in the anolyte
226 (Exp-05), the soil pH of all sections was kept at about 12.5 after EK tests. In all the tests, the pH
227 change of persulfate activated by the iron electrode was not significant. This was probably related
228 to the lack of the H^+ producing process in the anode as the water electrolysis was replaced by the
229 iron electrolysis, and also, the lower current inhibited the OH^- production on the cathode.

230 The initial soil EC was 0.08 mS cm^{-1} . The distribution of EC (as shown in Fig. 2b) decreased from
231 anode to cathode, which follows the same pattern as the soil pH, and the lower pH leads to the
232 higher EC. Besides the iron electrode activation, all of the activation methods enhanced the soil
233 EC compared to the treatment without activation.

234 3.3 The transport of persulfate and changes of soil solution pH

235 The spatial and temporal distribution of persulfate concentration and pH in soil solution is plotted

236 in Fig. 3. In the treatment without activation (Exp-01), persulfate can be delivered from the anode
237 toward the cathode by electroosmosis, the maximum transport distance of persulfate reached the
238 S4 section and the maximum average persulfate concentration transported in the soil was 127 g L^{-1}
239 at 9 d. With the consumption of oxidant, the persulfate concentration in S4 and S3 dropped
240 gradually to a minimum value. The pH variation in the soil solution is shown in Fig. 3b. As the
241 acid front resulting from water electrolysis and persulfate decomposition migrated into the soil
242 from anode, a pH decline was observed from the anode towards the cathode. From 12th to 15th
243 day, the pH in anolyte, S1 and S2 was below zero. However, the pH reduction ended in S3 section,
244 the location of which coincides with the location of a high persulfate front. At the pH jumping
245 location (S4), the pH increased to more than 12.0, and the OH^- produced from the cathode
246 migrating toward the anode by electromigration resulted in the alkaline condition. Under strong
247 alkaline conditions, a large amount of precipitates such as metal sulphates, phosphates and
248 hydroxides (especially calcium sulphate) will be produced to decrease the permeability of soil,
249 which in turn prevented the migration of persulfate towards the cathode (Suèr et al., 2003; Isosaari
250 et al., 2007; Fan et al., 2014a).

251 In Exp-02, 1 g of zero-valent iron was added in the anolyte on 3rd, 6th, 9th and 12th day to
252 activate persulfate (as shown in Fig. 3c). The addition of zero-valent iron significantly enhanced
253 the transport of persulfate towards the cathode. After 6 d, persulfate was detected throughout the
254 whole column length with a persulfate front concentration of 61.9 g L^{-1} in S5 section. All the other
255 sections had a concentration above 140 g L^{-1} . Moreover, at this time, the maximum average
256 persulfate concentration transported in soil was 144 g L^{-1} , which was higher than that of Exp-01.
257 The higher transfer mass was related to its higher EOF, which confirms that EOF is the main
258 transport mechanism of persulfate and its derivatives. Additionally, the mass of the zero-valent
259 iron added to the anolyte is 1 g, which is lower than the persulfate concentration. Although some
260 persulfate can be decomposed by the activator, most of the persulfate migrated towards the
261 cathode without being affected. As time goes by, the concentration of persulfate delivered into the
262 soil column decreased due to the discontinuous iron addition. Also, the persulfate in S4 and S5
263 sections was exhausted by activation due to the OH^- production on the cathode and encountering
264 the persulfate. The pH variation of the soil solution is in agreement with the transport of persulfate.
265 As shown in Fig. 3d, when persulfate got through the whole column on 6th day, the pH of soil

266 solution increased from the anode to the cathode with a range of 1.3-4.2. Moreover, after 9 d, the
267 pH in S4 and S5 sections rose to more than 12.0 due to the water electrolysis on the cathode.

268 When persulfate was activated by citric acid chelated Fe^{2+} (Exp-03), a large amount of activator
269 reacted with the oxidant immediately which resulted in the over consumption of oxidant before it
270 was delivered into the soil column (Fig. 3e). On 3rd day, the residual persulfate concentration in
271 the anolyte was only 42.2 g L^{-1} , and after 6 d, the persulfate was used up completely within. The
272 mass of persulfate transported into the soil was extremely low with a concentration of 2 g L^{-1} in S1
273 section. Due to the complete decomposition of persulfate, a large amount of acidic byproducts
274 such as HSO_4^- and H^+ entering into soil by electroosmosis and electromigration lead to the
275 decrease in pH (as shown in Fig. 3f). At the end of the test, the soil solution pH ranged from 0.04
276 to 2.4 in S1-S4 sections, and only S5 section had a pH of above 12.0.

277 In the treatment with an iron electrode to activate persulfate (Exp-04), the migration of persulfate
278 was inhibited due to the weak EOF, as well as the depletion of persulfate by iron electrolysis. In
279 Fig. 3g, the persulfate was only transported to S1 section with a concentration of 86.8 g L^{-1} on 3rd
280 day. After 6 d, the persulfate migrated to S3 section with a minimum front of 1.3 g L^{-1} , meanwhile,
281 the persulfate in the anolyte decreased to 61.7 g L^{-1} as a result of constant dissolution of the iron
282 electrode. The maximum average persulfate concentration transported in soil was 14.4 g L^{-1} ,
283 which occurred on 9th day. The changes of soil solution pH were related to the persulfate
284 transportation. As shown in Fig. 3h, on 3rd day, the pH of anolyte and S1 section reduced to 1.2
285 and 1.8, respectively, and the pH of other soil sections was above 5.0. At the end of the test, the
286 pH of S1 and S2 sections decreased to about 1.5, and the pH in S3 section was 4.0 due to the
287 lower amount of persulfate transported into the soil. Also, the pH of soil solution near the cathode
288 (S4 and S5) increased to about 6.5 as the result of water electrolysis. The relatively low pH near
289 the cathode was attributed to the weak water electrolysis resulting from the low current intensity.

290 As alkaline activation was used in Exp-05, the transport of persulfate was enhanced dramatically.
291 Fig. 3i shows that at the early stage (on 3rd day), the persulfate was delivered to S1 section with a
292 high concentration of over 300 g L^{-1} that is much more than the initial value. On 6th day, the
293 persulfate front reached S4 section and every section had an even persulfate concentration of
294 about 180 g L^{-1} . The maximum average persulfate concentration transported in soil (149 g L^{-1})
295 was also obtained, which is higher than all the other treatments. The improvement of persulfate

296 transport is highly dependent on the high EOF resulting from the high pH. Nevertheless, at the
297 later stage (on 9th, 12th and 15th day), the soil pH increased with the exhaustion of persulfate by
298 alkaline activation, which decreased the permeability of soil which prevented the soil solution
299 extraction (the blank spots in Fig. 3i). Fig. 3j shows the changes of soil solution pH. Under the pH
300 auto-control system, the pH of anolyte was kept around 12.0. With the transport of persulfate in
301 soil, the pH of soil solution in S1-S4 decreased to about 3.0 due to persulfate decomposition. Then,
302 the soil solution pH of the spots that could be extracted went up to more than 13.0 after the
303 persulfate in soil was exhausted.

304 In Exp-06, peroxide was used to activate persulfate. As shown in Fig. 3k, on 3rd day, persulfate
305 could be delivered to S1 section with a front of 109 g L⁻¹. After 6 d, the front approached the S4
306 section and every section (S1-S4) has a concentration of about 65 g L⁻¹. Compared to Exp-01, the
307 addition of peroxide improved the migration distance of persulfate at the same time. However, the
308 continuous addition of peroxide in the anolyte led to persulfate decomposition and on 6th day the
309 persulfate concentration in anolyte was reduced to 102 g L⁻¹. The maximum average persulfate
310 concentration transported in soil was only 53.2 g L⁻¹. At the end of the test, the persulfate
311 transported in soil dropped gradually to the minimum value. The activator intensified the
312 decomposition of persulfate and thus decreased the soil solution pH. As shown in Fig. 3l, the
313 anolyte pH after 9 d decreased to below zero, and the soil solution pH from S1 to S4 kept
314 dropping. The minimum value was obtained on 12th day with the soil solution pH in S1 to S4
315 ranging from 0.6 to 2.4. Only the soil solution pH in S5 increased above 12.0 after 9 d due to the
316 water electrolysis on the cathode.

317 From the above results, we can conclude that comparing to persulfate without activation,
318 zero-valent iron, alkaline and peroxide activation improved the transport of persulfate at the early
319 stage of EK test, and the longest delivery distance reached sections S4 or S5 on 6th day . The
320 transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent
321 activation > without activation > peroxide activation > iron electrode activation > citric acid
322 chelated Fe²⁺ activation.

323 3.4 Residual PCBs concentration in soil

324 Table 3 presents the distribution of residual PCBs in different treatments after EK tests. In general,
325 besides the iron electrode, all the other activation methods enhanced the degradation of PCBs in

326 the soil as compared to that without activation. The removal efficiency of PCBs in soil followed
327 the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation >
328 zero-valent iron activation > without activation > iron electrode activation, and the values were
329 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. As the persulfate and activators
330 were injected in the anode, the degradation of PCBs in soil was predominant on the section near
331 the anode, followed by the section near the cathode, while the degradation of PCBs in the central
332 part was minor.

333 In the control test without activation (Exp-01), the distribution of residual PCBs in soil increased
334 from the anode towards the cathode with the degradation of PCBs mainly concentrated on S1
335 section with a removal rate of 51.7%. In the other sections, the degradation of PCBs was
336 insignificant even with a high persulfate concentration (more than 100 g L^{-1}) in S2 until the end of
337 the test, and most of the PCBs were accumulated in the middle sections. In the location near the
338 cathode (S4 and S5), a relatively higher PCBs degradation efficiency was observed ($\approx 27\%$),
339 although the persulfate transported to these sections was limited. This can be probably attributed
340 to the alkaline hydrolysis function occurred in the cathode (Jeffers et al., 1989; Waisner et al.,
341 2008).

342 When zero-valent iron was added to activate persulfate (Exp-02), the removal of PCBs in soil was
343 not remarkably improved even though the transport distance and mass of persulfate was higher
344 than the control test. The residual PCBs in S1 to S3 section followed the same trend as Exp-01,
345 whereas, the removal rates of S4 (35%) and S5 (33%) were higher than that of the control test
346 (26%). This result was due to the lower amount of zero-valent iron added in the anolyte. The
347 molar ratio of persulfate and total iron we added is 5.88:1 and the optimum rate referenced is 1.5:1
348 (Lang et al., 2010), so, the mass of zero-valent iron added is not enough to break down persulfate
349 completely. When persulfate was delivered to S4 and S5 section, it could be activated by the high
350 pH near the cathode, which enhanced PCBs degradation in these sections.

351 In Exp-03, the distribution of residual PCBs in soil was uniform, with a removal rate of about 35%.
352 Although the mass of persulfate transported in soil was almost zero, as the result of the abundant
353 of citric acid chelated Fe^{2+} put into the oxidant solution, the activation products such as $\text{SO}_4^{\cdot-}$ or \cdot
354 OH radicals generated by persulfate decomposition were transported into soil by EOF, which
355 resulted in the degradation of PCBs in soil. The mass of $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ transported into the soil

356 could not be measured, but the extremely low pH distribution in this treatment confirmed that the
357 decomposition products had been transported into the soil column. Moreover, the drastic reaction
358 between activator and oxidant released much heat, which could also favored persulfate activation,
359 as well as the PCBs desorption from the soil.

360 The lowest PCBs degradation percentage was found in the treatment with an iron electrode to
361 activate persulfate (Exp-04). The activated persulfate transported in soil enhanced the degradation
362 of PCBs near the anode, and the degradation percentages of PCBs in S1, S2 and S3 were 44%, 33%
363 and 30%, respectively. However, the degradation of PCBs in S4 and S5 was low, only 21% and
364 25%. This distribution of residual PCBs in soil was consistent with the delivery of persulfate in
365 the soil. Besides, the low removal of PCBs was probably due to its low EOF, as the low EOF
366 inhibited the transportation of persulfate and its derivatives in the soil.

367 The treatment of alkaline activation yielded the highest PCBs degradation percentage (Exp-05). In
368 the section near the anode (S1), the removal reached as high as 53% with about 40% degradation
369 in the other sections. The relatively high PCBs degradation was based on the long transport
370 distance and high transfer mass of persulfate as well as the high pH. Also, during the alkaline
371 activation process, $\bullet\text{OH}$ was predominant while its oxidizing ability is more powerful than that of
372 $\text{SO}_4^{\bullet-}$. Meanwhile, on the condition of pH above 12.0, alkaline hydrolysis also plays an important
373 role in PCBs degradation.

374 When peroxide was used to activate persulfate (Exp-06), the distribution of residual PCBs in soil
375 increased first and decreased subsequently. The degradation of PCBs in soil was mainly focused
376 on the section near the anode (about 40%) and cathode (about 32%), and most of PCBs were
377 accumulated in the central part of the soil column (28%). Compared to the treatment without
378 activation, peroxide activation facilitated the degradation of PCBs in soil. This result indicated
379 that the radicals resulting from peroxide activating persulfate entered into the soil and led to the
380 degradation of PCBs. The low pH in S1 to S4 also confirms that the decomposition products
381 migrated from the anode towards the cathode, and also that lower pH is conducive to the
382 degradation of PCBs by persulfate (House, 1962; Liang et al., 2007; Fang et al., 2013).

383 In conclusion, the impact of different persulfate activation methods on the degradation of PCBs is
384 different, and PCBs degradation was related to persulfate transfer distance, transfer mass, and the
385 soil pH. The relationship between the degradation effect and weight factors with different

386 activation methods is summarized in Table 4. In essence, all these factors were based on the ratio
387 of oxidant and activator, which is controlled by the injection quantity and rate. In general,
388 persulfate activation did not enhance the degradation of PCBs significantly, and the highest
389 enhancement only increased by 10% compared with that without activation. The activation
390 parameters should be optimized in future studies. Although alkaline activation (pH control in the
391 anode) reached the highest enhancement, the high pH would damage the soil properties in field
392 remediation. Additionally, iron electrode activation has a good applicability for in-situ
393 remediation, but further research is needed on how to regulate its activation effect.

394 4. Conclusions

395 In this study, a series of experiments were undertaken to assess the transport behavior of activated
396 persulfate under electric field and the efficiency of remediation of PCBs polluted soil. The impact
397 of different activation methods, using zero-valent iron, citric acid chelated Fe^{2+} , iron electrode,
398 alkaline pH and peroxide on the persulfate migration was evaluated as well as the degradation of
399 PCBs in soil.

400 Electroosmotic flow was the main transfer mechanism for persulfate and its derivatives, the EOF
401 flowed from anode towards cathode (direct EOF) and followed the order of alkaline activation >
402 zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide
403 activation > iron electrode activation.

404 Zero-valent iron, alkaline, and peroxide activation improved the transport of persulfate at the early
405 stage of EK test, and the longest delivery distance reached S4 or S5 section on 6th day. The
406 transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent
407 activation > without activation > peroxide activation > iron electrode activation > citric acid
408 chelated Fe^{2+} activation.

409 The addition of an activator accelerated the decomposition of persulfate, and the persulfate
410 transported in soil decreased with its degradation. The decomposition of persulfate will decrease
411 the soil pH, and lower pH was beneficial for the degradation of PCBs.

412 Besides iron electrode activation, all the other activation methods enhanced the removal of PCBs
413 in soil in different extents. The removal efficiency of PCBs in soil followed the order of alkaline
414 activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation >

415 without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%,
416 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of oxidant
417 and activator.

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1 Electrokinetic delivery of persulfate to remediate PCBs polluted
2 soils: effect of different activation methods

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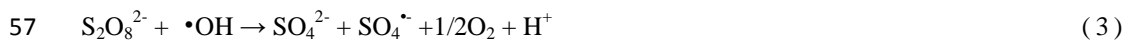
8 **ABSTRACT:** Persulfate-based in-situ chemical oxidation (ISCO) for the remediation of organic
9 polluted soils has gained much interest in last decade. However, the transportation of persulfate in
10 low-permeability soil is very low, which limits its efficiency in degrading soil pollutants.
11 Additionally, the oxidation-reduction process of persulfate with organic contaminants takes place
12 slowly, while, the reaction will be greatly accelerated by the production of more powerful radicals
13 once it is activated. Electrokinetic remediation (EK) is a good way for transporting persulfate in
14 low-permeability soil. In this study, different activation methods, using zero-valent iron, citric acid
15 chelated Fe²⁺, iron electrode, alkaline pH and peroxide, were evaluated to enhance the activity of
16 persulfate delivered by EK. All the activators and the persulfate were added in the anolyte. The
17 results indicated that zero-valent iron, alkaline, and peroxide enhanced the transportation of
18 persulfate at the first stage of EK test, and the longest delivery distance reached sections S4 or S5
19 (near the cathode) on the 6th day. The addition of activators accelerated decomposition of
20 persulfate, which resulted in the decreasing soil pH. The mass of persulfate delivered into the soil
21 declined with the continuous decomposition of persulfate by activation. The removal efficiency of
22 PCBs in soil followed the order of alkaline activation > peroxide activation > citric acid chelated
23 Fe²⁺ activation > zero-valent iron activation > without activation > iron electrode activation, and
24 the values were 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. The activation
25 effect was highly dependent on the ratio of activator and persulfate.

26 **Key words:** Polychlorinated biphenyls (PCBs), soil remediation, electrokinetics, persulfate
27 activation.

28 _____
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31 **Introduction**

32 Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that strongly adsorb in
33 soils and sediments. Developing cost-effective and sustainable solutions for the remediation of
34 PCB-contaminated soils is imperative (Gomes et al., 2014). The present technologies include
35 capping, solvent extraction, thermal desorption, Fe-promoted dechlorination, chemical oxidation,
36 biological remediation and many others still in development phase (Gomes et al., 2013).
37 Among these technologies, in-situ chemical oxidation (ISCO) is an emerging technology for soil
38 and groundwater remediation due to its wide applicability, relatively fast treatment, simplicity of
39 operation and cost effectiveness (ITRC, 2005; Watts and Teel, 2006; Rastogi et al., 2009b;
40 Tsitonaki et al., 2010). ISCO involves the introduction of chemical oxidant into the subsurface to
41 transform organic contaminants into less harmful chemical species. Hydrogen peroxide,
42 permanganate and ozone are widely used oxidants, but their practical applications are hindered
43 due to their low stability (hydrogen peroxide and ozone) or high soil affinity for natural soil
44 organics (permanganate) (Gates-Anderson et al., 2001; Li and Schwartz, 2004; Tsai et al., 2008;
45 Navalon et al., 2010). Persulfate is a strong oxidant with a redox potential (E_0) of 2.01 V and a
46 relatively long life in the subsurface due to its slow reaction kinetics with organics, which can
47 promote more favorable contact time (Tsitonaki et al., 2010). Also, upon activation, persulfate can
48 produce sulfate radicals ($SO_4^{\bullet-}$, $E_0=2.6$ V) and hydroxyl radicals ($\bullet OH$, $E_0=2.7$ V) which are more
49 powerful and kinetically faster than persulfate anions (Liang et al., 2004a). There are many
50 methods available for persulfate activation including the use of heat, chelated or unchelated
51 transition metals, hydrogen peroxide, or strong alkaline pH (Eqs. (1)-(4)) (Petri et al., 2011). But
52 the site conditions such as lithology (clay, sand, etc.), hydrogeology and the structure of the target
53 contamination will affect the oxidation effectiveness. Thus, the activation method selected must be
54 dependent on the contaminants to be treated and the subsurface environment (Block et al., 2004).

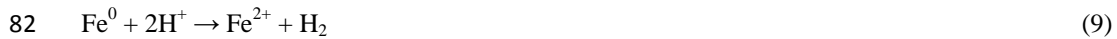


59 Fe(II) was used initially to activate persulfate. However, the activation by Fe^{2+} is not practical
60 because the reaction is almost instantaneously stopped due to the $SO_4^{\bullet-}$ scavenging by excess Fe^{2+}

61 or to the rapid conversion of Fe^{2+} to Fe^{3+} . As an alternative activator, zero-valent iron (an insoluble
 62 form of iron) has been employed to activate persulfate with promising results by directly reacting
 63 with persulfate to release Fe^{2+} , or releasing Fe^{2+} through the corrosion of zero-valent iron
 64 activation (Eqs. (5)-(7)) (Oh et al., 2009; Liang and Guo, 2010; Oh et al., 2010). On the other hand,
 65 aqueous Fe(II) is relatively insoluble at the ambient $\text{pH} \geq 5$ of most aquifer systems and Fe(II)
 66 chelated by chelating agents (e.g. ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic
 67 acid and citric acid) is effective in activating persulfate by maintaining iron in solution at neutral
 68 pH (Liang et al., 2004b; Crimi and Taylor, 2007; Rastogi et al., 2009a).



72 A significant difficulty in ISCO is promoting the contact between the oxidant and the contaminant,
 73 particularly in low-permeability subsurface. When ISCO is combined with EK, EK has the
 74 potential to increase the delivery of oxidant in soil and improve the remediation efficiency (Reddy
 75 and Cameselle, 2009). Also, in-situ electrolysis by iron electrodes allows to manipulate the
 76 reactivity of persulfate in EK + ISCO system. According to Yuan et al. (2013), Fe^{2+} can be
 77 continuously produced in situ by electrochemical corrosion (Eqs. (8) and (6)) and chemical
 78 corrosion (Eqs. (9) and (7)) when applying a positive current on an iron anode, and the electrolytic
 79 supply of Fe^{2+} will improve the utilization of both Fe^{2+} and persulfate (Yuan et al., 2013).



84 The effect of different activators on persulfate oxidation has been studied extensively. However,
 85 the persulfate activation in EK was rarely referred. Recently, Yukselen-Aksoy et al. (2012)
 86 investigated the effect of heat and alkaline activation on the electrokinetically enhanced persulfate
 87 oxidation of PCB44 in kaolin and glacial till soils. Persulfate (30%) was injected from a position 3
 88 cm away from the anode and the result showed that both activation methods (heat or heat and high
 89 pH) improved the degradation of PCB44 in kaolin, but not in glacial till soil due to its high
 90 buffering capacity, nonhomogeneous mineral contents and high organic content (Yukselen-Aksoy

91 and Reddy, 2012). Furthermore, we investigated the transport behaviors of inactivated persulfate
92 under electric field, and found that electroosmotic flow (EOF) was more effective for persulfate
93 delivery than electromigration and the anode was the best injection spot for high dosage of
94 persulfate (Fan et al., 2014a). However, the activity of persulfate in soil is relatively low without
95 activation, so choosing appropriate activators to accelerate the reaction kinetics of persulfate is a
96 key process for the application of EK + persulfate technology.
97 In this study, different activation methods, using zero-valent iron, citric acid chelated Fe^{2+} , iron
98 electrode, alkaline pH, and peroxide, were evaluated to enhance the activity of persulfate delivered
99 by EK. The transport behavior of activated persulfate under electric field and the remediation
100 efficiency of PCBs contaminated soil were also investigated.

101 **2. Experimental**

102 *2.1 Chemicals and materials*

103 PCBs standard solution containing 20 PCBs congeners ($> 99.4\%$) were obtained from
104 AccuStandard (New Haven, CT, USA). Sodium persulfate (99.0%) was purchased from Chengdu
105 Kelon Chemical Reagent Factory. Zero-valent iron powder (98.0%) was provided by Shanghai
106 Miura Chemical Co. Ltd., China. Sodium hydroxide ($>96\%$), citric acid ($>99.6\%$), acetone
107 (analytical reagent) and hexane (analytical reagent) were obtained from Nanjing Chemical Reagent
108 Co. Ltd., China. Hydrogen peroxide (30% solution, 99.0%) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99.0%) were
109 supplied by Sinopharm Chemical Reagent Co. Ltd., China. Deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$)
110 obtained from a Millipore Milli-Q system was used in all experiments.

111 The PCBs polluted soil was sampled from a place near a capacitor storage site in Zhejiang
112 province, which was diluted with a clean soil sampled from a farmland in Nanjing. The properties
113 of the two soils are shown in Table 1. Both soils belong to yellow brown soil and have similar
114 properties. The soils were air-dried, ground and passed through 20 mesh and 60 mesh sieves,
115 respectively. Approximately 100 g of PCBs polluted soil was mixed with 2200 g of clean soil
116 thoroughly, after that, the mixed soil was stored in the fume hood one week for equilibrium. Also,
117 the properties of the mixed soil were analyzed and shown in Table 1. The initial values of PCBs in
118 the final soil were determined before starting the experiments.

119 2.2 EK tests

120 The experimental setup used in this study was reported in our previous studies (Fan et al., 2014a).
121 The setup consisted of a direct-current power supply, a four-channel peristaltic pump, a cylindrical
122 soil column (12 cm L × 6.6 cm D), anode and cathode compartments with two titanium electrodes,
123 *in situ* soil solution samplers and a pH auto-control system. About 570 g of the dry soil was loaded
124 into the EK cell in layers and compacted manually using a rammer. During this process, five
125 *in-situ* soil solution samplers were also vertically embedded at target locations through the soil
126 column. According to our previous results, the anode was selected as the persulfate injection
127 location and 200 g L⁻¹ (20%) of persulfate was chosen as the optimum oxidation dosage injection
128 in the anode (Fan et al., 2014a; Fan et al., 2014b). A total of six tests were conducted under
129 different conditions as shown in Table 2. The initial PCBs concentration was 46 mg kg⁻¹. In the
130 control test (Exp-01), only 20% of persulfate was added in the anode to evaluate the performance
131 of transported persulfate by EK without activation. Exp-02 was performed with zero-valent iron
132 activation by adding 1 g of zero-valent iron powder in the anode compartment on 3rd, 6th, 9th and
133 12th day, and the molar ratio of persulfate and the total zero-valent iron we added was 5.88:1. The
134 discontinuous input of zero-valent iron aimed to avoid the over-consumption of persulfate by the
135 activator. In Exp-03, citric acid was selected as the Fe²⁺ chelator, injecting citric acid chelated Fe²⁺
136 in the anode at one time under the Na₂S₂O₈/ citric acid /Fe²⁺ molar ratio of 20/5/5 (Liang et al.,
137 2004b). In Exp-04, a 14# galvanized iron wire (2.03 mm D × 8 cm L) was used as the iron anode
138 to keep the current continuity. The iron anode was occasionally replaced by a new one after its
139 complete corrosion. Exp-05 was performed with alkaline activation using a pH controller to keep
140 the anode pH at 12.0. In Exp-06, 6 mL of 30% H₂O₂ was injected into the anolyte per day to keep
141 a molar ratio of the total H₂O₂ and Na₂S₂O₈ nearly 1:1 (Block et al., 2004). For all the treatments,
142 0.01 M NaNO₃ was used as the supporting electrolyte. Before application of electrical field, the
143 soil was saturated with 0.01 M NaNO₃ solution for 24 h. A voltage gradient of 1.0 V cm⁻¹ was
144 applied to the EK system by a DC power supply for a period of 15 d (14 d for Exp-03). During EK
145 tests, the electric current and the EOF were recorded and the soil solution and electrolytes were
146 sampled on 3rd, 6th, 9th, 12th and 15th day for persulfate concentration and pH analysis. At the
147 end of the tests, the soil was extruded from the column and divided into five sections, labeled as

148 S1 to S5 from anode to cathode. For each soil section, pH, EC (electrical conductivity) and
149 residual PCBs concentration were determined.

150 *2.3 Analytical methods*

151 The soil pH and EC were determined with a solid:water ratio of 1:2.5 (Lu, 2000). The soil
152 particle-size distribution was analyzed by laser particle analyzer (LS13320, Beckman Coulter Inc.
153 USA). The TOC (total organic carbon) of soil was measured by potassium dichromate oxidation
154 method at 100 °C for 90 min and determined by the UV-Vis spectrophotometer at 590 nm
155 (721-100, Jinghua Science and Technology Instrument Co., Ltd, China). Moreover, the OM
156 (organic matter) of soil was calculated after the soil TOC with a factor of 1.724 (Lu, 2000). The
157 CEC (cationic interchange capacity) of soil was measured by the ammonium acetate extraction
158 method (Lu, 2000). The metal concentration of soil was determined by ICP (Inductively Coupled
159 Plasma, Optima 8000, PerkinElme Inc., USA) after HF-HClO₄-HNO₃ digestion. After extracting
160 the soil solution, persulfate concentration was determined in the UV-Vis spectrophotometer
161 according to Liang et al. (Liang et al., 2008). This method was detailed in our previous study (Fan
162 et al., 2014a). For PCBs concentration measurement, the air-dried soil samples were ground and
163 passed through 20-mesh sieve, and then extracted by sonication using hexane:acetone (V/V, 1:1)
164 for three times. Three replicate samples were tested for each analysis to ensure accuracy. PCBs in
165 the supernatant was quantified by gas chromatography (GC-×ECD, Agilent 7890A, USA) coupled
166 with a micro-electron capture detector and a HP-5 (30 m × 0.25 mm × 0.25 μm) fused silica
167 capillary column. The oven temperature was programmed starting at 150 °C for 2 min, and then
168 increased to 280 °C at a rate of 5 °C min⁻¹ where it was hold for 2 min. The temperature of the
169 injector and detector was 250 °C and 300 °C, respectively. High pure nitrogen was used as the
170 carrier gas and the ECD makeup gas with a constant of 1.0 mL min⁻¹ and 30 mL min⁻¹,
171 respectively.

172 **3. Results and discussion**

173 *3.1 Electrical current and EOF*

174 The evolution of electric current and EOF is presented in Fig. 1. In the control test (Exp-01), the
175 current started increasing, reached a peak value of 66 mA at 121 h, and then decreased rapidly and

176 stabilized at around 8 mA at the end of the test (Fig. 1a). In Exp-02, the addition of zero-valent
177 iron activator every three days in the anolyte increased the current drastically with a peak value of
178 330 mA at 197 h. The periodic addition of zero-valent iron caused the decomposition of persulfate
179 into more ions (e.g. Fe^{2+} and SO_4^{2-}), and the increased ionic strength enhanced the current intensity.
180 When citric acid chelated Fe^{2+} was introduced into the persulfate solution in the anode chamber
181 (Exp-03), the current was relatively low with a small fluctuation (ranged from 10 to 34 mA). The
182 sharp contrast of the ionic concentration in the anodic and the counter compartment increased the
183 electric resistance that resulted in the low current (Yuan et al., 2013). In the presence of Fe^{2+}
184 chelator, once the activator is injected into the persulfate solution, a large amount of chelated Fe^{2+}
185 reacted and exhausted most of the persulfate in the anolyte before it could be transported in the
186 soil by EK. The treatment using an iron anode (Exp-04) yielded the lowest current, with a highest
187 current value about 20 mA at the initial and last stages. This was attributed to the small surface
188 area of the iron electrode as the current intensity is proportional to the electrode surface area. The
189 iron wire anode ($d = 2.03$ mm) used in Exp-04 had a much small surface area comparing to the
190 other electrodes ($4 \text{ cm} \times 4 \text{ cm}$) and needed to be replaced with a new one after it was completely
191 corroded within several hours. The highest current value was obtained in Exp-05 using alkaline
192 activate persulfate, and the current reached its peak value of 700 mA at 164 h. In order to maintain
193 the high pH value (12.0) of the anolyte, large amount of NaOH solution was applied in the anode,
194 which increased the ionic density and current of the system. In Exp-06, the current reached the
195 maximum value of 194 mA due to the addition of H_2O_2 in the anode every day, which can activate
196 persulfate and accelerate its decomposition to produce more acidity. The decreased soil pH may
197 cause more salts dissolving into the soil solution and also enhance the current.

198 Fig. 1b presents the variation of cumulative EOF during the experiments. EOF was required to
199 deliver persulfate and its derivatives into the soil from the anode to the cathode to interact with
200 PCBs in soil (Yukselen-Aksoy and Reddy, 2012; Fan et al., 2014a). In all treatments, the EOF was
201 directed and followed the order of alkaline activation > zero-valent iron activation > without
202 activation > citric acid chelated Fe^{2+} activation > peroxide activation > iron electrode activation. In
203 the treatment without activation (Exp-01), a EOF of 299 mL was obtained. Persulfate activated by
204 alkaline (Exp-05) yielded the highest EOF of 370 mL due to its high pH (Saichek and Reddy,
205 2005). Persulfate activated by zero-valent iron (Exp-02) has the second highest EOF of 327 mL

206 after Exp-05. The EOF was related to its current, and it was proportional to the current strength. In
207 the treatment of citric acid chelated Fe^{2+} activation and peroxide activation (Exp-03 and Exp-06),
208 the EOF was lower than that without activation. This was probably attributed to the exhaustion of
209 persulfate. The activator accelerated the decomposition of persulfate and the acidic by-product
210 (such as H^+ or HSO_4^-) enter into the soil solution, resulting in the decrease of soil pH (Liang and
211 Lai, 2008). As a result of lower pH, the zeta potential of the soil surface will also be reduced and
212 the EOF hampered. The Exp-04, using an iron electrode to activate persulfate obtained the lowest
213 EOF, only 164 mL. The relatively lower electric current was responsible for this weak EOF.

214 *3.2 Soil pH and EC*

215 Fig. 2 shows the pH and EC distribution of soil sections after EK tests. The initial soil pH was 5.7.
216 In the control test without activation (Exp-01), the soil pH ranged from 1.4 to 4.0 in S1-S3 with
217 the transport of persulfate from anode to cathode by electroosmosis, whereas in the pH jumping
218 location, the soil pH drastically increased to above 11.0 in S4 and S5 due to water electrolysis on
219 the cathode. Compared to Exp-01, the addition of zero-valent iron (Exp-02) decreased the soil pH
220 near the anode (S1-S3) to some extent, with pH in the range of 1.3 to 2.2 due to the persulfate
221 decomposition after activation. The pH reduction was also observed in the treatment with citric
222 acid chelated Fe^{2+} (Exp-04) and peroxide (Exp-06), and the pH in the pH jumping location
223 dropped to 2.6 and 3.6, respectively. This result indicated that the acidic by-products after
224 persulfate decomposition were transported to this section by electroosmosis and electromigration
225 and promoted the pH decrease. When persulfate was activated by pH control in the anolyte
226 (Exp-05), the soil pH of all sections was kept at about 12.5 after EK tests. In all the tests, the pH
227 change of persulfate activated by the iron electrode was not significant. This was probably related
228 to the lack of the H^+ producing process in the anode as the water electrolysis was replaced by the
229 iron electrolysis, and also, the lower current inhibited the OH^- production on the cathode.

230 The initial soil EC was 0.08 mS cm^{-1} . The distribution of EC (as shown in Fig. 2b) decreased from
231 anode to cathode, which follows the same pattern as the soil pH, and the lower pH leads to the
232 higher EC. Besides the iron electrode activation, all of the activation methods enhanced the soil
233 EC compared to the treatment without activation.

234 *3.3 The transport of persulfate and changes of soil solution pH*

235 The spatial and temporal distribution of persulfate concentration and pH in soil solution is plotted

236 in Fig. 3. In the treatment without activation (Exp-01), persulfate can be delivered from the anode
237 toward the cathode by electroosmosis, the maximum transport distance of persulfate reached the
238 S4 section and the maximum average persulfate concentration transported in the soil was 127 g L^{-1}
239 at 9 d. With the consumption of oxidant, the persulfate concentration in S4 and S3 dropped
240 gradually to a minimum value. The pH variation in the soil solution is shown in Fig. 3b. As the
241 acid front resulting from water electrolysis and persulfate decomposition migrated into the soil
242 from anode, a pH decline was observed from the anode towards the cathode. From 12th to 15th
243 day, the pH in anolyte, S1 and S2 was below zero. However, the pH reduction ended in S3 section,
244 the location of which coincides with the location of a high persulfate front. At the pH jumping
245 location (S4), the pH increased to more than 12.0, and the OH^- produced from the cathode
246 migrating toward the anode by electromigration resulted in the alkaline condition. Under strong
247 alkaline conditions, a large amount of precipitates such as metal sulphates, phosphates and
248 hydroxides (especially calcium sulphate) will be produced to decrease the permeability of soil,
249 which in turn prevented the migration of persulfate towards the cathode (Suèr et al., 2003; Isosaari
250 et al., 2007; Fan et al., 2014a).

251 In Exp-02, 1 g of zero-valent iron was added in the anolyte on 3rd, 6th, 9th and 12th day to
252 activate persulfate (as shown in Fig. 3c). The addition of zero-valent iron significantly enhanced
253 the transport of persulfate towards the cathode. After 6 d, persulfate was detected throughout the
254 whole column length with a persulfate front concentration of 61.9 g L^{-1} in S5 section. All the other
255 sections had a concentration above 140 g L^{-1} . Moreover, at this time, the maximum average
256 persulfate concentraion transported in soil was 144 g L^{-1} , which was higher than that of Exp-01.
257 The higher transfer mass was related to its higher EOF, which confirms that EOF is the main
258 transport mechanism of persulfate and its derivatives. Additionally, the mass of the zero-valent
259 iron added to the anolyte is 1 g, which is lower than the persulfate concentration. Although some
260 persulfate can be decomposed by the activator, most of the persulfate migrated towards the
261 cathode without being affected. As time goes by, the concentration of persulfate delivered into the
262 soil column decreased due to the discontinuous iron addition. Also, the persulfate in S4 and S5
263 sections was exhausted by activation due to the OH^- production on the cathode and encountering
264 the persulfate. The pH variation of the soil solution is in agreement with the transport of persulfate.
265 As shown in Fig. 3d, when persulfate got through the whole column on 6th day, the pH of soil

266 solution increased from the anode to the cathode with a range of 1.3-4.2. Moreover, after 9 d, the
267 pH in S4 and S5 sections rose to more than 12.0 due to the water electrolysis on the cathode.

268 When persulfate was activated by citric acid chelated Fe^{2+} (Exp-03), a large amount of activator
269 reacted with the oxidant immediately which resulted in the over consumption of oxidant before it
270 was delivered into the soil column (Fig. 3e). On 3rd day, the residual persulfate concentration in
271 the anolyte was only 42.2 g L^{-1} , and after 6 d, the persulfate was used up completely within. The
272 mass of persulfate transported into the soil was extremely low with a concentration of 2 g L^{-1} in S1
273 section. Due to the complete decomposition of persulfate, a large amount of acidic byproducts
274 such as HSO_4^- and H^+ entering into soil by electroosmosis and electromigration lead to the
275 decrease in pH (as shown in Fig. 3f). At the end of the test, the soil solution pH ranged from 0.04
276 to 2.4 in S1-S4 sections, and only S5 section had a pH of above 12.0.

277 In the treatment with an iron electrode to activate persulfate (Exp-04), the migration of persulfate
278 was inhibited due to the weak EOF, as well as the depletion of persulfate by iron electrolysis. In
279 Fig. 3g, the persulfate was only transported to S1 section with a concentration of 86.8 g L^{-1} on 3rd
280 day. After 6 d, the persulfate migrated to S3 section with a minimum front of 1.3 g L^{-1} , meanwhile,
281 the persulfate in the anolyte decreased to 61.7 g L^{-1} as a result of constant dissolution of the iron
282 electrode. The maximum average persulfate concentration transported in soil was 14.4 g L^{-1} ,
283 which occurred on 9th day. The changes of soil solution pH were related to the persulfate
284 transportation. As shown in Fig. 3h, on 3rd day, the pH of anolyte and S1 section reduced to 1.2
285 and 1.8, respectively, and the pH of other soil sections was above 5.0. At the end of the test, the
286 pH of S1 and S2 sections decreased to about 1.5, and the pH in S3 section was 4.0 due to the
287 lower amount of persulfate transported into the soil. Also, the pH of soil solution near the cathode
288 (S4 and S5) increased to about 6.5 as the result of water electrolysis. The relatively low pH near
289 the cathode was attributed to the weak water electrolysis resulting from the low current intensity.

290 As alkaline activation was used in Exp-05, the transport of persulfate was enhanced dramatically.
291 Fig. 3i shows that at the early stage (on 3rd day), the persulfate was delivered to S1 section with a
292 high concentration of over 300 g L^{-1} that is much more than the initial value. On 6th day, the
293 persulfate front reached S4 section and every section had an even persulfate concentration of
294 about 180 g L^{-1} . The maximum average persulfate concentration transported in soil (149 g L^{-1})
295 was also obtained, which is higher than all the other treatments. The improvement of persulfate

296 transport is highly dependent on the high EOF resulting from the high pH. Nevertheless, at the
297 later stage (on 9th, 12th and 15th day), the soil pH increased with the exhaustion of persulfate by
298 alkaline activation, which decreased the permeability of soil which prevented the soil solution
299 extraction (the blank spots in Fig. 3i). Fig. 3j shows the changes of soil solution pH. Under the pH
300 auto-control system, the pH of anolyte was kept around 12.0. With the transport of persulfate in
301 soil, the pH of soil solution in S1-S4 decreased to about 3.0 due to persulfate decomposition. Then,
302 the soil solution pH of the spots that could be extracted went up to more than 13.0 after the
303 persulfate in soil was exhausted.

304 In Exp-06, peroxide was used to activate persulfate. As shown in Fig. 3k, on 3rd day, persulfate
305 could be delivered to S1 section with a front of 109 g L^{-1} . After 6 d, the front approached the S4
306 section and every section (S1-S4) has a concentration of about 65 g L^{-1} . Compared to Exp-01, the
307 addition of peroxide improved the migration distance of persulfate at the same time. However, the
308 continuous addition of peroxide in the anolyte led to persulfate decomposition and on 6th day the
309 persulfate concentration in anolyte was reduced to 102 g L^{-1} . The maximum average persulfate
310 concentration transported in soil was only 53.2 g L^{-1} . At the end of the test, the persulfate
311 transported in soil dropped gradually to the minimum value. The activator intensified the
312 decomposition of persulfate and thus decreased the soil solution pH. As shown in Fig. 3l, the
313 anolyte pH after 9 d decreased to below zero, and the soil solution pH from S1 to S4 kept
314 dropping. The minimum value was obtained on 12th day with the soil solution pH in S1 to S4
315 ranging from 0.6 to 2.4. Only the soil solution pH in S5 increased above 12.0 after 9 d due to the
316 water electrolysis on the cathode.

317 From the above results, we can conclude that comparing to persulfate without activation,
318 zero-valent iron, alkaline and peroxide activation improved the transport of persulfate at the early
319 stage of EK test, and the longest delivery distance reached sections S4 or S5 on 6th day. The
320 transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent
321 activation > without activation > peroxide activation > iron electrode activation > citric acid
322 chelated Fe^{2+} activation.

323 *3.4 Residual PCBs concentration in soil*

324 Table 3 presents the distribution of residual PCBs in different treatments after EK tests. In general,
325 besides the iron electrode, all the other activation methods enhanced the degradation of PCBs in

326 the soil as compared to that without activation. The removal efficiency of PCBs in soil followed
327 the order of alkaline activation > peroxide activation > citric acid chelated Fe^{2+} activation >
328 zero-valent iron activation > without activation > iron electrode activation, and the values were
329 40.5%, 35.6%, 34.1%, 32.4%, 30.8% and 30.5%, respectively. As the persulfate and activators
330 were injected in the anode, the degradation of PCBs in soil was predominant on the section near
331 the anode, followed by the section near the cathode, while the degradation of PCBs in the central
332 part was minor.

333 In the control test without activation (Exp-01), the distribution of residual PCBs in soil increased
334 from the anode towards the cathode with the degradation of PCBs mainly concentrated on S1
335 section with a removal rate of 51.7%. In the other sections, the degradation of PCBs was
336 insignificant even with a high persulfate concentration (more than 100 g L^{-1}) in S2 until the end of
337 the test, and most of the PCBs were accumulated in the middle sections. In the location near the
338 cathode (S4 and S5), a relatively higher PCBs degradation efficiency was observed ($\approx 27\%$),
339 although the persulfate transported to these sections was limited. This can be probably attributed
340 to the alkaline hydrolysis function occurred in the cathode (Jeffers et al., 1989; Waisner et al.,
341 2008).

342 When zero-valent iron was added to activate persulfate (Exp-02), the removal of PCBs in soil was
343 not remarkably improved even though the transport distance and mass of persulfate was higher
344 than the control test. The residual PCBs in S1 to S3 section followed the same trend as Exp-01,
345 whereas, the removal rates of S4 (35%) and S5 (33%) were higher than that of the control test
346 (26%). This result was due to the lower amount of zero-valent iron added in the anolyte. The
347 molar ratio of persulfate and total iron we added is 5.88:1 and the optimum rate referenced is 1.5:1
348 (Lang et al., 2010), so, the mass of zero-valent iron added is not enough to break down persulfate
349 completely. When persulfate was delivered to S4 and S5 section, it could be activated by the high
350 pH near the cathode, which enhanced PCBs degradation in these sections.

351 In Exp-03, the distribution of residual PCBs in soil was uniform, with a removal rate of about 35%.
352 Although the mass of persulfate transported in soil was almost zero, as the result of the abundant
353 of citric acid chelated Fe^{2+} put into the oxidant solution, the activation products such as $\text{SO}_4^{\cdot-}$ or \cdot
354 OH radicals generated by persulfate decomposition were transported into soil by EOF, which
355 resulted in the degradation of PCBs in soil. The mass of $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ transported into the soil

356 could not be measured, but the extremely low pH distribution in this treatment confirmed that the
357 decomposition products had been transported into the soil column. Moreover, the drastic reaction
358 between activator and oxidant released much heat, which could also favored persulfate activation,
359 as well as the PCBs desorption from the soil.

360 The lowest PCBs degradation percentage was found in the treatment with an iron electrode to
361 activate persulfate (Exp-04). The activated persulfate transported in soil enhanced the degradation
362 of PCBs near the anode, and the degradation percentages of PCBs in S1, S2 and S3 were 44%, 33%
363 and 30%, respectively. However, the degradation of PCBs in S4 and S5 was low, only 21% and
364 25%. This distribution of residual PCBs in soil was consistent with the delivery of persulfate in
365 the soil. Besides, the low removal of PCBs was probably due to its low EOF, as the low EOF
366 inhibited the transportation of persulfate and its derivatives in the soil.

367 The treatment of alkaline activation yielded the highest PCBs degradation percentage (Exp-05). In
368 the section near the anode (S1), the removal reached as high as 53% with about 40% degradation
369 in the other sections. The relatively high PCBs degradation was based on the long transport
370 distance and high transfer mass of persulfate as well as the high pH. Also, during the alkaline
371 activation process, $\bullet\text{OH}$ was predominant while its oxidizing ability is more powerful than that of
372 $\text{SO}_4^{\bullet-}$. Meanwhile, on the condition of pH above 12.0, alkaline hydrolysis also plays an important
373 role in PCBs degradation.

374 When peroxide was used to activate persulfate (Exp-06), the distribution of residual PCBs in soil
375 increased first and decreased subsequently. The degradation of PCBs in soil was mainly focused
376 on the section near the anode (about 40%) and cathode (about 32%), and most of PCBs were
377 accumulated in the central part of the soil column (28%). Compared to the treatment without
378 activation, peroxide activation facilitated the degradation of PCBs in soil. This result indicated
379 that the radicals resulting from peroxide activating persulfate entered into the soil and led to the
380 degradation of PCBs. The low pH in S1 to S4 also confirms that the decomposition products
381 migrated from the anode towards the cathode, and also that lower pH is conducive to the
382 degradation of PCBs by persulfate (House, 1962; Liang et al., 2007; Fang et al., 2013).

383 In conclusion, the impact of different persulfate activation methods on the degradation of PCBs is
384 different, and PCBs degradation was related to persulfate transfer distance, transfer mass, and the
385 soil pH. The relationship between the degradation effect and weight factors with different

386 activation methods is summarized in Table 4. In essence, all these factors were based on the ratio
387 of oxidant and activator, which is controlled by the injection quantity and rate. In general,
388 persulfate activation did not enhance the degradation of PCBs significantly, and the highest
389 enhancement only increased by 10% compared with that without activation. The activation
390 parameters should be optimized in future studies. Although alkaline activation (pH control in the
391 anode) reached the highest enhancement, the high pH would damage the soil properties in field
392 remediation. Additionally, iron electrode activation has a good applicability for in-situ
393 remediation, but further research is needed on how to regulate its activation effect.

394 **4. Conclusions**

395 In this study, a series of experiments were undertaken to assess the transport behavior of activated
396 persulfate under electric field and the efficiency of remediation of PCBs polluted soil. The impact
397 of different activation methods, using zero-valent iron, citric acid chelated Fe^{2+} , iron electrode,
398 alkaline pH and peroxide on the persulfate migration was evaluated as well as the degradation of
399 PCBs in soil.

400 Electroosmotic flow was the main transfer mechanism for persulfate and its derivatives, the EOF
401 flowed from anode towards cathode (direct EOF) and followed the order of alkaline activation >
402 zero-valent iron activation > without activation > citric acid chelated Fe^{2+} activation > peroxide
403 activation > iron electrode activation.

404 Zero-valent iron, alkaline, and peroxide activation improved the transport of persulfate at the early
405 stage of EK test, and the longest delivery distance reached S4 or S5 section on 6th day. The
406 transfer mass of persulfate in soil followed the order of alkaline activation > zero-valent
407 activation > without activation > peroxide activation > iron electrode activation > citric acid
408 chelated Fe^{2+} activation.

409 The addition of an activator accelerated the decomposition of persulfate, and the persulfate
410 transported in soil decreased with its degradation. The decomposition of persulfate will decrease
411 the soil pH, and lower pH was beneficial for the degradation of PCBs.

412 Besides iron electrode activation, all the other activation methods enhanced the removal of PCBs
413 in soil in different extents. The removal efficiency of PCBs in soil followed the order of alkaline
414 activation > peroxide activation > citric acid chelated Fe^{2+} activation > zero-valent iron activation >

415 without activation > iron electrode activation, and the values were 40.5%, 35.6%, 34.1%, 32.4%,
416 30.8% and 30.5%, respectively. The activation effect was highly dependent on the ratio of oxidant
417 and activator.

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Table and figure captions

Table 1 Physical and chemical characteristics of the soils used.

Table 2 Experimental design of the electrokinetic tests.

Table 3 The distribution of residual PCBs in soil (C/C_0).

Table 4 Relationship between degradation effect and weight factors in different treatments.

Figure 1 Change of (a) electric current and (b) electroosmotic flow at different time in various treatments.

Figure 2 Soil (a) pH and (b) electrical conductivity.

Figure 3 Variation of $\text{Na}_2\text{S}_2\text{O}_8$ concentration and pH in soil solution at different time.

Tables

Table 1 Physical and chemical characteristics of the soils used.

Parameters	Clean soil	PCBs polluted soil	Mixed soil
Location	a farmland, Nanjing	a landfill, Taizhou,	–
Sand (%)	12.0	4.2	7.7
Silt (%)	66.9	83.2	50.1
Clay (%)	21.1	12.6	42.2
pH	5.7	6.3	5.74
OM content (g kg ⁻¹)	7.08	11.0	7.30
CEC (cmol kg ⁻¹)	20.4	20.1	20.1
Total metal concentration (mg kg ⁻¹)			
Ca	9848	2259	9760
Mg	7330	3430	7238
Cu	47	89	46
Zn	159	183	160
Fe	33130	86950	34570
Mn	701	867	724

Table 2 The experimental design of the electrokinetic tests.

Treatments	Anolyte	Catholyte	Treatment (in the anolyte)	Voltage /V cm ⁻¹	Duration time /d	PCBs concentration /mg kg ⁻¹
Exp-01	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	–	1	15	46
Exp-02	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	Add 1g Fe on 3rd,6th,9th,12th day (Mol Na ₂ S ₂ O ₈ :Fe=5.88:1)	1	15	46
Exp-03	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	Citric acid/Fe ²⁺ (Mol Na ₂ S ₂ O ₈ :Citric acid:Fe ²⁺ =20:5:5)	1	14	46
Exp-04	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	Iron anode electrode (Mol Na ₂ S ₂ O ₈ :Fe≈1:1)	1	15	46
Exp-05	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	Control anode pH at 12.0	1	15	46
Exp-06	200 g L ⁻¹ Na ₂ S ₂ O ₈	0.01M NaNO ₃	Add 6 mL of 30% H ₂ O ₂ at anode per day (Mol H ₂ O ₂ :Na ₂ S ₂ O ₈ =1:1)	1	15	46

Table 3 The distribution of residual PCBs in soil (C/C_0).

Soil section	Exp-01	Exp-02	Exp-03	Exp-04	Exp-05	Exp-06
S1	46.3±7.0	50.3±6.9	59.0±3.9	55.9±1.6	47.2±0.5	57.8±1.5
S2	72.3±8.3	72.2±6.9	69.5±3.0	67.1±8.8	59.0±2.5	59.8±0.9
S3	80.2±3.6	83.5±4.9	68.5±1.8	70.2±5.8	63.0±1.3	72.1±2.4
S4	73.7±4.7	65.4±6.0	63.9±1.4	79.4±7.0	61.6±3.4	68.6±5.5
S5	73.6±2.7	66.7±2.0	68.8±7.5	74.7±8.0	66.7±5.3	63.9±2.9
Removal rate (%)	30.8	32.4	34.1	30.5	40.5	35.6

Table 4 Relationship between degradation effect and weight factors in different treatments.

Treatments	Removal rate (%)	Transport distance	Transport mass	pH
Without activation	30.8	○	○	○
zero-valent activation	32.4	√	√	○
citric acid chelated Fe ²⁺ activation	34.1	×	×	√
iron electrode activation	30.5	×	×	×
alkaline activation	40.5	√	√	√
peroxide activation	35.6	√	○	√

Notes: ○ average, √ above average, × below average.

Figures

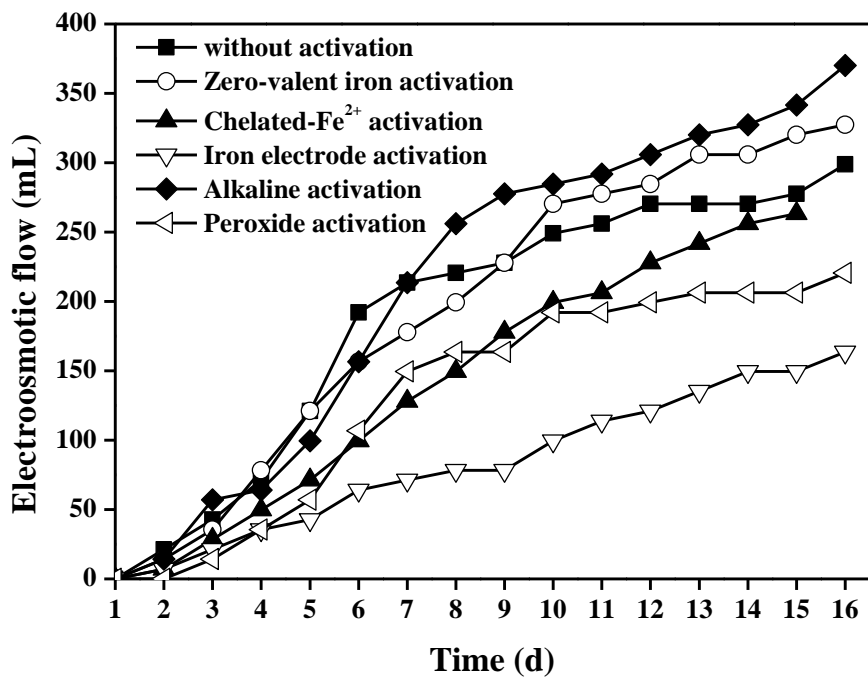
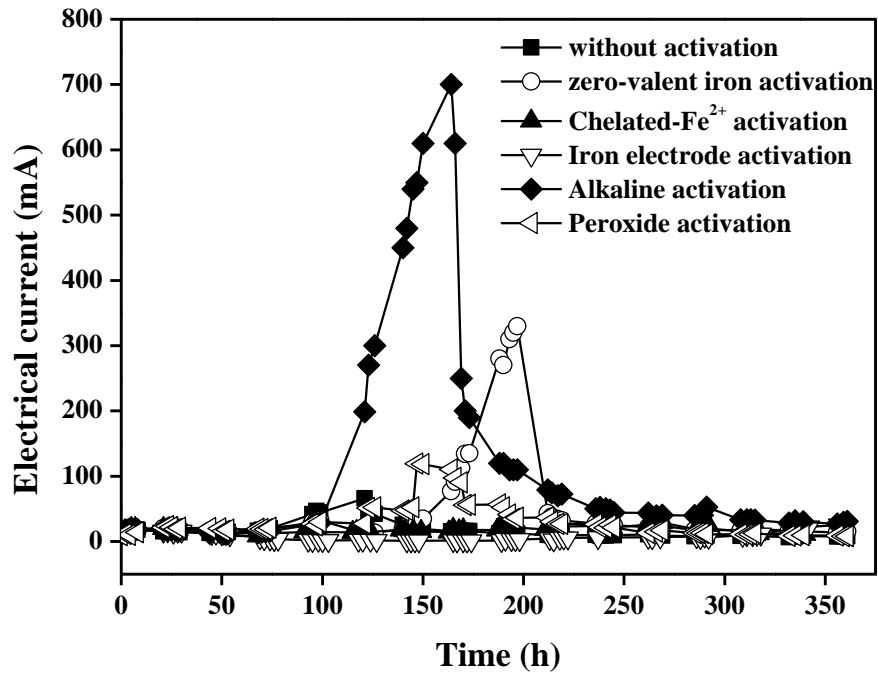


Figure 1 Variation of (a) electric current and (b) electroosmotic flow at different time in various treatments.

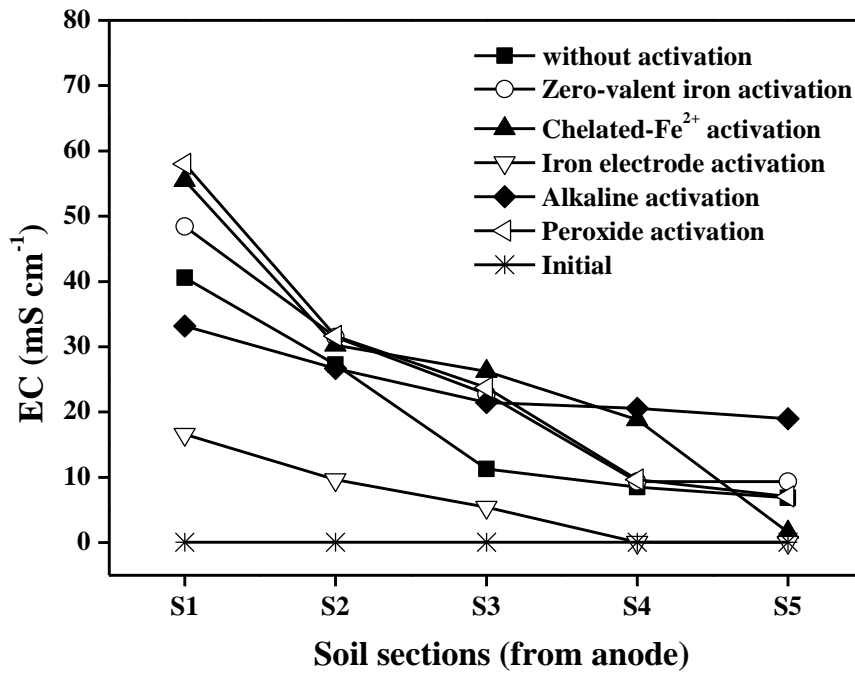
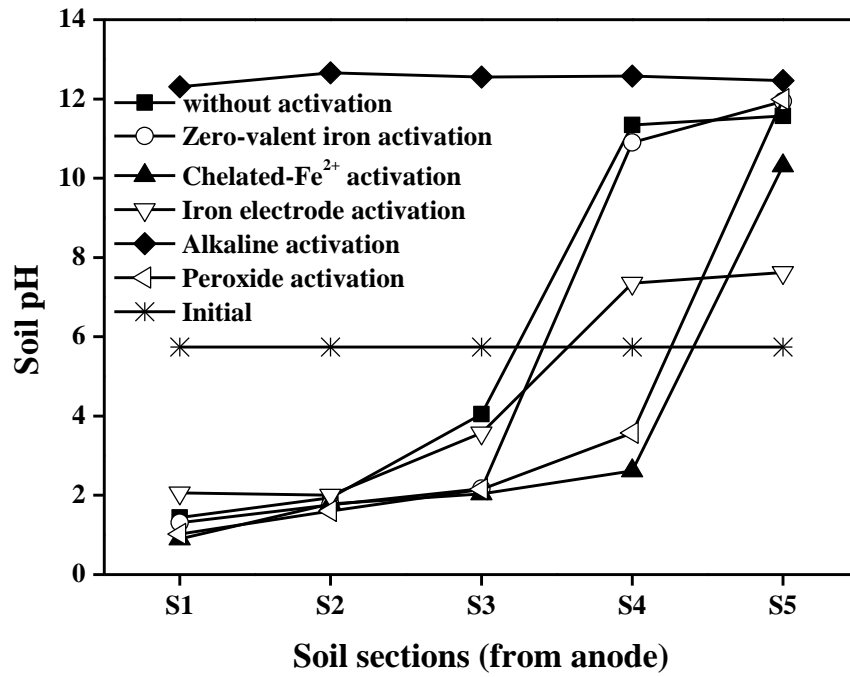
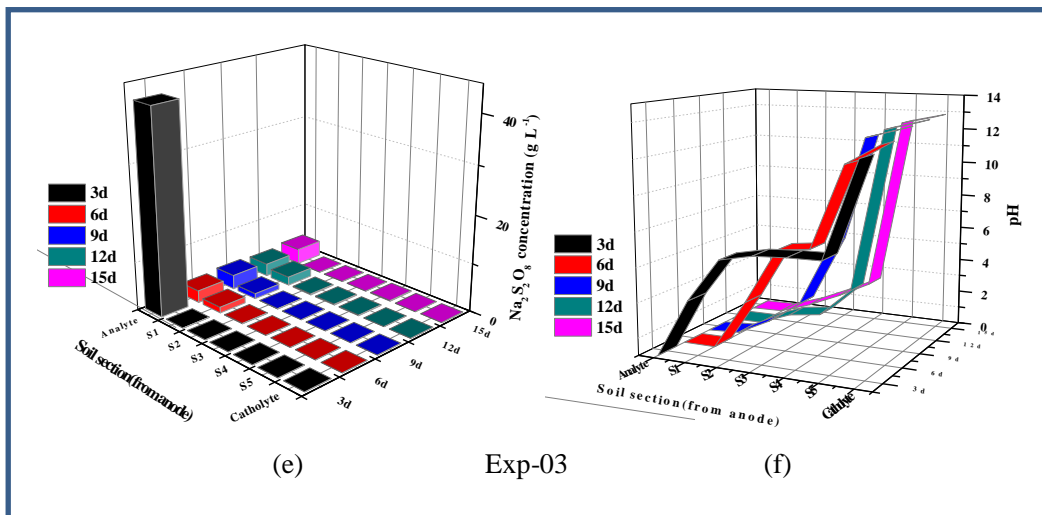
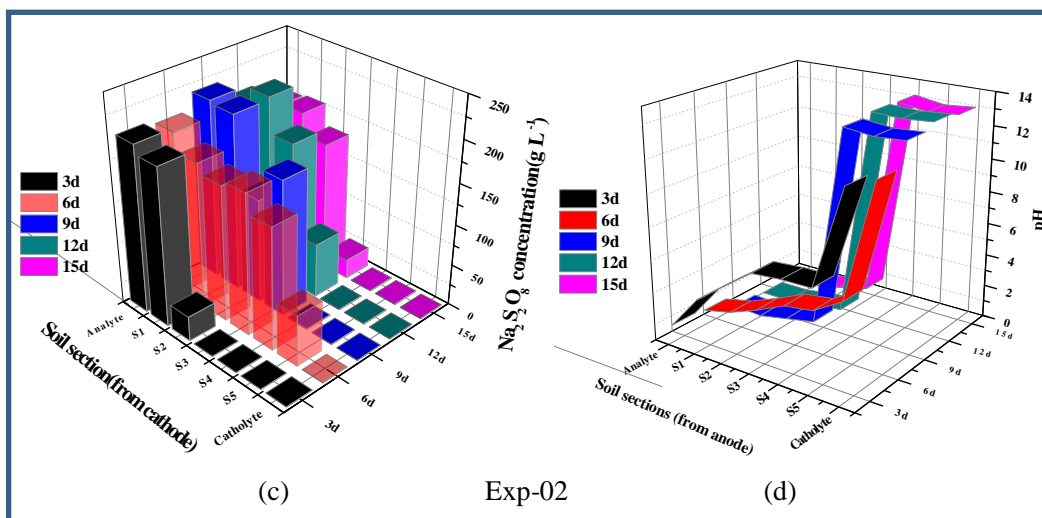
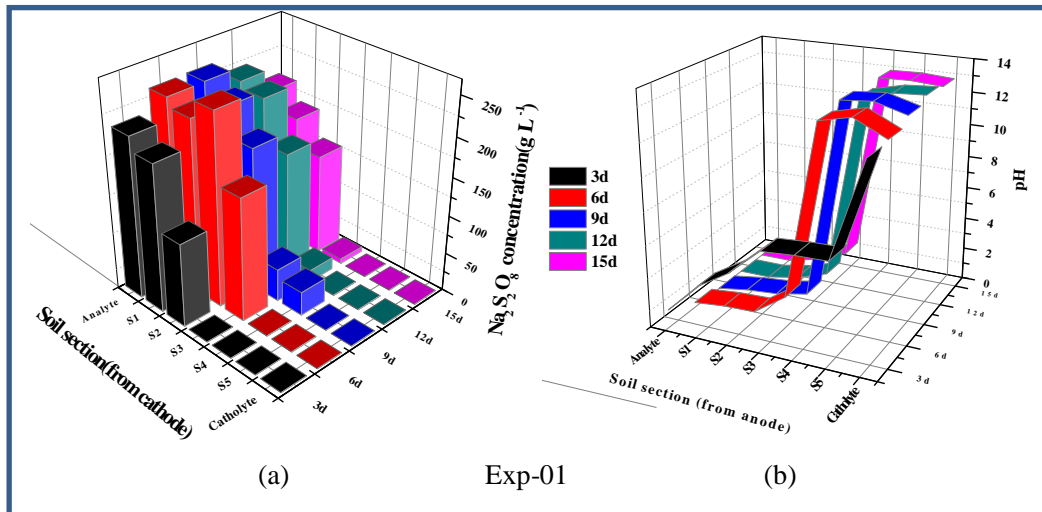


Figure 2 Soil (a) pH and (b) electrical conductivity.



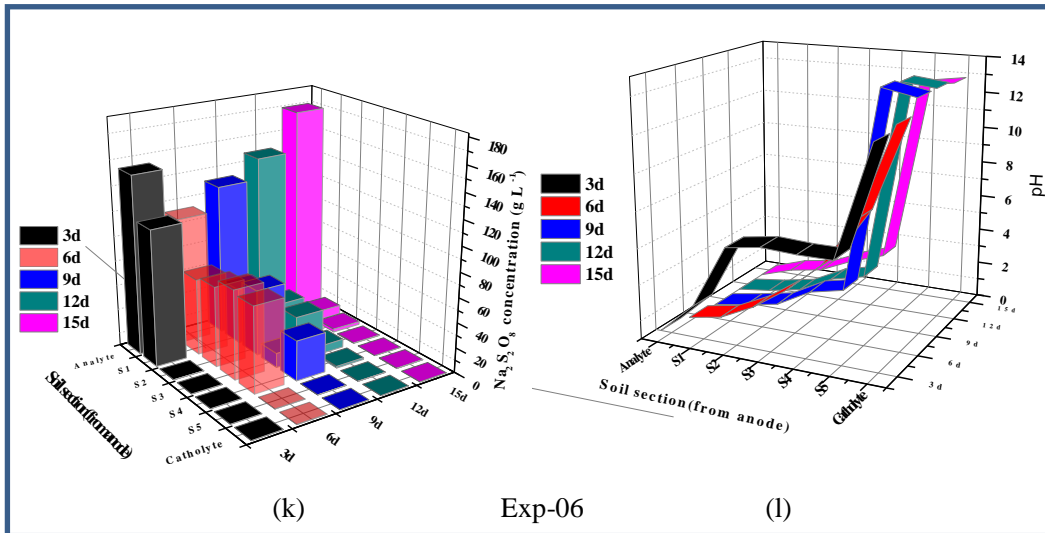
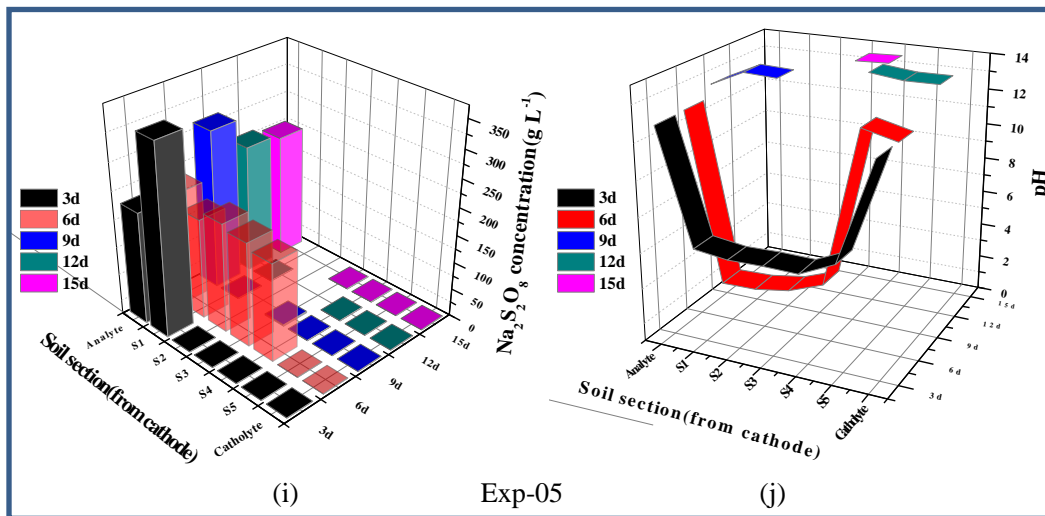
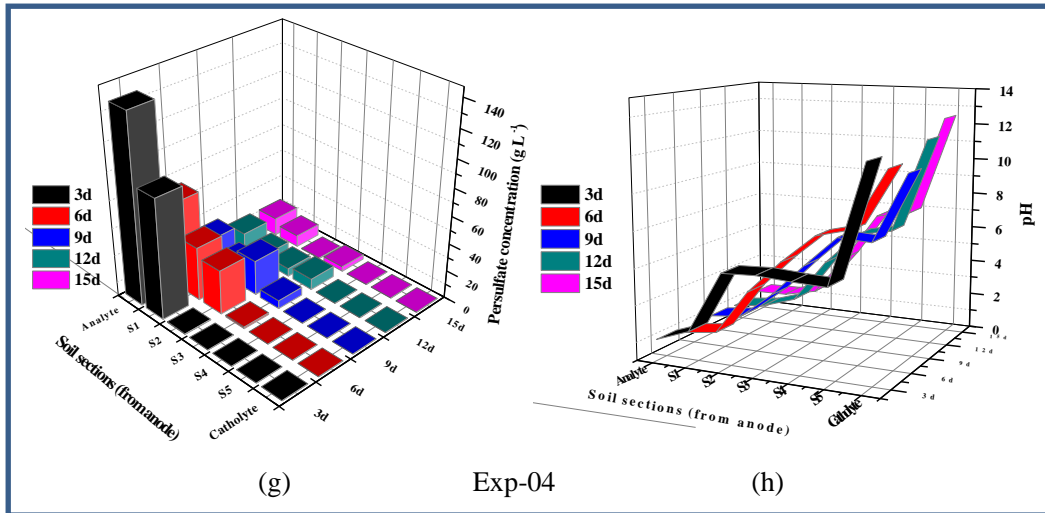


Figure 3 Variation of Na₂S₂O₈ concentration and pH in soil solution at different time.