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1 **Phenanthrene degradation using Fe(III)-EDDS photoactivation**  
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3 **treatment**

4  
5 **Yufang Tao<sup>a,b</sup>, Marcello Brigante<sup>a</sup>, Hui Zhang<sup>b\*</sup>, Gilles Mailhot<sup>a\*</sup>**

6  
7 <sup>a</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de  
8 Clermont-Ferrand, 63000 Clermont–Ferrand, France

9 <sup>b</sup> Department of Environmental Engineering, School of Resources and Environmental Science,  
10 Wuhan University, 430079, P. R. China

11 \*Corresponding author:

12 Pr. Gilles Mailhot :

13 Present/permanent address: Institut de Chimie de Clermont-Ferrand, Université Clermont  
14 Auvergne, 24 avenue Blaise Pascal, 63178 Aubière Cedex, France.

15 Tel : 00 33 (0)6 61 63 99 20

16 E-mail: [gilles.mailhot@uca.fr](mailto:gilles.mailhot@uca.fr)

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23  
24 <sup>a</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de  
25 Clermont-Ferrand, 63000 Clermont–Ferrand, France

26 <sup>b</sup> Department of Environmental Engineering, School of Resources and Environmental Science,  
27 Wuhan University, 430079, P. R. China

28 **Abstract**

29 In this work, for the first time, the nonionic surfactant polyoxyethylene-(20)-sorbitan  
30 monooleate (Tween 80, C<sub>64</sub>H<sub>124</sub>O<sub>26</sub>) aided soil washing effluent was treated by enhanced  
31 activation of persulfate (PS) using Fe(III)-EDDS (EDDS: ethylenediamine-N, N-disuccinic  
32 acid) complexes under simulated solar light irradiation. The performance of this system was  
33 followed via the production and reactivity of radical species (SO<sub>4</sub><sup>•-</sup>, HO<sup>•</sup>, Cl<sub>2</sub><sup>•-</sup>) and  
34 degradation of phenanthrene (PHE) used as a model pollutant in soils. Different  
35 physico-chemical parameters such as the concentration of reactive species and pH were  
36 investigated through the PHE degradation efficiency. The second-order rate constants of the  
37 reactions for generated radicals with PHE and Tween 80 in solution were identified through  
38 competitive reaction experiments under steady-state conditions and application of nanosecond  
39 laser flash photolysis (LFP) as well. A kinetic approach was applied to assess the selectivity

40 and reactivity of photo-generated radicals in aqueous medium in order to explain the observed  
41 degradation trends. This work proposes an innovative technology of management of soil  
42 washing solutions using Fe(III)-EDDS complexes and solar light for the activation of  
43 persulfate.

44 **Keywords:** Advanced oxidation processes, sulfate radical, iron complexes, soil depollution,  
45 photochemistry.

## 46 **1. Introduction**

47 Soil contamination is known to be a severe and ubiquitous problem worldwide. Specially, soil  
48 pollution caused by hydrophobic organic compounds (HOCs) have attracted more attention  
49 and been taken seriously by governments and enterprises due to the characters of high-toxicity  
50 and long-refractory of this kind of pollutant. Polycyclic aromatic hydrocarbons (PAHs) are  
51 typical representatives of HOCs, which are notable and distinguished by their high health  
52 risks of mutability, carcinogenicity and teratogenicity through long-term bioaccumulation in  
53 the environment (Yap et al., 2011; Li et al., 2012; Trelu et al., 2016). The characteristics of  
54 low solubility in water and poor mobility in soil of PAHs impede the elimination of this type  
55 of compound from soils. Comprehensive researches of *in-situ* technologies such as  
56 bioremediation (Tiehm et al., 1997), phytoremediation (Huang et al., 2004) and electrokinetic  
57 remediation (Reddy et al., 2006) technologies are available in the literature (Gan et al., 2009a).  
58 In Ye's (Ye et al., 1995) study of biodegradation of PAHs by *Sphingomonas paucimobilis*,  
59 after 16 h of incubation of pyrene, benz[a]anthracene (B[a]A), benzo[a]pyrene (B[a]P),  
60 benzo[b]fluoranthene (B[b]F) for each with 10mg/L, the degradation percentage was  $1.3 \pm$   
61  $0.4$ ,  $1.8 \pm 0.1$ ,  $9.6 \pm 1$ ,  $5.0 \pm 0.6$ , respectively. Lee's group (Lee et al., 2008) compared four  
62 native Korean plant species for phytoremediation of phenanthrene (PHE) and pyrene, the  
63 maximum removal efficiency of phenanthrene was >99%, for pyrene was 94% in planted soil

64 after 80 days of experiments. Maturi's group (Maturi and Reddy, 2006) investigated modified  
65 cyclodextrin enhanced electrokinetic remediation of PHE and Nickel contaminated soil, the  
66 optimal 10% removal efficiency of PHE was achieved with 1% cyclodextrin addition after  
67 around 166 days elapsed duration. However, all these in-situ techniques present at least one  
68 non-negligible disadvantages such as time-consuming treatment requirements, low  
69 remediation efficiency and high economic input. In this case, *ex-situ* techniques represented  
70 by surfactant aided soil washing processes appeal to more and more researchers. During the  
71 past several decades, *ex-situ* soil washing (SW) and *in-situ* soil flushing (SF) techniques,  
72 improved by application of surfactants as the extracting agents, have exhibited high  
73 performances for PAH elimination from soils (Gan et al., 2009b; Mousset et al., 2014a).  
74 Nonionic surfactant Polyoxyethylene (20) sorbitan monooleate (Tween 80), Dodecyl  
75 polyglycol ether(Brij 35), Polyoxyethylene (10) isooctylphenyl ether (Triton X-100),  
76 anionic surfactant sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulphonate  
77 (SDBS) are commonly used in the literature of surfactant enhanced soil remediation (Mao et  
78 al., 2015). Among these surfactants, the application of Tween 80 (TW80) was more extensive  
79 and prominent due to its lower toxicity and higher solubility capacity (Cheng et al., 2008).  
80 Except for the common application for PAHs, TW80 was supposed to be an excellent  
81 alternative for numerous hydrophobic contaminants such as PAHs anthracene, fluoranthene,  
82 pyrene and phenanthrene (Alcántara et al., 2008; Peng et al., 2011), Petroleum Hydrocarbons  
83 (Huguenot et al., 2015), p-cresol (Rosas et al., 2011), Decabromodiphenyl ether (Zhou et al.,  
84 2007), 4,4'-dichlorobiphenyl (Chu and Kwan, 2003), p-Nitrochlorobenzene (Guo et al., 2009)  
85 and pesticides like Diazinon (Hernández-Soriano et al., 2012), DDT (Zheng et al., 2012). The  
86 application of TW80 in the remediation of PAHs contaminated soil is especially ubiquitous  
87 owing to its better solubilization characteristic than other surfactants. It was reported that  
88 TW80 was efficient for solubilizing a plenty of PAHs such as Pyrene, PHE, Fluorene,

89 Acenaphthene, Naphthalene and TW80 exhibited superior capacity than other nonionic  
90 surfactants such as Tween 20, Triton X-100, Triton X-305, Triton X-405 (Zhu and Zhou,  
91 2008). In another work, TW80 was suggested as the highest solubilization capacity than  
92 Brij35, TX100 and SDS for PHE on the basis of molar solubilization ratios (MSR) (Zhao et  
93 al., 2005). Nevertheless, as a consequence of these soil washing/flushing processes, a  
94 complicated mixture of waste liquids containing great loads of extractants, PAHs and other  
95 accompanying organics is generated and should be further treated to reduce the potential  
96 environment concern of discharge the effluent into environment. Owing to the complexity of  
97 the mixed components of SW solutions, the management and disposal are a tremendous  
98 challenge for environmental engineering (Rosas et al., 2013; Trellu et al., 2016). Soil washing  
99 effluent could be treated with biological method, adsorption techniques as well as Advanced  
100 oxidation process (AOPs). However, biological treatments bear the drawbacks of long  
101 duration and low efficiency (Gharibzadeh et al., 2016), while adsorption technologies possess  
102 potential risks since contaminants could not be completely decomposed (Ahn et al., 2008;  
103 Zhou et al., 2013; Li et al., 2014). In this case, AOPs including electrochemical oxidation  
104 (Gómez et al., 2010; Mousset et al., 2014c, b; Trellu et al., 2017a), ozone oxidation (Liu,  
105 2018), photocatalytic oxidation (Zhang et al., 2011; Bai et al., 2019) have been developed to  
106 the most popular and common applied technology for PAHs and various surfactant involved  
107 soil washing effluent treatments. As reviewed in Table S1, AOPs based on radical oxidation  
108 mechanism could effectively decompose PAHs into various products during the processes of  
109 soil washing effluent treatment with PAHs dosage from  $1\text{ mg L}^{-1}$  to around  $200\text{ mg L}^{-1}$  and  
110 optimal surfactants ranging from  $1\text{ g L}^{-1}$  to  $10\text{ g L}^{-1}$ . Among multiple AOPs, Sulfate radicals  
111 based advanced oxidation processes (SR-AOPs) have been widely applied as effective and  
112 practicable techniques for remediation of contaminated waters and soils (Yen et al., 2011;  
113 Waclawek et al., 2017). Persulfate ( $\text{S}_2\text{O}_8^{2-}$ , PS) is an ideal alternative oxidant ( $E_0 = 2.01\text{ V}$ ),

114 which can be activated to produce stronger sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) ( $E_0 = 2.6 \text{ V}$ ) by various  
115 chemical or physical methods (Usman et al., 2012). In addition to its strong oxidation capacity,  
116 sulfate radical has revealed several advantages over other oxidants.  $\text{SO}_4^{\bullet-}$  is more stable than  
117 hydroxyl radical ( $\text{HO}^{\bullet}$ ) and exhibits a longer half-life time as well as a wider pH range for the  
118 application (Anipsitakis and Dionysiou, 2004).

119 Iron, one of the chemical activators of PS, is the most abundant transition metal present in the  
120 earth's crust and exists in a variety of forms in water such as soluble, colloidal and particulate  
121 forms. In natural water, insoluble iron-containing oxides account for a large proportion (Faust  
122 and Zepp, 1993), while dissolved iron is only found in a small percentage and most of them  
123 exists in the form of complex with organic ligands (Zhou et al., 2004). Polycarboxylates and  
124 (amino-)polycarboxylates like citrate, malonate, oxalate, EDTA, etc. can react with ferric ions  
125 ( $\text{Fe}^{3+}$ ) to form stable and strong complexes and improve its solubility and stability in natural  
126 water (Chen et al., 2007). Moreover, such (amino-)polycarboxylate complexes are reported to  
127 have strong and fast photochemical reactivity under sunlight irradiation giving rise to  
128 oxidative species (Zhang et al., 2009). Those iron complexes such as Fe(III)-EDTA,  
129 Fe(III)-EDDS, Fe(III)-oxalate or Fe(III)-citrate have exhibited high efficiency as  
130 photo-catalysts and as persulfate and hydrogen peroxide activators for the elimination of a  
131 variety of contaminants (Manenti et al., 2015; Miralles-Cuevas et al., 2018; Soriano-Molina et  
132 al., 2019). Ethylenediamine-N,N-disuccinic acid (EDDS) is a structural isomer of EDTA, and  
133 [S,S]-EDDS, [R,R]-EDDS and [R,S/S,R]-EDDS are three stereo isomers of EDDS. Among  
134 those isomers, [S,S]-EDDS is recognized and employed as a environmentally safe and  
135 friendly substitution for EDTA for environmental restoration since it is easier biodegradable  
136 than EDTA (Nagaraju et al., 2007).

137 In this work, Fe(III)-EDDS complex was used to improve the PS photo-activation for the  
138 phenanthrene (PHE) degradation in soil washing solution. Main physico-chemical parameters

139 such as concentration of chemical species and pH were investigated using simulated solar  
140 radiation to generate the sulfate radical from PS. This work provides a novel proposal of  
141 application of Fe(III)-EDDS for soil washing effluent treatments.

## 142 **2. Experimental Details**

### 143 **2.1 Chemicals**

144 Tween 80 (TW80), phenanthrene (PHE) and ferric perchlorate ( $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ ) were  
145 obtained from Sigma-Aldrich. Ethylenediamine-N,N-disuccinic acid trisodium salt solution  
146 (35% in water) was purchased from Fluka. All the other used reagents and chemicals were of  
147 analytical grade and all the solutions employed in this work were prepared with purified water  
148 from Millipore Ultra-Pure System (18.2 M $\Omega$  cm). The stock solutions of Fe(III)-EDDS were a  
149 mixture of appropriate amount of newly prepared aqueous solutions of ferric perchlorate and  
150 EDDS at a stoichiometry ratio of 1:1.

### 151 **2.2 Preparation of the synthetic SW solution**

152 TW80 is one of the suggested and most applied enhancing-solubility nonionic surfactants that  
153 increases the solubility of HOCs due to its notable features of lower soil sorption capacity and  
154 critical micellar concentration (CMC), low toxic property as well as higher solubilization  
155 ability and higher cost-effectiveness (Mulligan et al., 2001). It is known that above CMC, the  
156 surface tension of HOCs varies with a much smaller slope and the solubility of HOCs is  
157 strongly improved (Trellu et al., 2016). The CMC of TW80 is equal to 0.016 g L<sup>-1</sup>  
158 (López-Vizcaíno et al., 2012) which is much lower compared to other surfactants. Due to the  
159 above advantages, TW80 was chosen as the aiding compound and its solubilization capacity  
160 of PHE was investigated.

### 161 **2.3 Irradiation experiments and degradation kinetic**

162 50 mL of samples were irradiated in a jacketed cylindrical Pyrex reactor connected to water

163 cooling system and placed in a rectangular wood box to prevent the interference from the  
164 external light sources. Four tubular lamps (Sylvania, F15W/350BL), used as irradiation  
165 sources, were fixed on the top of the wood box. The irradiation energy was determined  
166 employing an optical fiber with a charge coupled device (CCD) spectrophotometer (Ocean  
167 Optics USD 2000 + UV-vis) previously calibrated with a DH-2000-CAL reference lamp. The  
168 energy reaching the reactor determined between 300 and 400 nm ( $1390 \mu\text{W cm}^{-2}$ ) was very  
169 closed to the typical solar emission in the same wavelength range (Bianco et al., 2016).

170 In Figure 1 emission spectrum of light sources and UV-vis absorption spectra of chemical  
171 species (carried out with a Cary 300 UV-visible spectrophotometer) were presented. An  
172 overlap between the emission spectrum of the lamps and the absorption spectrum  
173 Fe(III)-EDDS complex was highlighted. PHE absorbed in the ultraviolet region with two  
174 maxima at 252 nm and 295 nm. The main absorption region was located at  $\lambda < 250$  nm for PS  
175 and  $\lambda < 300$  nm for PHE in TW80 solution. Fe(III)-EDDS clearly exhibited a broad but  
176 gradual decrease absorption at the region of wavelengths up to approximately 400 nm and the  
177 overlapping absorption with the lamp emission spectrum from 300 nm and 400 nm as well.

178 All experiments were carried out at  $293 \pm 2$  K and solutions were magnetically stirred with a  
179 magnetic bar to insure the homogenous mixture of the solution. At regular intervals, 0.5 mL of  
180 sample was withdrawn and analyzed by an UPLC-UV system (Alliance) equipped with a  
181 photodiode array detector. The eluent was a mixture of water and acetonitrile (30/70, v/v)  
182 with isocratic mode in a flow rate of  $1 \text{ mL min}^{-1}$ . The column was a Nucleodur 100-5 C18 of  
183  $150 \text{ mm} \times 4.6 \text{ mm}$  with particle size  $5 \mu\text{m}$ . The pseudo-first-order decay of PHE was  
184 determined using the following exponential equation:

185 
$$\frac{[PHE]}{[PHE]_0} = \exp(-k't)$$

186 Where  $[PHE]_0$  and  $[PHE]$  are the initial and residual concentrations of PHE at time  $t$ ,  $k'$  is the  
187 pseudo-first-order apparent rate constant ( $s^{-1}$ ). The initial conversion rate of PHE ( $R_{PHE}$ ) was  
188 calculated as  $R_{PHE} (M s^{-1}) = k' \times [PHE]_0$ . The retention time and the analysis of PHE were not  
189 modified by the presence of TW80. The pHs of the solutions were adjusted with 0.1 M of  
190  $HClO_4$  or NaOH solutions and no significant pH variation was observed during irradiation.

## 191 **2.4 Laser flash photolysis**

192 The determination of the second order rate constants were carried out with the nanosecond  
193 laser flash photolysis (LFP) apparatus from Applied Photophysics (LKS60). A 266 nm  
194 excitation was used to generate radicals from solution and apparatus description as well as  
195 competition kinetic approaches have been reported elsewhere and a brief description is given  
196 in the supplementary materials section (Huang et al., 2018).

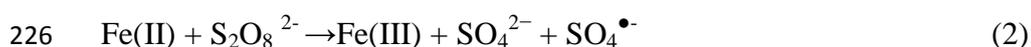
## 197 **3. Results and discussion**

### 198 **3.1 PHE degradation under various systems**

199 The solubility of PHE was tested using different concentration of TW80 in water. The results  
200 reported in Figure SM1 indicate that PHE solubility increased with the concentration of  
201 TW80 and a maximum of PHE solubility was reached around  $16 \text{ mg L}^{-1}$  (corresponding to a  
202 concentration of  $90 \text{ }\mu\text{M}$ ). This maximum of solubility of PHE was obtained from  $0.5 \text{ g L}^{-1}$  of  
203 TW80. This concentration of TW80 was then used to prepare PHE solution for all  
204 experiments.

205 The PHE degradation under simulated solar light at pH 3.5, using different mixture of  
206 Fe(III)–EDDS, Fe(III) and PS is reported in Figure 2. Control experiments showed that very

207 low degradation of PHE (less than 5%) occurred with the involvement of Fe(III)-EDDS  
208 complex and PS in the dark. Under irradiation, the direct photolysis (without PS and iron  
209 complexes) of PHE was negligible, less than 8% and addition of Fe(III)-EDDS (0.5 mM) not  
210 significantly changed the efficiency of PHE degradation after 150 min of irradiation. As a  
211 contrary, about 30% removal of PHE was being achieved in the presence of PS (5 mM) with  
212 UVA light due to the photogeneration of sulfate radicals that contributed to PHE degradation.  
213 Under UVA irradiation with addition of Fe(III) to PS solution, almost 35% of PHE removal  
214 was obtained under irradiation. So, although Fe(III) can be photo-reduced to Fe(II) (Brand et  
215 al., 1998) which is able to activate PS leading to the generation of sulfate radicals (Anipsitakis  
216 and Dionysiou, 2004; Liang et al., 2004), only 5% of PHE degradation was promoted  
217 compared to PS/UV system. In the system with replacement of Fe(III) by Fe(III)-EDDS (0.5  
218 mM) to PS solution, the performance was much more pronounced and PHE removal was  
219 remarkably strengthened under irradiation, especially in the first 30 minutes. This difference  
220 can be explained by the lower photoreactivity of Fe(III) aquacomplexes in comparison with  
221 Fe(III)-EDDS at pH around 3.5 (Catastini et al., 2004; Huang, 2012) since Fe(II) formation  
222 from Fe(III) aquacomplexes is lower than from Fe(III)-EDDS at  $\lambda > 300$  nm. Therefore, in the  
223 presence of PS, sulfate radical formation is more important with Fe(III)-EDDS (reactions 1  
224 and 2):



228 Under sun-simulated irradiation in the presence of Fe(III)-EDDS, PHE kinetic exhibited two

229 different decay steps (Figure 2). In the first 30 mins of irradiation, Fe(III)-EDDS was almost  
230 completely degraded at pH 3.5 (Figure 3) to produce Fe(II) which represented the  
231 rate-limiting parameter for  $\text{SO}_4^{\bullet-}$  formation. In the second step, after complete decomposition  
232 of Fe(III)-EDDS, iron remained in the form of Fe(III) aquacomplexes, and under the influence  
233 of UVA light, hydroxyl radical and Fe(II) could be generated as well (reaction 3) (Mailhot et  
234 al., 2002; Krýsová et al., 2003). In the presence of PS, Fe(II) led to Fe(III) again (reaction 2)  
235 and we were in the presence of the (photo)chemical cycle involving Fe(III) and Fe(II). In this  
236 system, the degradation of PHE was mainly attributed to the formation of  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$   
237 through analogous reactions obtained with Fe(III) aquacomplexes in solution and the  
238 subsequent cycle of Fe(III)/Fe(II). In fact, the degradation kinetic after 30 minutes followed  
239 the same profile compared with those obtained where PS was mixed with Fe(III)  
240 aquacomplexes.

241 Same experiments conducted at pH 7.0 (Figure SM2) indicated that an enhancement of PHE  
242 degradation was still acquired with Fe(III)-EDDS, suggesting that the iron complex is  
243 photoactive also at higher pH (Wu et al., 2014). As a contrary, a strong inhibition of PHE  
244 degradation occurred with the dosing of Fe(III) aquacomplexes and PS. This effect could be  
245 ascribed to the precipitation of Fe(III) at  $\text{pH} > 4.0$ , resulting in absorption of light by iron  
246 particles and a potential screening effect for the photolysis of PS and also a very low  
247 photoreactivity of precipitated iron species.

248 What should be noted is on the contrary of many studies involving iron species, in our system  
249 UV/PS/Fe(III)-EDDS no significant effect of pH in the range 3.0 to 8.5 was obtained (Figure  
250 SM3). This observation was quite surprising, if we compare with former studies (Wu et al.,

251 2014; Wu et al., 2015) but could be due to the presence of TW80 which modified the  
252 reactivity of radical species (see following results).

### 253 **3.2 Effect of Fe(III)-EDDS and PS concentrations**

254 The effects of persulfate (PS) and Fe(III)-EDDS concentrations were investigated on the PHE  
255 degradation efficiency. PHE degradation involving different concentrations of Fe(III)-EDDS  
256 with 5 mM PS are reported in Figure 3A. An enhancement of PHE degradation, after 30 min  
257 of irradiation, more than 3 times was achieved with the Fe(III)-EDDS concentration increased  
258 from 0 to 0.5 mM (Figure 3B). However, the degradation efficiency of PHE decreased with  
259 the further increase of iron complex concentration. In fact, a scavenging effect of  
260 Fe(III)-EDDS and Fe(II) toward  $\text{SO}_4^{\bullet-}$  was expected at higher concentrations (Peng et al.,  
261 2017; Yu et al., 2018). Considering that a second order rate constant of  $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  has  
262 been determined for the reaction between sulfate radical and Fe(II) (E. et al., 1966), it was  
263 possible to argue that scavenging effect of ferrous ions, that were more stable in solution at  
264 pH 3.5, became significant at higher dosage of Fe(III)-EDDS. The maximum degradation of  
265 PHE (33%) after 30 mins was reached using 0.5 mM Fe(III)-EDDS, while after 150 minutes  
266 the highest degradation efficiency (55%) was obtained with 0.25 mM of Fe(III)-EDDS  
267 (Fig.3B). This shift of the maximum efficiency after 30 min was attributed to the higher load  
268 of Fe(II) and EDDS at higher concentration of Fe(III)-EDDS and so stronger scavenging  
269 effect of sulfate radicals.

270 To further explore the degradation performance of PHE in the system PS/Fe(III)-EDDS, the  
271 effect of persulfate concentration was investigated. As shown in Figure 4, PHE degradation  
272 efficiency was strongly promoted by increasing PS loading from 0 to 30 mM both for the  
273 photolysis of PS alone in solution and in the presence of Fe(III)-EDDS. The influence of  
274 Fe(III)-EDDS was much pronounced at higher concentration of persulfate. In the presence of  
275 Fe(III)-EDDS and after 150 min of irradiation, the enhancement of PHE degradation with 2

276 mM of PS was less than 2% while with 5 mM of PS the enhancement was around 18% and  
277 more than 50% with 15 and 30 mM of PS.

278 These results suggested that Fe(III)-EDDS had stronger impact at higher concentration of PS  
279 showing that the generation of sulfate radical through reaction between PS and Fe(II) was the  
280 main contribution of the efficiency of the system.

### 281 **3.3. Effect of Fe(III)/EDDS ratio**

282 According to previously reported works; the ratio of Fe(III) and EDDS concentrations  
283 represented a key parameter for the efficiency of the pollutants removal in water (Li et al.,  
284 2010). The concentration of PS was kept constant at 5 mM while various initial loads of Fe(III)  
285 were applied. As shown in Figure SM4, the initial degradation rate of PHE increased with a  
286 higher concentration of Fe(III). At 1 mM of Fe(III) the final elimination of PHE was higher  
287 than at 0.5 or 0.25 mM. This observation was resulted from the fact that at 1 mM of Fe(III),  
288 there were in solution 0.5 mM of Fe(III)-EDDS and 0.5 mM of Fe(III) aquacomplexes. The  
289 two iron species were photo-transformed into Fe(II) which could activate PS to generate  
290 sulfate radicals and moreover Fe(III) aquacomplexes generated photochemically also  
291 hydroxyl radicals. So in these conditions, a higher amount of sulfate and hydroxyl radicals  
292 were generated increasing the degradation of PHE. At concentrations of Fe(III) of 0.25 or 0.5  
293 mM, the final removals of PHE were very close with a little higher efficiency at 0.25 mM.  
294 During the first step of reactions, Fe(III) was reduced into Fe(II) and EDDS was oxidized.  
295 However if there were some residual EDDS remaining in solution, Fe(II) species were easily  
296 re-oxidized to Fe(III) and combined with EDDS to generate Fe(III)-EDDS complex (Li et al.,  
297 2010). As a consequence, the formation of  $\text{SO}_4^{\bullet-}$  and the degradation of PHE photoinduced by  
298 Fe(III)-EDDS complex could continue.

### 299 **3.4 Effect of TW80 concentration.**

300 To better explore the role of TW80 in this system, experiments with 0.5, 0.75 and 1 g L<sup>-1</sup> of

301 TW80 were carried out. The increase of the surfactant concentration from 0.5 to 1.0 g L<sup>-1</sup>  
302 inhibited significantly PHE degradation (Figure SM5A). In fact, when TW80 concentration  
303 increased to a factor of 1.5 and 2, the apparent rate constant of PHE degradation was reduced  
304 by a factor 1.8 and 3.3 (Figure SM5B). The negative effect acquired at higher TW80  
305 concentrations could be ascribed to the competition between TW80 and PHE for the reactivity  
306 with photogenerated sulfate radicals. In fact, as reported in Table 1, a second order rate  
307 constant between SO<sub>4</sub><sup>•-</sup> and TW80 ( $k_{TW80,SO_4^{\bullet-}}$ ) of  $4.6 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  has been determined  
308 (see SM for more details). At 0.5 g L<sup>-1</sup> of TW80 and considering the reactivity between SO<sub>4</sub><sup>•-</sup>  
309 and Fe(III)-EDDS and PS (Neta et al., 1988; Bianco et al., 2017) reported in literature, we can  
310 argue that about 33 % of photogenerated SO<sub>4</sub><sup>•-</sup> reacted with TW80 while only 7 % with PHE  
311 in solution. However, increasing the concentration of TW80 to 1 g L<sup>-1</sup>, the values were  
312 respectively 49 and 5 %. Moreover, in previously works it has been suggested that PHE was  
313 trapped into the micelle core of the surfactant, leading to a lower availability toward oxidizing  
314 radicals (Trellu et al., 2016; Trellu et al., 2017b). The significant sulfate radical selectivity  
315 between TW80 and PHE clearly demonstrated that the concentration of TW80 was the major  
316 parameter determining the efficiency of oxidative treatment adopted for PHE removal.

### 317 **3.5 Effect of chloride ions addition**

318 Inorganic species such as chloride ions are widely present in soil, resulting in the presence of  
319 such ions into the effluent of the procedure of soil washing. However, the existence of  
320 chloride ions (Cl<sup>-</sup>) in wastewater has been reported to affect the degradation efficiency of  
321 contaminants during the advanced oxidation processes and more particularly in PS oxidation  
322 treatments (Huang et al., 2018; Zhang et al., 2018). Different roles of chloride ions (Cl<sup>-</sup>) are

323 reported in the literature on the efficiency of  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$  based oxidations. Generally, it is  
324 reported that  $\text{Cl}^-$  acts as a radical scavenger that substantially inhibits the efficiency of UV  
325 based activation of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  (Tsuneda et al., 2002). However, some researchers find  
326 that reactive species produced from chloride ions, chlorine and dichlorine radicals ( $\text{Cl}^{\bullet}/\text{Cl}_2^{\bullet-}$ ),  
327 show high selectivity when react with organic pollutants and increase the efficiency of  
328 removal (Yang et al., 2014). Moreover, in other investigations it is suggested that  $\text{Cl}^-$  could  
329 react with  $\text{SO}_4^{\bullet-}$  to generate  $\text{HO}^{\bullet}$  in circumneutral and alkaline pH (Kiwi et al., 2000). In  
330 addition, the involvement of  $\text{Cl}^-$  is reported to modify the degradation mechanism using  
331  $\text{SO}_4^{\bullet-}$  based oxidation processes (Fang et al., 2012). As reported in Figure 5, complete  
332 degradation of PHE was achieved in 150 min of irradiation with 10 mM of  $\text{Cl}^-$ , while with 50  
333 mM or 100 mM of  $\text{Cl}^-$ , the same efficiency could be obtained within 60 min, demonstrating  
334 that the presence of higher dosages of  $\text{Cl}^-$  remarkably enhanced PHE degradation using  
335 Fe(III)-EDDS under UVA irradiation. This result was totally distinguished with other studies  
336 where  $\text{Cl}^-$  acted as an inhibitor or where its effect was negligible (Yang et al., 2016). To  
337 better understand the mechanism, for the first time, we determined the second order rate  
338 constants of  $\text{Cl}_2^{\bullet-}$  with PHE ( $k_{\text{PHE},\text{Cl}_2^{\bullet-}}$ ) and TW80 ( $k_{\text{TW80},\text{Cl}_2^{\bullet-}}$ ) respectively at  $4.6 \pm 0.3 \times 10^8$   
339  $\text{M}^{-1} \text{s}^{-1}$  and  $7.1 \pm 0.1 \times 10^6 \text{M}^{-1} \text{s}^{-1}$  (table 1). This results suggested that second order rate constant  
340 between PHE and dichlorine radical anion ( $k_{\text{PHE},\text{Cl}_2^{\bullet-}}$ ) was almost 65 times higher than the  
341 one between TW80 and the same radical ( $k_{\text{TW80},\text{Cl}_2^{\bullet-}}$ ). Therefore,  $\text{Cl}_2^{\bullet-}$  generated by  $\text{Cl}^-$   
342 exhibited much more selectivity to PHE in our soil washing solution. Moreover, the form of  
343 kinetics demonstrated that reactivity between  $\text{SO}_4^{\bullet-}$  and  $\text{Cl}^-$  played an important role to  
344 maintain PHE degradation, especially after 30 min of irradiation.

345 If we simplified our chemical system considering that generated radical species ( $\text{HO}^\bullet$ ,  $\text{SO}_4^{\bullet-}$ ,  
346  $\text{Cl}_2^{\bullet-}$ ) could react only with TW80 or PHE in solution, it was possible to explain, from a  
347 chemical kinetic point of view the impact of chloride on the system efficiency. In fact, in the  
348 absence of chloride ions mainly  $\text{SO}_4^{\bullet-}$  was generated in solution through reaction (2) and  
349 photolysis of persulfate ions. Considering the concentration of chemical species (i.e. TW80  
350 and PHE) and reactivity constant, about 82% of  $\text{SO}_4^{\bullet-}$  were trapped by TW80. However, if we  
351 considered that all  $\text{SO}_4^{\bullet-}$  was significantly converted into  $\text{Cl}_2^{\bullet-}$  (about 90% using 100 mM of  
352  $\text{Cl}^-$ ), in this case, the stronger reactivity between  $\text{Cl}_2^{\bullet-}$  and PHE compared to those determined  
353 for TW80 suggested that only 6% of  $\text{Cl}_2^{\bullet-}$  react with the surfactant and 94% with PHE.

### 354 **3.6 Radical species involvement**

355 In order to clearly clarify the significance of the different radicals formed during the process  
356 and their roles in this system and so further elucidate the oxidation mechanism of PHE  
357 degradation, free radicals scavenging tests were carried out. Methanol (MeOH) was employed  
358 as scavenger for both  $\text{HO}^\bullet$  ( $k_{\text{HO}^\bullet, \text{MeOH}} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $\text{SO}_4^{\bullet-}$  ( $k_{\text{SO}_4^{\bullet-}, \text{MeOH}} = 1.0 \times$   
359  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), and tert-Butanol (t-But) has higher selectivity for reactivity with  $\text{HO}^\bullet$   
360 ( $k_{\text{HO}^\bullet, \text{t-But}} = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) than with  $\text{SO}_4^{\bullet-}$  ( $k_{\text{SO}_4^{\bullet-}, \text{t-But}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ )  
361 (Buxton et al., 1988; Neta et al., 1988). With the addition of 50 mM of tert-Butanol, PHE  
362 oxidation decreased (Figure.6), which revealed that  $\text{HO}^\bullet$  was partly responsible for PHE  
363 oxidation. PHE removal was more attenuated with methanol addition indicating that  $\text{SO}_4^{\bullet-}$   
364 was also radical species involved in the transformation of PHE. The degradation efficiency of  
365 PHE reduced from 48% (without scavenger) to 40% and 23% with tert-Butanol and methanol,  
366 respectively.

367 With the different rate constants and concentrations of chemicals (TW80 and PHE) present in  
368 solution, we can deduce that, without scavengers about 18% of photogenerated  $\text{SO}_4^{\bullet-}$  and 13%  
369 of  $\text{HO}^{\bullet}$  reacted with PHE. However, i) In the presence of tert-Butanol (50 mM),  $\text{HO}^{\bullet}$  radicals  
370 were almost completely trapped, only 0.3% of  $\text{HO}^{\bullet}$  still reacted on PHE. There was no effect  
371 on the percentage of  $\text{SO}_4^{\bullet-}$  reacting with PHE. The addition of tert-Butanol resulted in 40%  
372 PHE degradation instead of 48%. ii) With the addition of methanol (50 mM), about 1% of  
373  $\text{HO}^{\bullet}$  and 15% of  $\text{SO}_4^{\bullet-}$  still reacted with PHE in solution. In this condition PHE concentration  
374 decreased by 25%.

375 As a consequence, in the presence of tert-Butanol almost no more  $\text{HO}^{\bullet}$  reacted on PHE and  
376 the percentage of PHE degradation decreased by 8%, while with the dosing of methanol only  
377 1% of  $\text{HO}^{\bullet}$  and 15% of  $\text{SO}_4^{\bullet-}$  reacted on PHE and the percentage of PHE degradation  
378 decreased by 25%. With these data, we can evaluate that 1% of  $\text{SO}_4^{\bullet-}$  contributed to 6% of  
379 PHE degradation and 1% of  $\text{HO}^{\bullet}$  contributed only to 0.6% of PHE degradation. In another  
380 word  $\text{SO}_4^{\bullet-}$  radicals contributed 10 times more than the  $\text{HO}^{\bullet}$  for the degradation of PHE in the  
381 presence of surfactant TW80. This result was not in agreement with the rate constant which  
382 was 1.4 times higher with  $\text{HO}^{\bullet}$  than with  $\text{SO}_4^{\bullet-}$  (table 1). Thus, this result highlighted the  
383 surrounding environment of the pollutant for the efficiency of the radical species. PHE in  
384 surfactant presented an opposite reactivity with  $\text{HO}^{\bullet}$  and  $\text{SO}_4^{\bullet-}$  if you compared with PHE  
385 alone in aqueous solution.

386

#### 387 **4 Conclusion**

388 A novel application of Fe(III) complexes was studied to improve the photochemical activation  
389 of persulfate for treatments of soil washing effluent. Experimental parameters such as

390 Fe(III)-EDDS concentration, PS concentration, TW80 concentration exhibited great effects on  
391 the PHE photodegradation in this system. The PHE degradation included two stages and the  
392 first period of Fe(III)-EDDS decomposition was the rate-limiting step. Quenching  
393 experiments proved that  $\text{SO}_4^{\bullet-}$  played a more important role than  $\text{HO}^{\bullet}$  on PHE degradation  
394 more particularly in the presence of surfactant which completely modified the reactivity of  
395 radical species. Moreover, we provided the evidence that the presence of chloride ions could  
396 significantly improve the PHE removal in this system. The higher selectivity of  $\text{Cl}_2^{\bullet-}$  between  
397 PHE and TW80 was responsible for the efficiency increase.

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406

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589 Table 1: Second-order rate constants ( $M^{-1} s^{-1}$ ) of TW80 and PHE with different radicals

590 determined using LFP and competition kinetic method.

<b>Compounds</b>	$k_{HO\cdot}$	$k_{SO_4^{\cdot-}}$	$k_{Cl_2^{\cdot-}}$
<b>TW80</b>	$9.9 \pm 0.1 \times 10^9$	$4.6 \pm 0.2 \times 10^9$	$7.1 \pm 0.1 \times 10^6$
<b>PHE</b>	$6.1 \pm 0.2 \times 10^9$	$4.3 \pm 0.4 \times 10^9$	$4.6 \pm 0.3 \times 10^8$

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593 **Figures Caption**

594 1) Absorption spectra of Fe(III)-EDDS (0.5 mM),  $S_2O_8^{2-}$  (5 mM) and 90  $\mu$ M of PHE in  
595 0.5 g L<sup>-1</sup> of TW80. Emission spectrum of the adopted irradiation lamps with a maximum  
596 centred at 365 nm.

597 2) Degradation of PHE in TW80 0.5 gL<sup>-1</sup> and degradation of Fe(III)-EDDS in different  
598 systems ( Blue marked ). Initial conditions are: [PS] = 5 mM, [Fe(III)] = 0.5 mM,  
599 [Fe(III)-EDDS] = 0.5mM, [TW80] = 0.5 g L<sup>-1</sup> , pH: 3.5±0.2.

600 3) **A)** Influence of Fe(III)-EDDS concentration on the photodegradation of PHE in  
601 aqueous solution. **B)** Degradation percentage of PHE after 30 and 150 minutes of  
602 irradiation as a function of different Fe(III)-EDDS concentrations. Initial conditions are:  
603 [PS] = 5 mM, [TW80] = 0.5 g L<sup>-1</sup> and pH: 3.5±0.2.

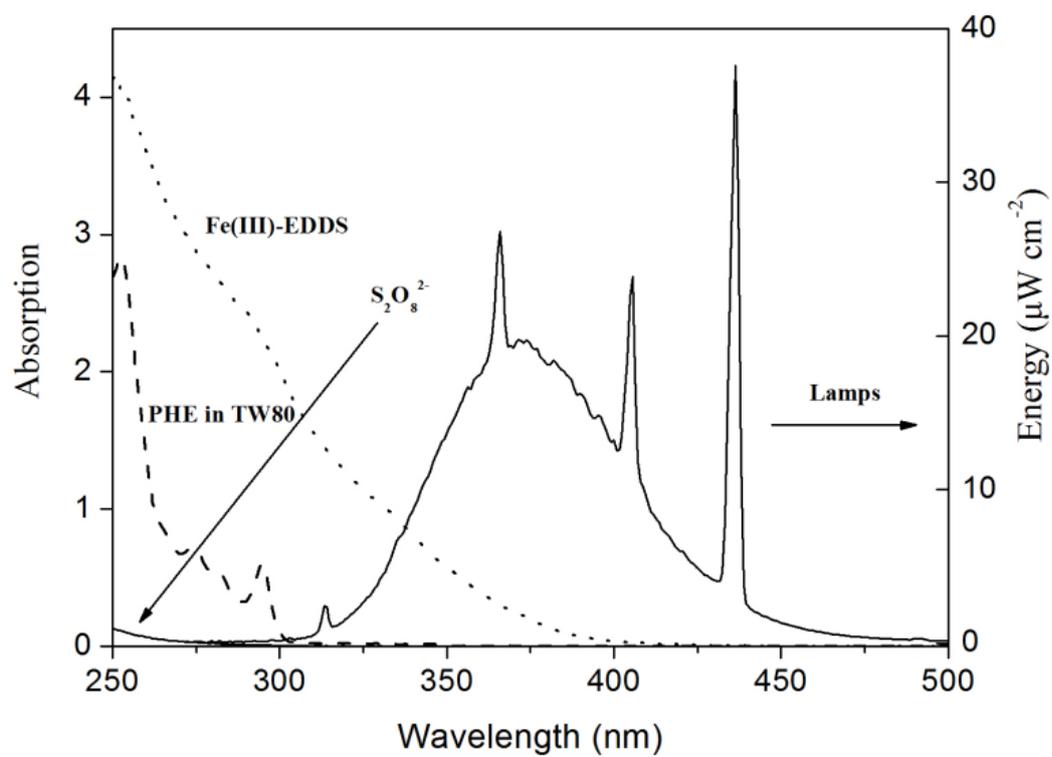
604 4) Influence of PS concentration on the photodegradation of PHE in aqueous solution.  
605 Initial conditions are: [Fe(III)-EDDS] = 5 mM, [TW80] = 0.5 g L<sup>-1</sup> and pH: 3.5±0.2.

606 5) Influence of concentration of Cl<sup>-</sup> for photodegradation of PHE in aqueous solution.  
607 [PS]=5mM, [Fe(III)-EDDS] = 5 mM, [TW80] = 0.5 g L<sup>-1</sup> and pH: 3.5±0.2.

608 6) Free radical scavenging tests photodegradation of PHE in aqueous solution. [PS] =  
609 5mM, [Fe(III)-EDDS] = 0.5 mM. [tert-Butanol] = 50 mM, [Methanol] = 50 mM, pH:  
610 3.5±0.2.

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612 **Figure 1**



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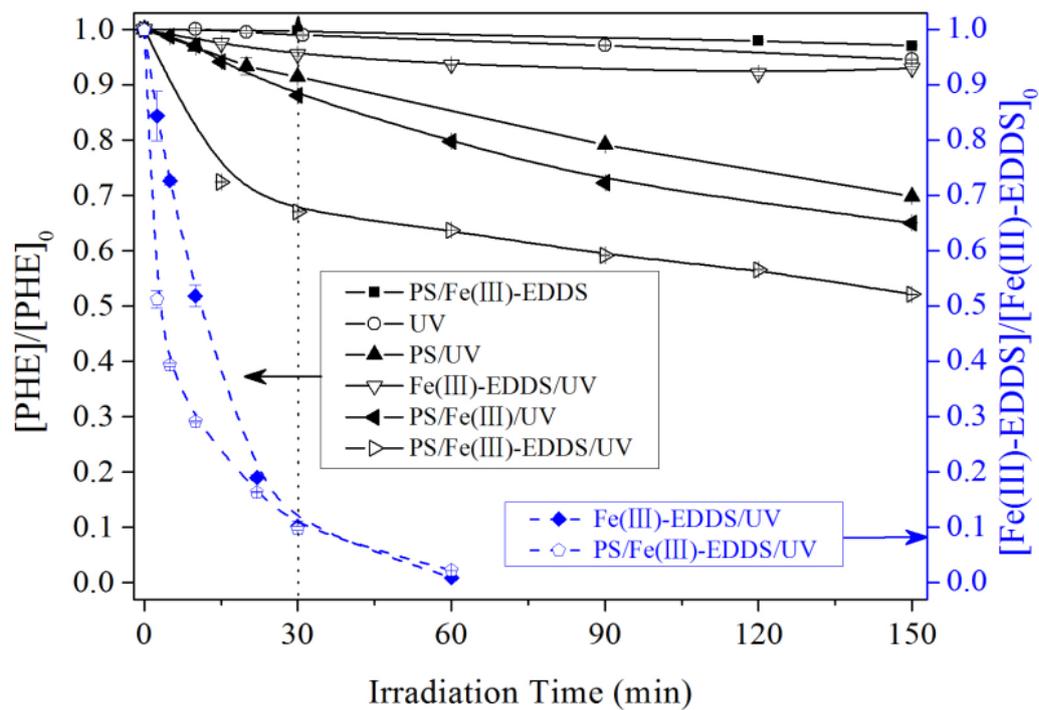
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626 **Figure 2**



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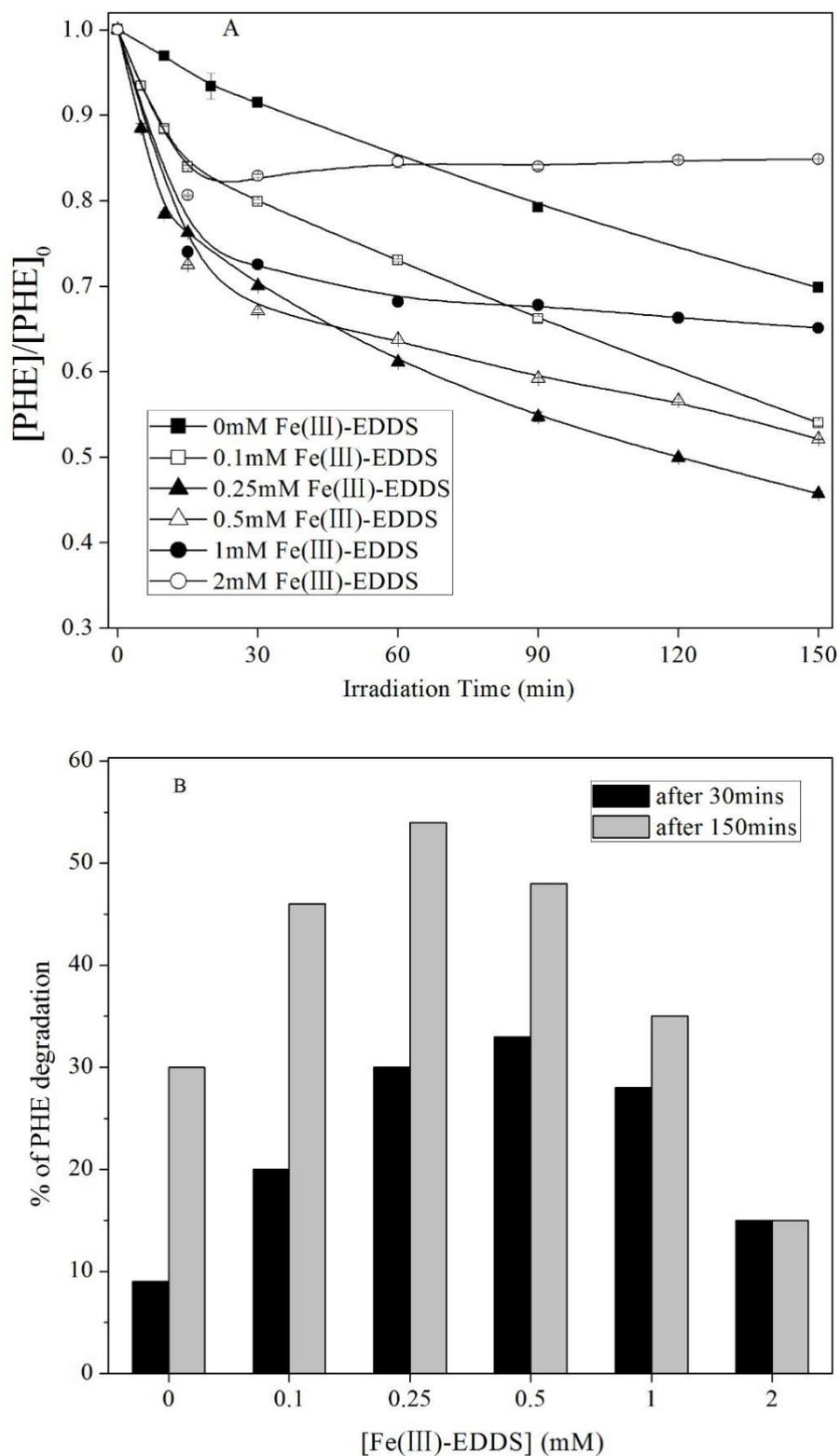
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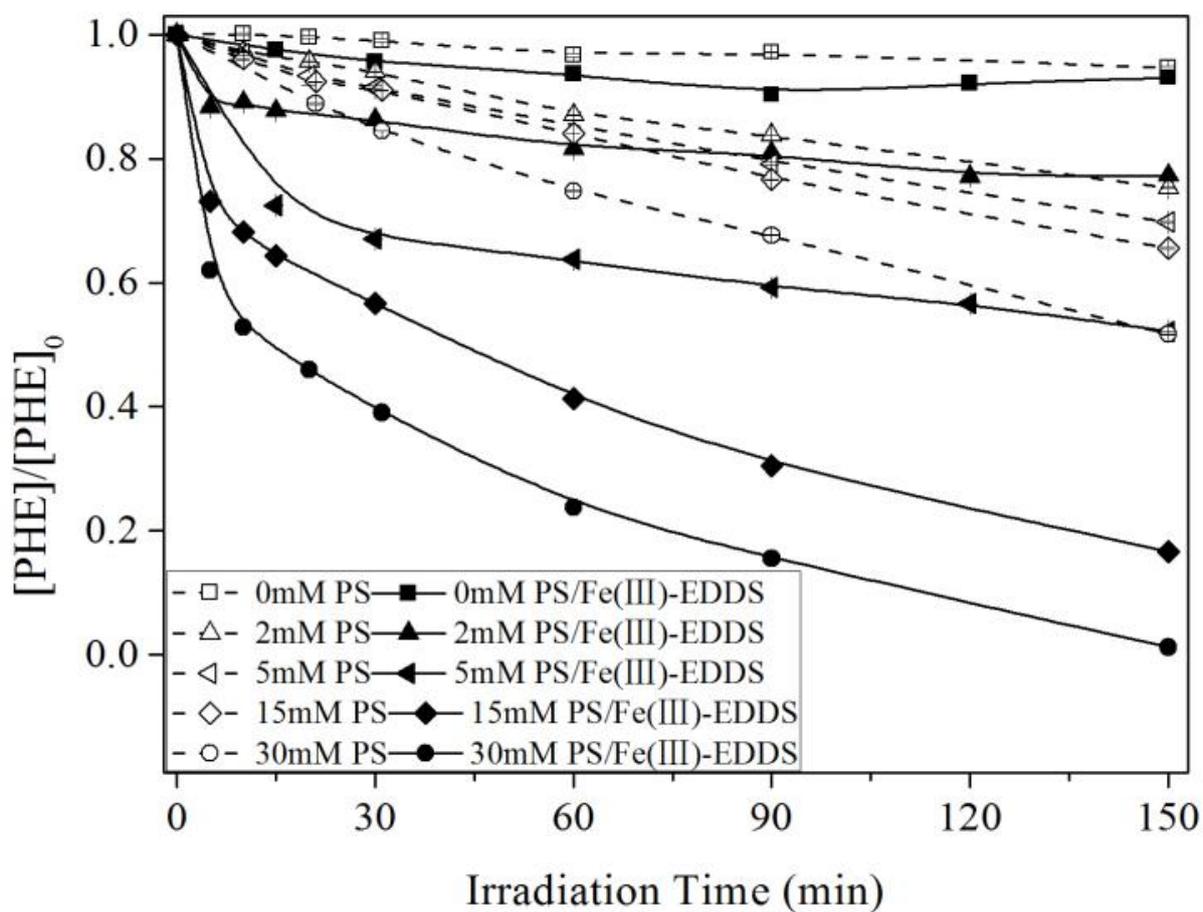
641 **Figure 3**



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643 **Figure 4**

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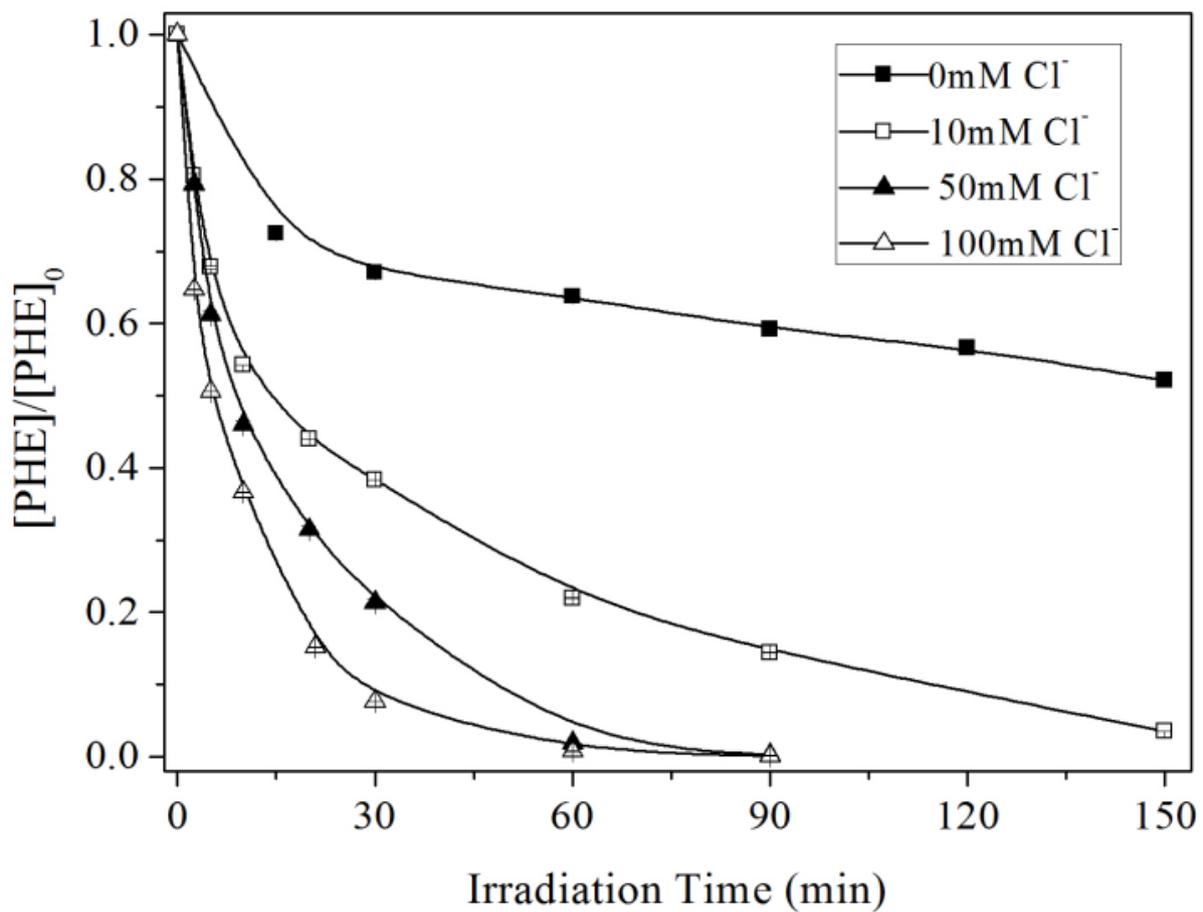
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656 **Figure 5**



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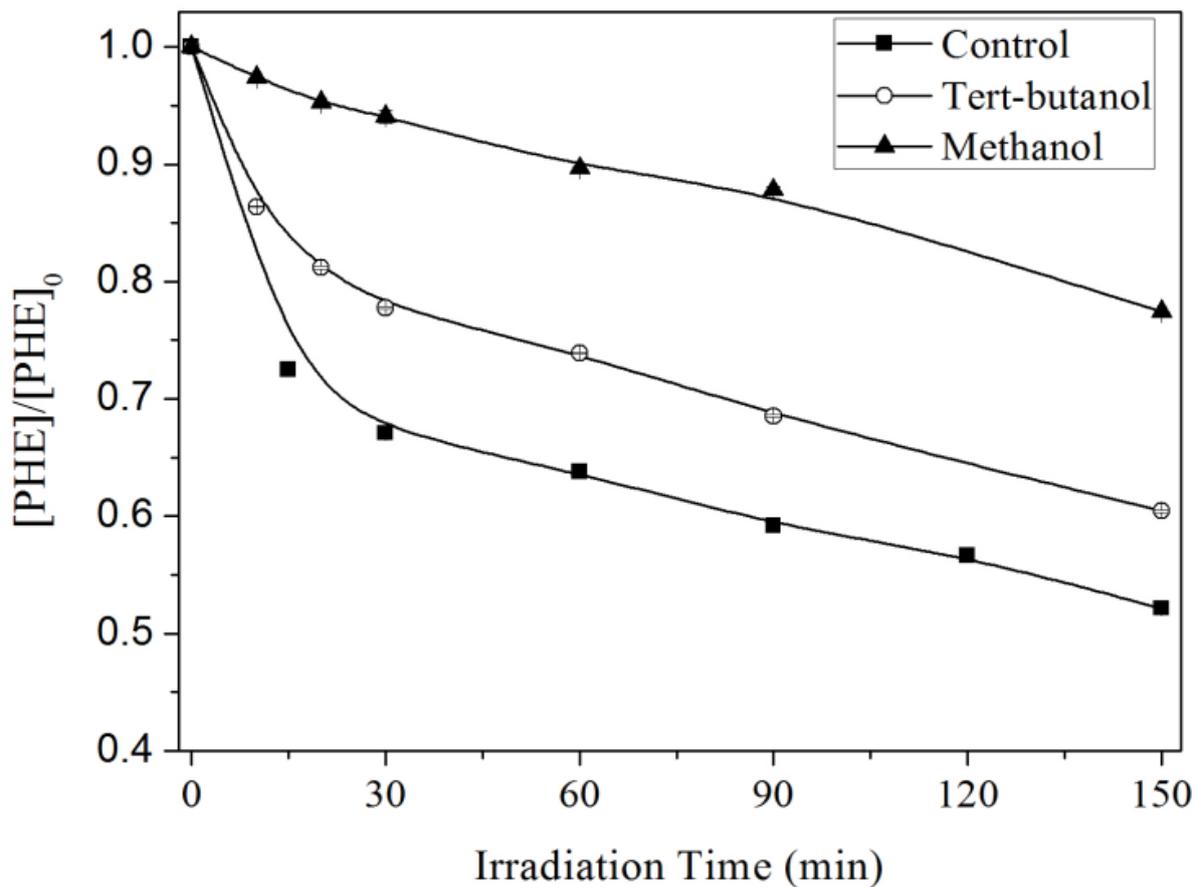
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668 **Figure 6**



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