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# Journal Pre-proof

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**Abstract**

In this work, the decomposition of phenanthrene (PHE) in mimic and real soil washing (SW) effluents was investigated using UVB light assisted activation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and peroxydisulfate (PDS) oxidation processes. The impact of oxidant concentration, initial pH, and coexisting inorganic anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ ) on PHE removal was evaluated. PHE degradation efficiency under UVB irradiation followed the order of UVB/PDS > UVB/ $\text{H}_2\text{O}_2$  > UVB. The increase of PHE decomposition efficiency was observed with increasing oxidant dose in the range of 2–30 mM upon the two processes. It was found  $\text{Cl}^-$  played different roles in the two activation systems depending on the solution pH and  $\text{Cl}^-$  concentration. The influence of  $\text{HCO}_3^-$  on PHE elimination was negligible in the UVB/PDS process, while an inhibitory effect was observed in the UVB/ $\text{H}_2\text{O}_2$  system. Nitrate inhibited the PHE decay in both UVB/ $\text{H}_2\text{O}_2$  and UVB/PDS processes at the investigated pH 3.3, 7.1 and 8.6. Finally, the application of the two activation processes to the treatment of real SW effluents indicated that up to 85.0% of PHE degradation could be reached under 6 h UVB irradiation with PDS, indicating UVB/PDS process is a promising alternative for SW effluent treatment.

**Keywords:** Soil washing effluent; Phenanthrene; Peroxydisulfate; Hydrogen peroxide; Photodegradation.

1 **Phenanthrene decomposition in soil washing effluents using UVB activation of**  
2 **hydrogen peroxide and peroxydisulfate**

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10 **Abstract**

11 In this work, the decomposition of phenanthrene (PHE) in mimic and real soil  
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13 hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and peroxydisulfate (PDS) oxidation processes. The impact  
14 of oxidant concentration, initial pH, and coexisting inorganic anions (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and  
15 NO<sub>3</sub><sup>-</sup>) on PHE removal was evaluated. PHE degradation efficiency under UVB  
16 irradiation followed the order of UVB/PDS > UVB/H<sub>2</sub>O<sub>2</sub> > UVB. The increase of  
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18 range of 2–30 mM upon the two processes. It was found Cl<sup>-</sup> played different roles in  
19 the two activation systems depending on the solution pH and Cl<sup>-</sup> concentration. The  
20 influence of HCO<sub>3</sub><sup>-</sup> on PHE elimination was negligible in the UVB/PDS process,  
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22 the PHE decay in both UVB/H<sub>2</sub>O<sub>2</sub> and UVB/PDS processes at the investigated pH 3.3,  
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## 29 **1. Introduction**

30 Contamination of soils by toxic pollutants, especially by the recalcitrant hydrophobic  
31 organic compounds (HOCs) is a matter of significant public, scientific and regulatory  
32 concern. Polycyclic aromatic hydrocarbons (PAHs), as a class of HOCs, are ubiquitous  
33 in the soil environment due to their low solubility in water and long-term persistence in  
34 soils (Manoli and Samara 1999; Shin et al., 2006; Trellu et al., 2016). Phenanthrene  
35 (PHE), containing three benzene rings, is one of the most widely detected PAHs in the  
36 contaminated sites (Bezza and Chirwa 2017; Gou et al., 2019; Li et al., 2019; Petrová  
37 et al., 2017), especially those located in manufactured gas plants and coal tar refinery  
38 (Li et al., 2019; Reddy et al., 2006; Yeom et al., 1995). Therefore, it is urgent and  
39 essential to develop effective remediation strategies to restore PAHs contaminated  
40 soil.

41 Surfactant-enhanced *ex-situ* soil washing (SW) has been proposed as a promising  
42 technology for elimination of PHE from contaminated soils due to its high extraction  
43 efficiency and low remediation cost (Kuhlman and Greenfield 1999; Ortega et al.,  
44 2008). Among various surfactants, Tween 80 (TW80) was the most commonly used  
45 non-ionic surfactant for washing PHE and other PAHs from soil due to its high  
46 solubilization capacity, low cost and low toxicity (Cheng et al., 2017; Lamichhane et  
47 al., 2017). Nevertheless, the SW process generates a large amount of effluent  
48 containing soil pollutant and surfactant, which should be further treated with

49 appropriate methods for the complete elimination of soil pollutant (Mousset et al.,  
50 2014; Trellu et al., 2017).

51 In the past few decades, advanced oxidation processes (AOPs) have been  
52 developed and widely applied as alternative technologies for the degradation of  
53 recalcitrant pollutants in waters and soils (Liu et al., 2016; Mousset et al., 2014; Wan et  
54 al., 2018; Wu et al., 2015). This is mainly attributed to the formation of reactive  
55 species with high standard redox potential such as hydroxyl radical ( $\text{HO}^\bullet$ ,  $E^0 = 1.8\text{-}2.7$   
56 V) or sulfate radical ( $\text{SO}_4^{\bullet-}$ ,  $E^0 = 2.5\text{-}3.1$  V) (Buxton et al., 1988; Neta et al., 1988). As  
57 efficient and environmental friendly techniques,  $\text{HO}^\bullet$  or  $\text{SO}_4^{\bullet-}$  based AOPs have been  
58 extensively investigated for the treatment of contaminants in water under UV  
59 irradiation (UVA, UVB and UVC) (Huang et al., 2018; Minella et al., 2019; Mosteo et  
60 al., 2020; Xiao et al., 2016; Xu et al., 2016; Yang et al., 2016; Zhang et al., 2015; Zhou  
61 et al., 2017b). Compared with UVA and UVC, UVB based oxidation has great  
62 potential due to: *i*) possible use of LED *ii*) considerably less energy requirement than  
63 UVC (Beck et al., 2017) and *iii*) higher efficiency for contaminant degradation than  
64 UVA (Joseph et al., 2016). After reviewing the literature, it is found that the  
65 investigation on HOCs decomposition by UVB-based oxidation is pretty limited and  
66 no studies for systematic comparison of SW effluent treatment by UVB activation of  
67 PDS and  $\text{H}_2\text{O}_2$  are reported before.

68 The presence of inorganic anions has been reported to exert strong impacts on the  
69 oxidative degradation of contaminants (Bennedsen et al., 2012; Liu et al., 2016; Yang  
70 et al., 2014). However, the effect of these anions on the photo-degradation of PHE in  
71 the SW effluent has not been investigated before. In this study, for the first time, UVB  
72 irradiation was used to activate  $\text{H}_2\text{O}_2$  and PDS for PHE decomposition in a surfactant  
73 co-existing SW effluent. The aims of this work were: (1) to investigate the PHE

74 decomposition efficiency in the present of TW80 by direct UVB radiation, UVB/H<sub>2</sub>O<sub>2</sub>,  
75 and UVB/PDS processes; (2) to evaluate the impact of operating factors including the  
76 oxidant dosage, the initial pH and the coexisting anions on PHE treatment efficiency;  
77 (3) to assess the performance of UVB, UVB/H<sub>2</sub>O<sub>2</sub> and UVB/PDS systems on PHE  
78 oxidation in the real SW solutions.

## 79 **2. Materials and methods**

### 80 **2.1 Chemicals**

81 TW80, phenanthrene (PHE), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, ≥ 99.0%), sodium  
82 chorine (NaCl, ≥ 99.5%), sodium bicarbonate (NaHCO<sub>3</sub>, ≥ 99.7%) and sodium nitrate  
83 (NaNO<sub>3</sub>, ≥ 99.0%) were purchased from Sigma-Aldrich. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>,  
84 30%) was obtained from Fluka, France. Perchloric acid (HClO<sub>4</sub>) and sodium  
85 hydroxide (NaOH) were applied for adjusting the initial pH of the solutions. Millipore  
86 Ultra-Pure System purified water (18.2 MΩ cm) was used to prepare solutions. All the  
87 chemical reagents were of analytical grade and employed without further purification.

### 88 **2.2 Preparation of the mimic and real SW solutions**

89 One liter of mimic SW solution was prepared as previously reported (Tao et al.,  
90 2019). Briefly, 10 mg of PHE was added to 1 L aqueous solution containing 0.5 g L<sup>-1</sup>  
91 TW80. The mixed solution was vigorously stirred for one week to obtain complete  
92 PHE dissolution before irradiation experiments.

93 Natural soil samples were obtained from Wuhan of Hubei Province (soil 1), Chuzhou  
94 of Anhui Province (soil 2) and Huaian of Jiangsu Province (soil 3), respectively. The  
95 collected soils were air dried and ground to obtain particles less than 2 mm before use.  
96 The PHE contaminated soil samples were prepared according to the literature (Yang et  
97 al., 2006). Briefly, the three PHE free soils were spiked with PHE dissolved in acetone

98 solutions and vigorously stirred for 30 minutes to obtain homogeneous distribution of  
99 PHE in the soil. The spiked soil samples were placed in three hoods for 5 days at room  
100 temperature to evaporate the solvent. The final PHE concentrations of each spiked soil  
101 were 4000 mg kg<sup>-1</sup>.

102 To obtain the real SW solutions, 3 grams of each contaminated soil were separately  
103 weighed into 150 mL conical flasks with stoppers and 60 mL TW80 solutions (10 g L<sup>-1</sup>)  
104 were added. The flasks were then placed into a constant temperature shaker for 24h  
105 with a speed of 200 rpm at 25 °C. Then, the mixtures were centrifuged at 8000 rpm for  
106 15 min and the supernatants were filtered with 0.22 µm PTFE filters before analysis and  
107 the sequent irradiation experiments.

### 108 **2.3 Irradiation experiments**

109 Irradiations experiments were carried out in a cylindrical Pyrex reactor (100 mL)  
110 which was placed into a rectangular glass jacket vessel with cooling water flowing  
111 between interlayers ensuring a constant temperature of 20 ± 2 °C through a  
112 thermostat-controlled cooling system. Four UVB tubes (G15T8E, Japan) were fixed  
113 on the top of the photo-reactor as the light resource, and the distance between  
114 photoreactor and the lamps was around 24 cm. The schematic diagram of  
115 experimental set-up is shown in Figure S1.

116 The polychromatic UVB irradiation energy was recorded by an optical fiber with a  
117 charge coupled device spectrophotometer (Ocean Optics USD 2000 + UV-vis). The  
118 total irradiance reaching the solution was then estimated to be 1393 µW cm<sup>-2</sup> in the  
119 UVB range (between 270 and 400 nm). The absorption spectra of PDS, H<sub>2</sub>O<sub>2</sub> and  
120 PHE solution in TW80 were recorded with a UV-visible spectrophotometer Cary 300.  
121 Emission spectrum of adopted UVB lamps reaching the solution was recorded using a  
122 calibrated CCD camera (Huang et al., 2018) as presented in Figure S2.



123 During the irradiation, the SW solution was continuously magnetically stirred at a  
124 fixed speed with a magnetic stirrer. At fixed interval times, 1 mL of sample was  
125 withdrawn and analyzed by a high performance liquid chromatography (HPLC,  
126 Alliance) equipped with a Waters 2998 photodiode array detector. The flow rate was 1  
127 mL min<sup>-1</sup> and an isocratic elution with water and acetonitrile (15/85, v/v) was used.  
128 The column was a Nucleodur 100-5 C18 of 150 mm × 4.6 mm, with particle size of 5  
129 μm.

130 The pseudo-first order rate constant of PHE decomposition ( $k_1$ ) was determined  
131 from Eq. (1):

$$132 \quad [\text{PHE}]/[\text{PHE}]_0 = \exp(-k_1 t) \quad (1)$$

133 where  $[\text{PHE}]_0$  and  $[\text{PHE}]$  were the PHE initial concentration and PHE concentration  
134 at time  $t$ , respectively.

135 Inorganic components of three real SW effluents were determined by ion  
136 chromatography. For anions, a Dionex DX320 system equipped with an IonPac AS11  
137 column and a KOH elution in gradient mode were used. For cations, a Dionex  
138 ICS-1500 system equipped an Ion-Pac CS16 column and a metasulfonic acid (MSA)  
139 eluent were employed (Marion et al., 2018).

140 TW80 concentration after soil washing process was quantified by a  
141 spectrophotometric method using cobalt ammonium thiocyanate as the chromogenic  
142 agent (Crabb and Persinger 1964).

### 143 **3. Results and discussion**

#### 144 **3.1 Comparison of UVB activation of H<sub>2</sub>O<sub>2</sub> and PDS**

145 In Figure 1, the decomposition of PHE (10 mg L<sup>-1</sup> corresponding to ~56 μM in 0.5  
146 g L<sup>-1</sup> TW80 solution) is reported. Under direct photolysis (UVB alone), about 23.0%

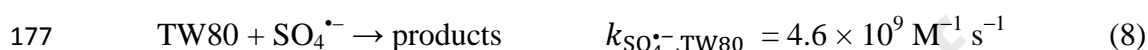
147 of PHE decay was observed after 3 h irradiation with a first order rate constant ( $k_1$ ) of  
 148  $1.5 \times 10^{-3} \text{ min}^{-1}$ , which is equivalent to a half-life of 7.8 h (Table S4). When the  
 149 oxidant ( $\text{H}_2\text{O}_2$  or PDS) was applied to the irradiation system,  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  were  
 150 generated through photo-dissociation of  $\text{H}_2\text{O}_2$  and PDS under UVB irradiation (Eqs. 2  
 151 and 3) (Mark et al., 1990; Yu and Barker 2003).



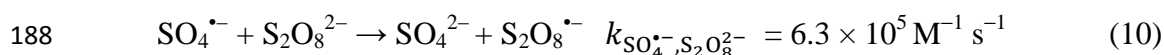
154 The evolution of HPLC chromatograms during UVB/ $\text{H}_2\text{O}_2$  and UVB/PDS  
 155 processes is presented in Figure S3, and PHE removal reached up to 34.0% and  
 156 72.0%, respectively. The pseudo-first order rate constants were  $2.3 \times 10^{-3} \text{ min}^{-1}$  with  
 157  $\text{H}_2\text{O}_2$  and  $7.1 \times 10^{-3} \text{ min}^{-1}$  with PDS. The correspondent half-lives of PHE were  
 158 calculated to be 5.0 h and 1.6 h in the UVB/ $\text{H}_2\text{O}_2$  and UVB/PDS systems,  
 159 respectively (Table S4). The different performance between UVB/ $\text{H}_2\text{O}_2$  and  
 160 UVB/PDS systems could be ascribed to the following aspects. Firstly, the  
 161 photo-dissociation quantum yield of PDS is higher than that for  $\text{H}_2\text{O}_2$ . In fact, near the  
 162 maximum emission wavelength of UVB (313 nm in Figure S2), the reported  $\text{SO}_4^{\bullet-}$   
 163 formation quantum yield from PDS photolysis ( $\Phi_{\text{SO}_4^{\bullet-}}$ ) is  $1.1 \pm 0.2$  (Herrmann 2007),  
 164 which is higher than the quantum yield for  $\text{HO}^\bullet$  generation from  $\text{H}_2\text{O}_2$ , i.e.,  $0.98 \pm 0.2$   
 165 (Zellner et al., 1990) or  $0.8 \pm 0.2$  (Yu and Barker 2003) at the wavelength of 308 nm.  
 166 Secondly, the selectivity of  $\text{SO}_4^{\bullet-}$  towards PHE is superior to that of  $\text{HO}^\bullet$  (Tao et al.,  
 167 2019). To verify this point, the selectivity coefficient  $\zeta_{\text{PHE}}$  is defined as Eq. (4) based  
 168 on the reactions of radicals with PHE, TW80 (Eqs. 5-8) and other species in the  
 169 system (see Text S1).

$$170 \quad \zeta_{\text{PHE}} = \frac{k_{\text{X}^\bullet, \text{PHE}}[\text{PHE}]_0}{k_{\text{X}^\bullet, \text{PHE}}[\text{PHE}]_0 + k_{\text{X}^\bullet, \text{S}}[\text{S}]_0} \quad (4)$$

171 where  $k_{X^{\bullet},\text{PHE}}$  and  $k_{X^{\bullet},\text{S}}$  are the second order rate constants of radicals with PHE and  
 172 other components S (PHE, TW80, oxidant, etc.) in the system, respectively.  $[\text{PHE}]_0$   
 173 and  $[\text{S}]_0$  are their initial concentrations.



178 In the UVB/H<sub>2</sub>O<sub>2</sub> system, HO<sup>•</sup> is the main generated radical, and  $\zeta_{\text{PHE}}$  was calculated  
 179 to be around 8.1%, while the selectivity coefficient was about 12.1 % in the  
 180 UVB/PDS system with SO<sub>4</sub><sup>•-</sup> as the major radical. This means the selectivity  
 181 coefficient  $\zeta_{\text{PHE}}$  for SO<sub>4</sub><sup>•-</sup> towards PHE (12.1%) is about 1.5 times higher than that of  
 182 HO<sup>•</sup> (8.1%). The result confirms SO<sub>4</sub><sup>•-</sup> was more selective than HO<sup>•</sup> to the oxidation of  
 183 PHE in the presence of TW80 (Tao et al., 2019). Lastly, the rate constant of H<sub>2</sub>O<sub>2</sub> and  
 184 HO<sup>•</sup> is around 43 times higher than that of PDS and SO<sub>4</sub><sup>•-</sup> ( $k_{\text{HO}^{\bullet},\text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ M}^{-1}$   
 185  $\text{s}^{-1}$ ,  $k_{\text{SO}_4^{\bullet-},\text{S}_2\text{O}_8^{2-}} = 6.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ), indicating HO<sup>•</sup> would be more prone to be  
 186 quenched by H<sub>2</sub>O<sub>2</sub> than SO<sub>4</sub><sup>•-</sup> scavenged by PDS (Eqs. 9 and 10).



### 189 3.2 Effect of oxidant concentration

190 Effects of initial concentration of H<sub>2</sub>O<sub>2</sub> or PDS on PHE degradation were evaluated  
 191 as reported in Figure 2. In the UVB/H<sub>2</sub>O<sub>2</sub> process, it can be seen from Figure 2A that  
 192 PHE decomposition after 3 hours reached around 28.0% with 2 mM H<sub>2</sub>O<sub>2</sub> and 51.0%  
 193 with 30 mM H<sub>2</sub>O<sub>2</sub>, and the corresponding PHE oxidation rate constant increased  
 194 around 1.95 folds from  $2.0 \times 10^{-3}$  to  $3.9 \times 10^{-3} \text{ min}^{-1}$ . In the UVB/PDS process as

195 illustrated in Figure 2B, with 2 mM of PDS, the PHE decomposition efficiency  
196 reached around 61.0% and rate constant was  $5.1 \times 10^{-3} \text{ min}^{-1}$ . With further addition of  
197 PDS to 30 mM, the PHE elimination efficiency was around 83.0% and  $k_1$  increased  
198 around 1.90 folds to  $9.7 \times 10^{-3} \text{ min}^{-1}$ . In comparison with the effect of oxidant type,  
199 the results indicated that the decomposition efficiency of PHE followed the order of  
200  $\text{PDS} > \text{H}_2\text{O}_2$  at the same oxidant dosage.

201 Some researchers reported that the decomposition rate of contaminant increased  
202 linearly with the oxidant dosage (Deng et al., 2013; Tan et al., 2013; Xu et al., 2016),  
203 while others found that the removal rate would drop when the oxidant concentration  
204 exceeds its threshold level (Olmez-Hanci and Arslan-Alaton 2013; Yang et al., 2010;  
205 Zhou et al., 2017a). In our case, PHE removal increased almost linearly with  
206 increasing  $\text{H}_2\text{O}_2$  concentration from 2 to 30 mM, probably because more  $\text{HO}^\bullet$  radicals  
207 were formed for PHE decomposition with higher  $\text{H}_2\text{O}_2$  concentration and the  
208 maximum dosage (30 mM) was still below its threshold level. In the UVB/PDS  
209 system, PHE removal efficiency also increased with the increasement of PDS.  
210 However, insignificant improvement of PHE decomposition was observed at PDS  
211 concentration higher than 10 mM, which possibly because the PDS concentration was  
212 beyond the threshold and quenching effect of  $\text{SO}_4^{\bullet-}$  radicals via Eq. (10) (Herrmann  
213 et al., 1995) became pronounced.

### 214 3.3 Effect of initial pH

215 The influence of initial pH on the photo-degradation of PHE by the UVB/ $\text{H}_2\text{O}_2$  and  
216 UVB/PDS processes is given in Figure 3. In the UVB/ $\text{H}_2\text{O}_2$  system, a slight difference  
217 (less than 10.0%) was obtained from pH 3.3 to pH 10.1, though the maximum PHE  
218 decomposition extent of 40.0% and a first order rate constant of  $2.8 \times 10^{-3} \text{ min}^{-1}$  were

219 observed at pH 4.5 (Figure 3A). In the UVB/PDS system, pH had insignificant effect  
220 on PHE decay, and the difference of PHE photo-degradation efficiency was less than  
221 5.0% with pH value ranging from acidic to basic (Figure 3B). The little difference of  
222 PHE degradation with pH is probably due to the chemical stability of PHE with pH  
223 ranging from 3.3 to 10.1 and also the photolysis of H<sub>2</sub>O<sub>2</sub> or PDS is not pH dependent.  
224 Moreover, although the PHE degradation was performed in a quite wide initial pH  
225 range (from 3.3 to 10.1), the pH varied from 3.4 to 6.6 after UVB/H<sub>2</sub>O<sub>2</sub> process, or from  
226 3.3 to 3.8 after UVB/PDS process as indicated in Table S5. The difference of final pH  
227 (3.3~3.8) in the UVB/PDS system is less than that (3.4~6.6) in the UVB/H<sub>2</sub>O<sub>2</sub> system.  
228 It is probably due to the higher degradation efficiency of PHE and more production of  
229 acidic intermediates in the UVB/PDS system than in the UVB/H<sub>2</sub>O<sub>2</sub> system.

### 230 **3.4 Effect of inorganic anions**

231 Inorganic species (such as carbonate, chloride and nitrate) are widely found in the  
232 soil due to many factors: (i) the parent soil substrate, (ii) depositions through  
233 fertilization, and (iii) other human activities such as irrigation (Du et al., 2013; Wang  
234 et al., 2019). These anions are generally considered to be freely mobile in soils and  
235 can be released into groundwater *via* rainfall (Bastviken et al., 2006; Lu et al., 2019).  
236 Therefore, inorganic species (Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) are inevitably dissolved in the  
237 SW effluent and they may exert impact on the PHE decomposition by UVB/H<sub>2</sub>O<sub>2</sub> and  
238 UVB/PDS processes.

#### 239 **3.4.1 Chloride**

240 The PHE elimination as a function of Cl<sup>-</sup> dosage at pH 3.3 of the two AOP systems  
241 is presented in Figure 4. The results clearly revealed that the presence of Cl<sup>-</sup> had  
242 adverse effect on the two AOPs. In the UVB/H<sub>2</sub>O<sub>2</sub> process as shown in Figure 4A, the  
243 effect of 2 and 10 mM Cl<sup>-</sup> on PHE oxidation was insignificant, while PHE decay was

244 inhibited by around 10.0% with addition of 50 mM  $\text{Cl}^-$ . In the UVB/PDS process as  
 245 depicted in Figure 4B, PHE oxidation gradually increased by 9.0% when  $\text{Cl}^-$   
 246 concentration ranging from 0 to 10 mM and no further improvement of PHE removal  
 247 can be achieved with 50 mM  $\text{Cl}^-$ . At pH 7.1, the influence of  $\text{Cl}^-$  from 2 to 50 mM on  
 248 PHE removal is negligible in the UVB/ $\text{H}_2\text{O}_2$  system (Figure S4A), while PHE  
 249 removal increased by 15.0% with  $\text{Cl}^-$  dose varying from 0 to 50 mM in the UVB/PDS  
 250 process (Figure S4B). At alkaline pH 8.6,  $\text{Cl}^-$  exerted negative effect on PHE  
 251 oxidation and larger inhibition was observed with higher  $\text{Cl}^-$  concentration in the  
 252 UVB/ $\text{H}_2\text{O}_2$  system and PHE decomposition decreased by 17.0% in the presence of 50  
 253 mM  $\text{Cl}^-$  (Figure S4C). Under the same pH condition, the effect of 2 mM  $\text{Cl}^-$  on PHE  
 254 removal was insignificant and PHE removal was slightly promoted by around 6.0%  
 255 with 10 and 50 mM  $\text{Cl}^-$  in the UVB/PDS system (Figure S4D).

256 Various conflicting results were reported in the different UV based AOPs with the  
 257 presence of  $\text{Cl}^-$  as indicated in Table S1. Usually,  $\text{Cl}^-$  can react with  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  to  
 258 yield secondary active chlorine radical species such as  $\text{ClOH}^{\bullet-}$ ,  $\text{Cl}^\bullet$ , and  $\text{Cl}_2^{\bullet-}$  through  
 259 a series of intricate chain reactions (Eqs. 11, 13-15) (Grigor'ev et al., 1987; Jayson et  
 260 al., 1973; Neta et al., 1988).



267 The negligible effect of low  $\text{Cl}^-$  concentration (2–10 mM) on PHE removal in the  
 268 UVB/ $\text{H}_2\text{O}_2$  system was mainly due to the reaction of Eq. (12). The negative effect of

269 50 mM  $\text{Cl}^-$  on PHE oxidation observed can be ascribed to the consumption of  $\text{H}_2\text{O}_2$   
 270 by  $\text{Cl}^\bullet$  and  $\text{Cl}_2^{\bullet-}$  (Eqs.17 and 18) (Hasegawa and Neta 1978; Klänning and Wolff 1985).  
 271 These reactions reduced the amount of available  $\text{HO}^\bullet$  and  $\text{Cl}_2^{\bullet-}$  radicals reacting with  
 272 PHE (Eqs.5 and 16) (Tao et al., 2019), leading to the lower PHE elimination.  
 273 Moreover, the finding of inhibition of PHE at pH 8.6 could be explained by the  
 274 reduction of  $\text{Cl}_2^{\bullet-}$  triggered by Eqs. (19) and also the higher consumption of  $\text{H}_2\text{O}_2$  via  
 275 Eqs. (17) and (18) at alkaline pH, which restrained active species reacting with PHE  
 276 and consequently retarded PHE oxidation.



280 In the UVB/PDS system, the weak enhancement of PHE decay was attributed to the  
 281 production of  $\text{Cl}_2^{\bullet-}$  radicals through a series of chain reactions (Eqs.14 and 20).  
 282 According to our previous study (Tao et al., 2019),  $\text{Cl}_2^{\bullet-}$  was more selective towards  
 283 PHE than  $\text{SO}_4^{\bullet-}$  in the presence of TW80 (Eqs. 16 and 21), therefore PHE elimination  
 284 could be promoted.



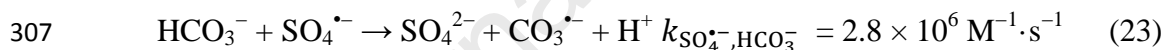
### 287 3.4.2 Bicarbonate

288 Figure 5 depicts the elimination efficiency of PHE in the presence of various  
 289 concentrations of bicarbonate ( $\text{HCO}_3^-$ ) in the UVB/ $\text{H}_2\text{O}_2$  and UVB/PDS processes at  
 290 initial pH of around 8.6. As presented in Figure 5A, the oxidation of PHE was  
 291 obviously inhibited with the addition of  $\text{HCO}_3^-$ , which is in accordance with most  
 292 reports investigated in aqueous phase in the absence of surfactant (Table S2). With the  
 293 addition of 50 mM bicarbonate, the PHE removal efficiency decreased by almost

294 one-half in comparison with 33.0% removal in the absence of bicarbonate.  $\text{HCO}_3^-$   
 295 could react with  $\text{HO}^\bullet$  to generate carbonate radicals ( $\text{CO}_3^{\bullet-}$ ) via Eq. (22). However, the  
 296 generated  $\text{CO}_3^{\bullet-}$  are considered to be a weaker oxidant and the reactions with most  
 297 organic pollutants are insignificant (Crittenden et al., 1999; Zuo et al., 1999). As a  
 298 consequence, available  $\text{HO}^\bullet$  was reduced and PHE decomposition was depressed.



300 The effect of bicarbonate in the UVB/PDS system is illustrated in Figure 5B.  
 301 Insignificant effect of  $\text{HCO}_3^-$  was observed, which may be ascribed to the negligible  
 302 scavenging effect of  $\text{SO}_4^{\bullet-}$  by  $\text{HCO}_3^-$  (Eq. 23) since the rate constant between  $\text{SO}_4^{\bullet-}$   
 303 and  $\text{HCO}_3^-$  is around 3 orders of magnitudes smaller than that between PHE and  
 304  $\text{SO}_4^{\bullet-}$ . In the meanwhile, the little influence of  $\text{HCO}_3^-$  on the performance of  
 305 UVB/PDS system was ascribed to the unpronounced variation of selectivity  
 306 coefficient (12.1% ~ 11.3%) with the  $\text{HCO}_3^-$  concentration ranging from 0 ~ 50 mM.



### 308 3.4.3 Nitrate

309 The influence of  $\text{NO}_3^-$  with different doses and pH conditions on the  
 310 decomposition of PHE in the UVB/PDS and UVB/ $\text{H}_2\text{O}_2$  systems were studied.  $\text{NO}_3^-$   
 311 led to a strong inhibitory effect on the two AOPs, which is in agreement with other  
 312 reports as summarized in Table S3. At pH 3.3, with the concentration of  $\text{NO}_3^-$  ranging  
 313 from 0 to 50 mM, the PHE decomposition efficacy decreased from 34.5% to 19.0% in  
 314 the UVB/ $\text{H}_2\text{O}_2$  system (Figure 6A), while it dropped from 73.0% to 42.0% in the  
 315 UVB/PDS system (Figure 6B).

316 The stronger inhibition of  $\text{NO}_3^-$  on PHE decomposition can be explained by the  
 317 screen effect of light due to the photoreactivity of  $\text{NO}_3^-$  (Eqs. 24 and 25) (Keen et al.,  
 318 2012) and its secondary substance (i.e.  $\text{NO}_2^-$ ), leading to competition with  $\text{H}_2\text{O}_2$  and



319 PDS for UVB radiation. It is reported that both  $\text{NO}_3^-$  and  $\text{NO}_2^-$  have absorption in the  
 320 range of UVB light (around 260 – 330 nm) (Mack and Bolton 1999). This is  
 321 supported by the strong decrease of the direct photolysis of PHE under UVB  
 322 irradiation in presence of 5 mM  $\text{NO}_3^-$ . In the UVB alone, PHE removal was 23.0%  
 323 while it dropped to only 7.0% with the addition of 5 mM  $\text{NO}_3^-$ . The production of  
 324  $\text{HO}^\bullet$  from the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  photolysis (Eqs. 26-28) (Keen et al., 2012; Lyon et al.,  
 325 2012; Sørensen and Frimmel 1997) probably did not compensate the negative screen  
 326 effect. On the other hand,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  had quenching effect for both  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^\bullet$   
 327 via Eqs. (29)-(31), which could also restrain PHE degradation.



336 The influence of 5 mM  $\text{NO}_3^-$  on PHE degradation at different initial pH was also  
 337 investigated in the two AOPs. As displayed in Figure S5, in comparison with the  
 338 absence of  $\text{NO}_3^-$ , the decrease of PHE removal at pH 3.3, 7.1 and 8.6 was respectively  
 339 5.0%, 14.5%, 13.6% in the UVB/ $\text{H}_2\text{O}_2$  system, while it was respectively 10.7%, 10.3%  
 340 and 14.3% in the UVB/PDS system.

### 341 3.5 Treatment of real SW effluent by the UVB/ $\text{H}_2\text{O}_2$ and UVB/PDS systems

342 The treatment of real effluents after washing three types of soils spiked with PHE  
343 was further carried out to evaluate the feasibility of UVB/H<sub>2</sub>O<sub>2</sub> and UVB/PDS  
344 systems. The various ions and constituents in the soils are listed in Table S6, and the  
345 results of SW effluent treatment are displayed in Figure 7. As can be seen, UVB/PDS  
346 system was more effective for PHE decomposition than UVB/H<sub>2</sub>O<sub>2</sub> and UVB alone  
347 for the three SW samples, corroborating our former results with mimic SW samples.  
348 Direct PHE photolysis in the UVB system was less than 10.0% for all the three SW  
349 effluents. The lower efficiency compared with synthetic SW samples (around 23.0%)  
350 could be ascribed to the screening effect of light due to the diverse mixture of  
351 substances in the solution. For UVB/H<sub>2</sub>O<sub>2</sub> or UVB/PDS process the efficiencies of  
352 PHE degradation in the SW effluents from soil 1 and 2 were comparable with those in  
353 the synthetic SW effluents, while for soil 3, the PHE removal efficiency was lower in  
354 both UVB/H<sub>2</sub>O<sub>2</sub> and UVB/PDS systems. In fact, with H<sub>2</sub>O<sub>2</sub>, PHE degradation  
355 efficiencies after 6 h irradiation were 47.5%, 51.6% and 33.5% in soil 1, 2 and 3  
356 respectively. With PDS the removal of PHE achieved around 85.0% for soil 1 and 2  
357 and 78.0% for soil 3.

358 The results of PHE degradation with the three real SW effluents using the two  
359 AOPs validated our previous observations on the mimic SW solutions and the effects  
360 of the main co-existing inorganic species. Moreover, although the intricate mixed  
361 effects of the various soil components in real SW effluent, the PHE oxidation  
362 efficiency with UVB/PDS is similar to the removal in the synthetic solutions,  
363 implying UVB/PDS remains to be the most efficient process for PHE elimination.

#### 364 **4. Conclusion**

365 The results obtained from this study indicate that the UVB based AOPs, e.g.,  
366 UVB/PDS and UVB/H<sub>2</sub>O<sub>2</sub>, can eliminate PHE in both simulated and real SW

367 effluents. The photo-degradation efficiency of PHE is influenced by various  
368 parameters including the concentration of oxidants, initial pH and widespread soil  
369 inorganic anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ ). Opposite results are obtained for the effect  
370 of  $\text{Cl}^-$  for UVB assisted  $\text{H}_2\text{O}_2$  and PDS activation. The presence of  $\text{Cl}^-$  at alkaline pH  
371 inhibits PHE degradation in UVB/ $\text{H}_2\text{O}_2$ , while slightly enhances PHE elimination in  
372 the UVB/PDS process at different pH. The experimental results reveal the negligible  
373 effect of  $\text{HCO}_3^-$  in the UVB/PDS system but negative effect in the UVB/ $\text{H}_2\text{O}_2$  process.  
374 Nitrate has negative effect on the PHE degradation in both AOPs. Overall, the  
375 UVB/PDS process is much more efficient than UVB/ $\text{H}_2\text{O}_2$  due to the formation of  
376 sulfate radical which is less sensitive to the main inorganic ions present in soil, and  
377 could be a promising process to be applied for real SW effluents treatment.

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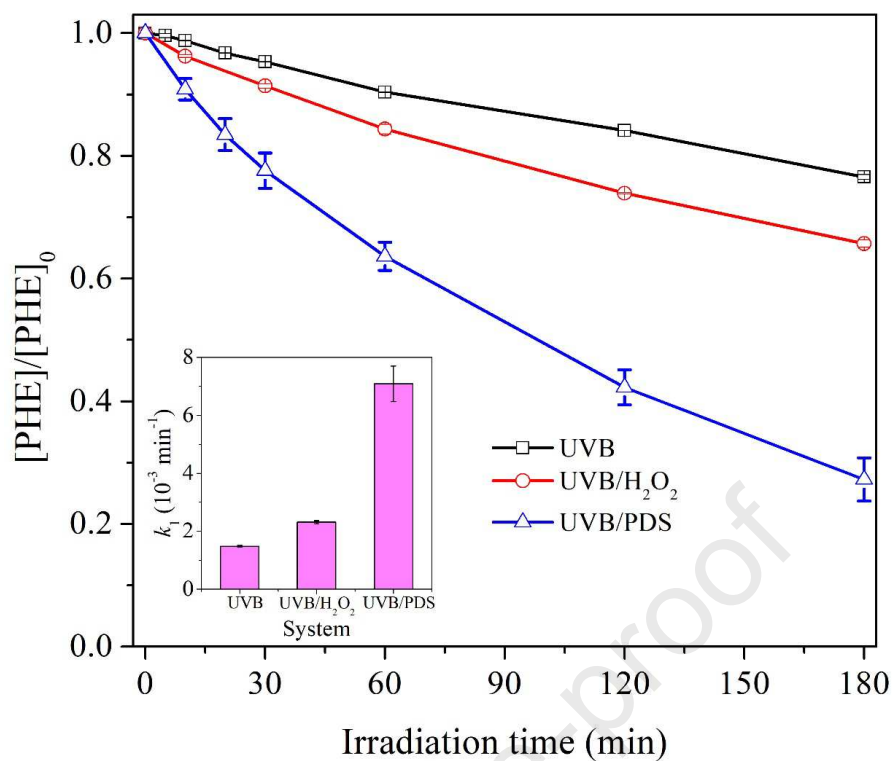
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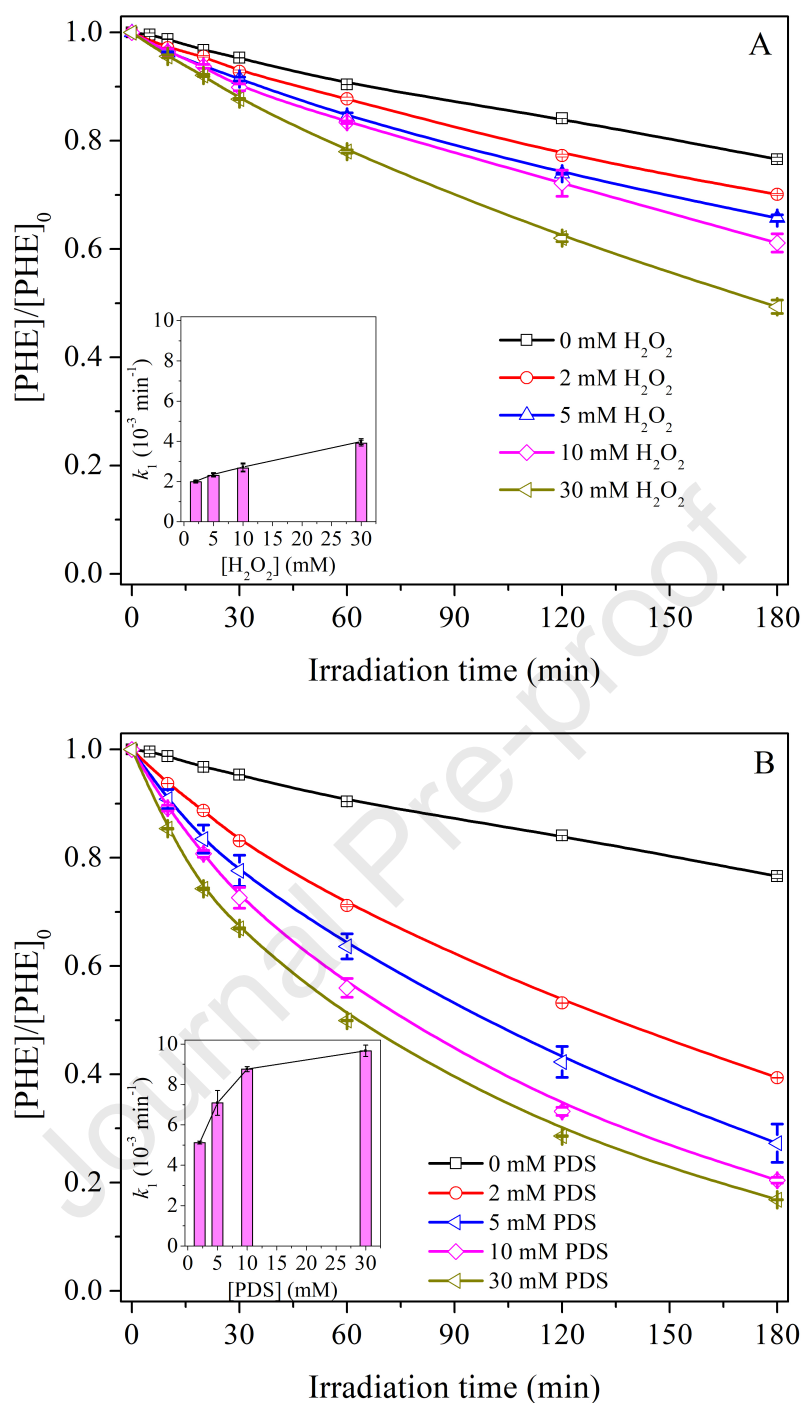
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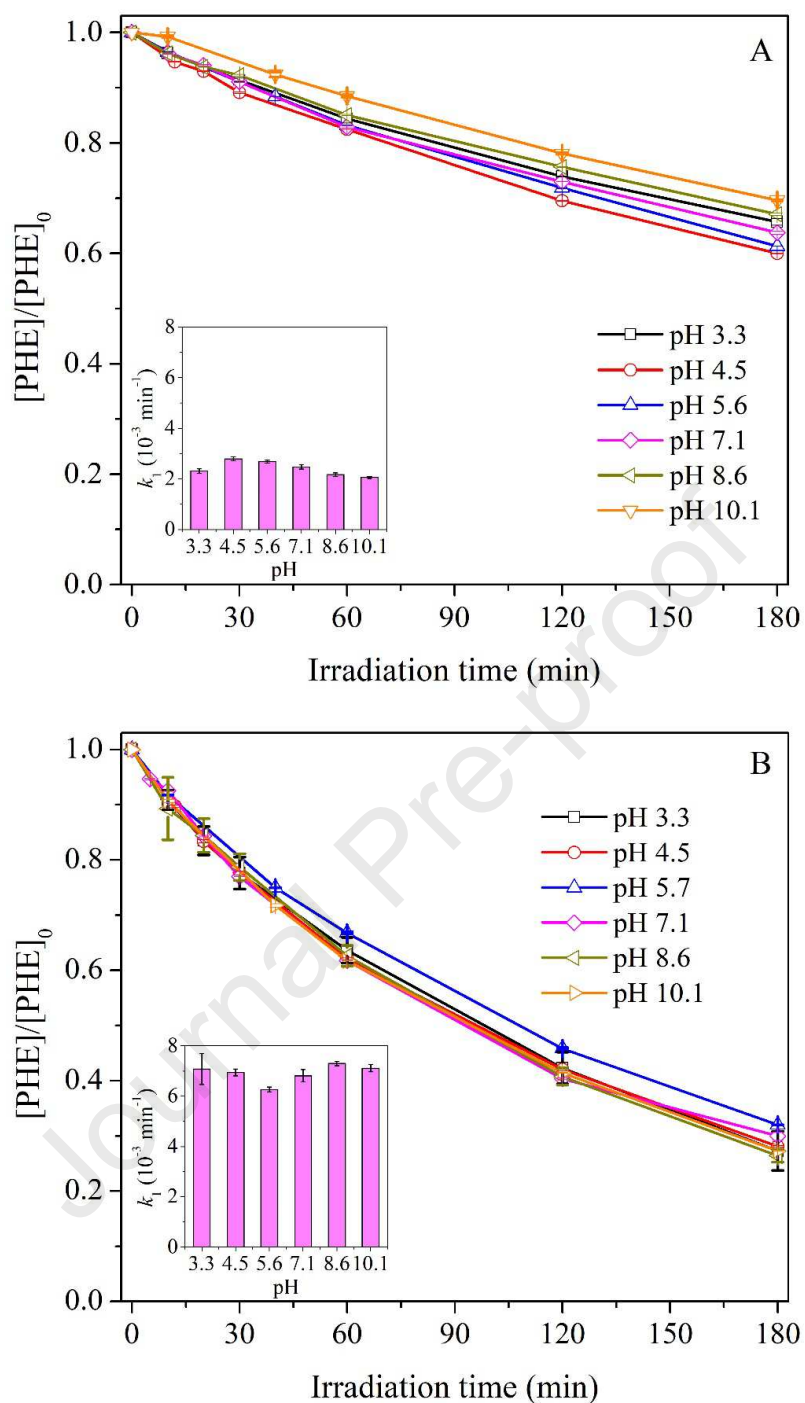


**Figure 1.** Degradation of PHE in the presence of TW80 in different systems. Inserts are the corresponding pseudo-first order rate constants. Initial conditions are  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 3.3 \pm 0.1$ .

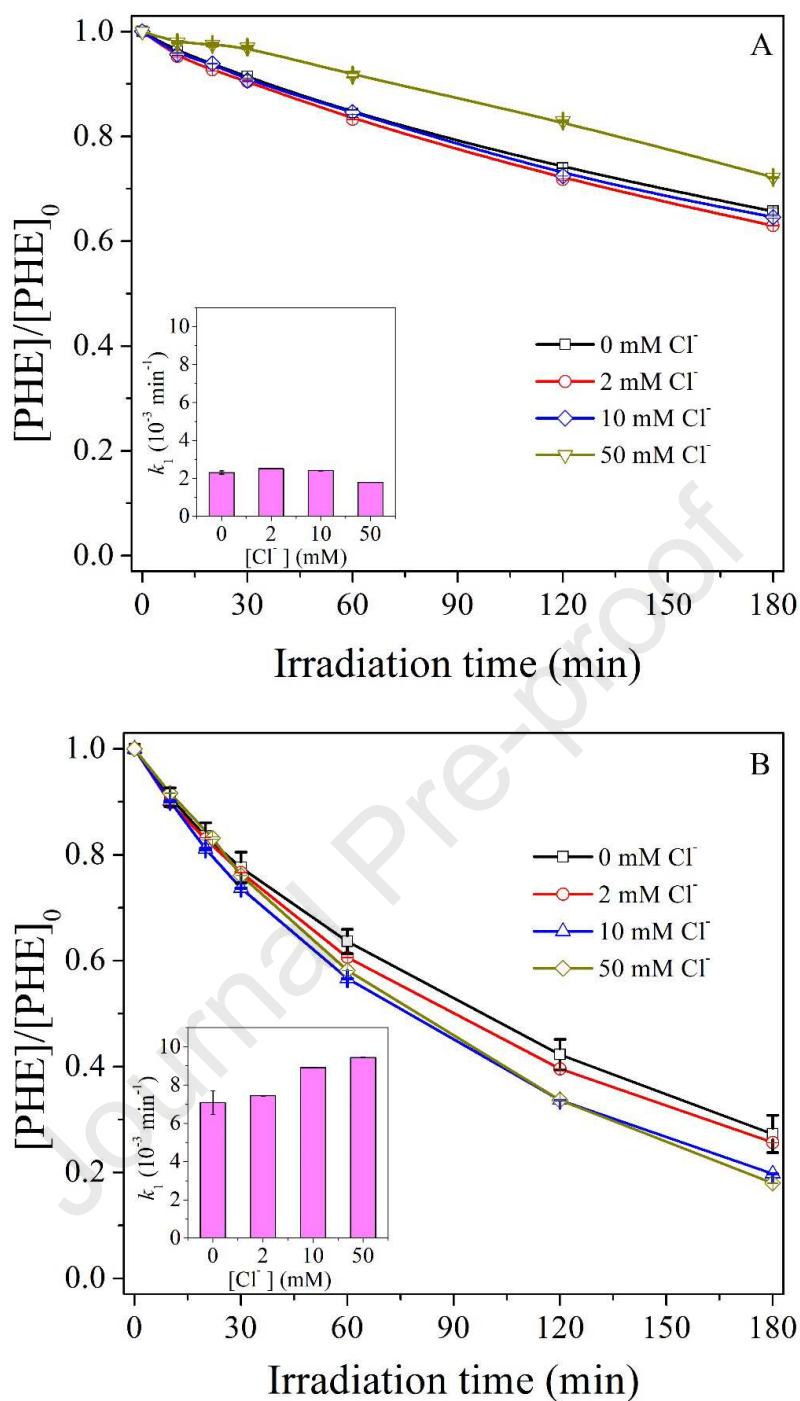


**Figure 2.** Influence of oxidant concentration on the photo-degradation of PHE. Inserts are the corresponding pseudo first order rate constants. A) UVB/H<sub>2</sub>O<sub>2</sub>; B) UVB/PDS.

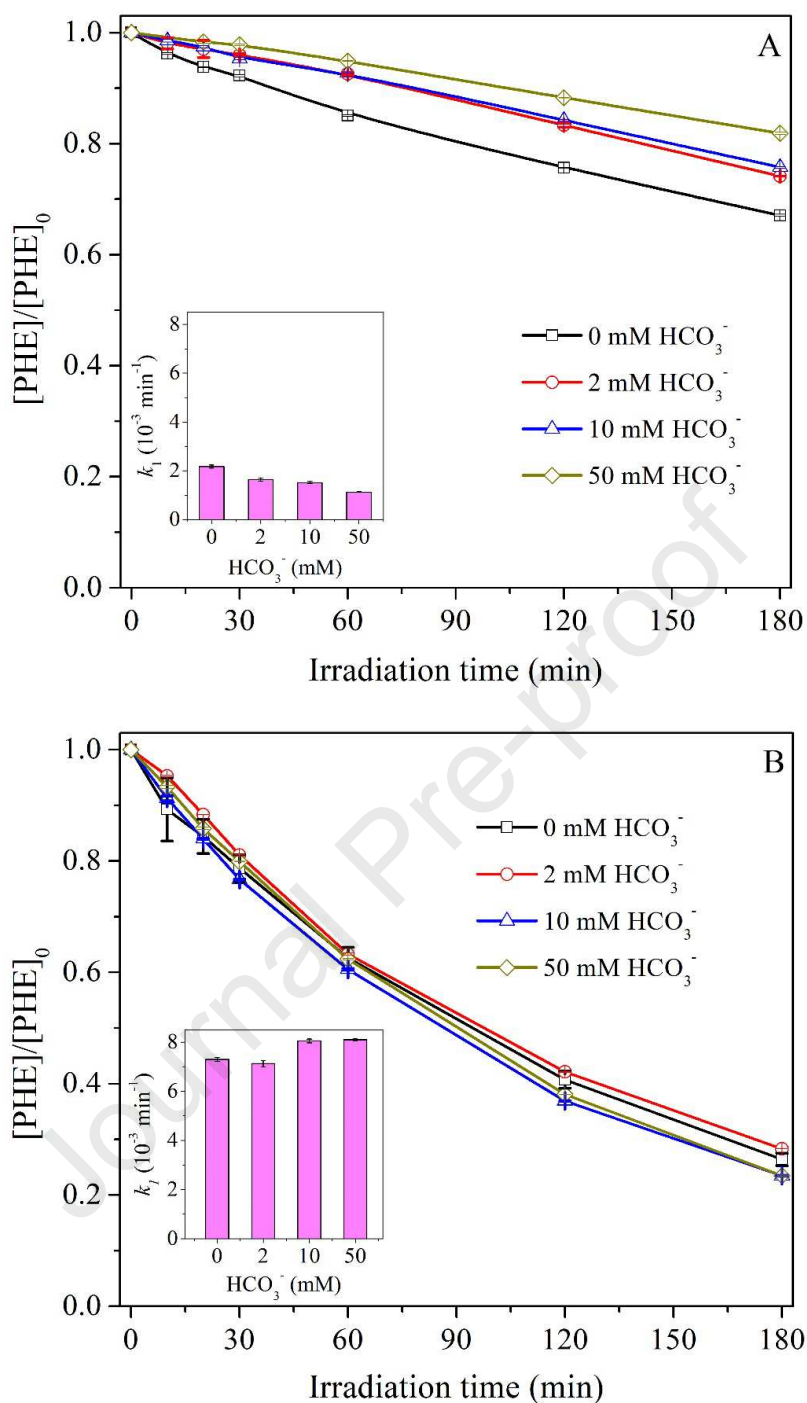
Initial conditions are [PHE] = 10 mg L<sup>-1</sup>, [TW80] = 0.5 g L<sup>-1</sup>, pH 3.3 ± 0.1.



**Figure 3.** Influence of initial solution pH on the photo-degradation of PHE. Inserts are the corresponding pseudo first order rate constants. A) UVB/ $H_2O_2$ ; B) UVB/PDS. Initial conditions are:  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ .

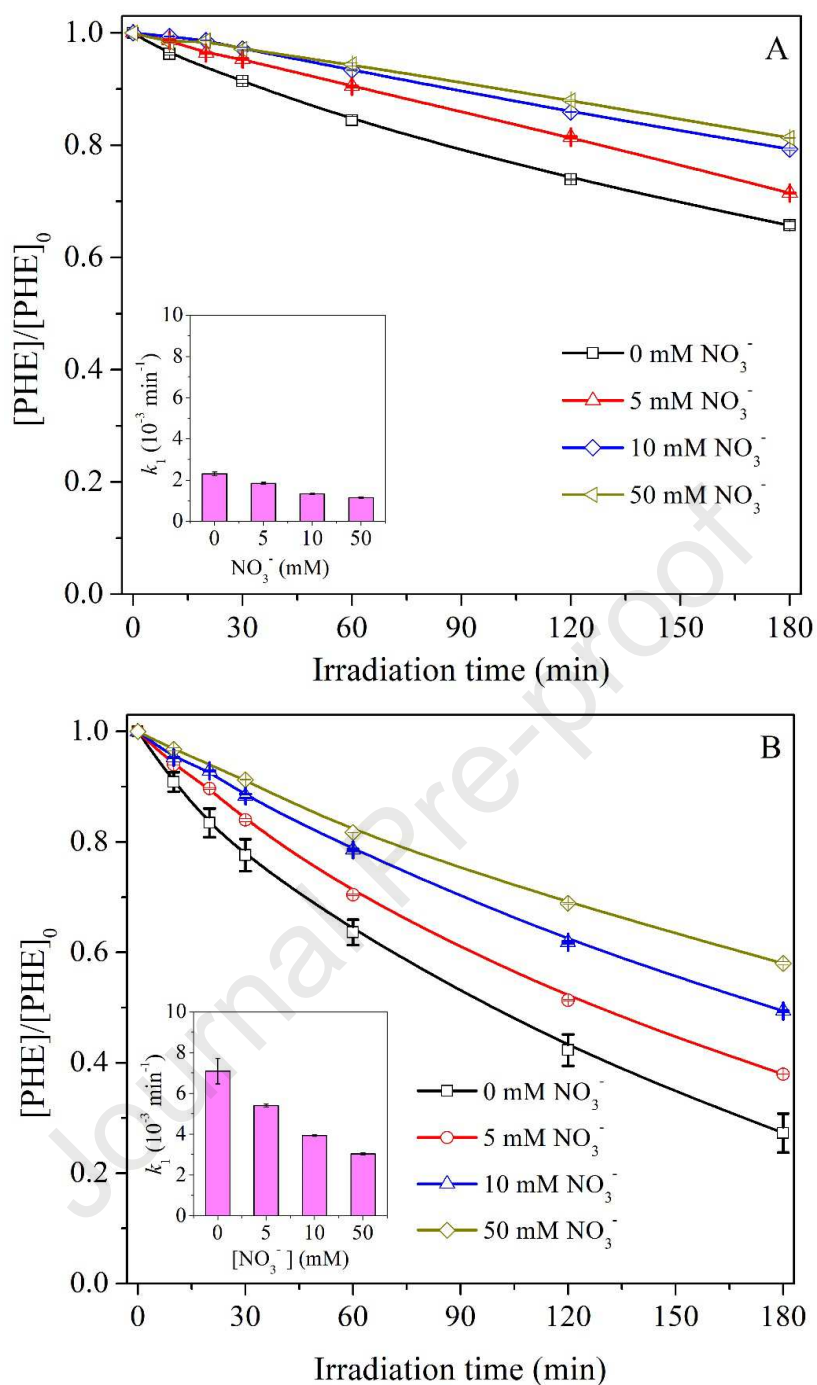


**Figure 4.** Influence of  $Cl^-$  concentration on the photo-degradation of PHE. A) UVB/ $H_2O_2$ ; B) UVB/PDS. Insets are the corresponding first-order rate constants. Initial conditions are:  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 3.3 \pm 0.1$ .

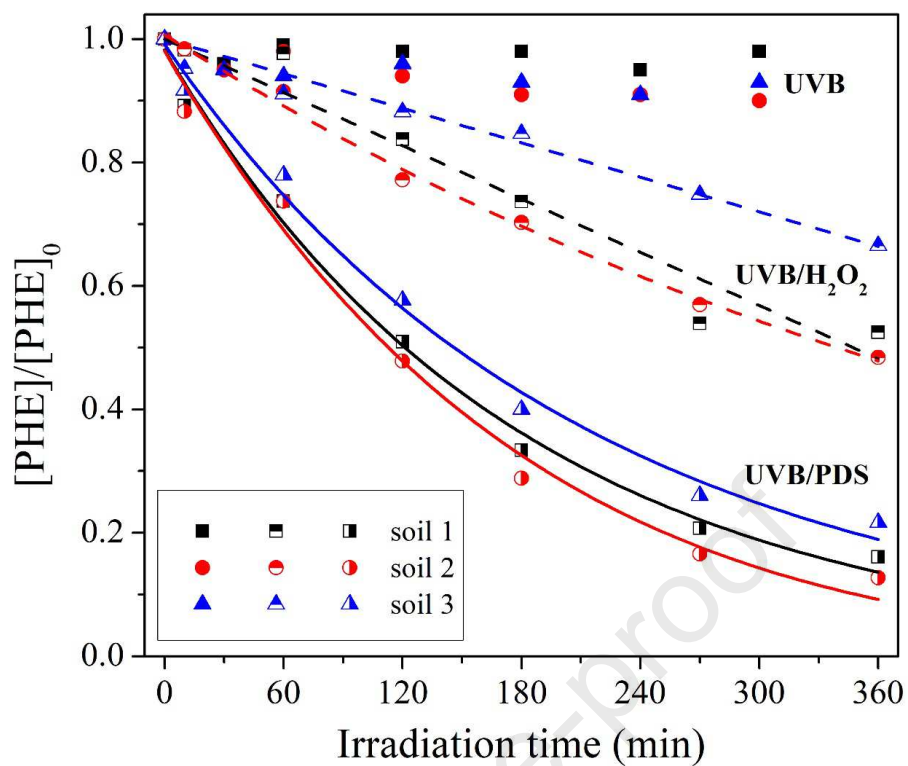


**Figure 5.** Influence of  $\text{HCO}_3^-$  concentration on the photo-degradation of PHE. A) UVB/ $\text{H}_2\text{O}_2$ ; B) UVB/PDS. Insets are the corresponding first-order rate constants. Initial conditions are:  $[\text{PHE}] = 10 \text{ mg L}^{-1}$ ,  $[\text{TW80}] = 0.5 \text{ g L}^{-1}$ ,  $[\text{PDS}] = [\text{H}_2\text{O}_2] = 5 \text{ mM}$ ,  $\text{pH } 8.6 \pm 0.1$ .





**Figure 6.** Influence of  $NO_3^-$  concentration on the photo-degradation of PHE. A) UVB/ $H_2O_2$ ; B) UVB/PDS. Insets are the corresponding first-order rate constants. Initial conditions are:  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 3.3 \pm 0.1$ .



**Figure 7.** Degradation of PHE with three real SW effluents in different systems.

Initial conditions are  $[PDS] = [H_2O_2] = 5$  mM.

### Highlights

- PDS is more efficient than  $\text{H}_2\text{O}_2$  for UVB decay of PHE in soil washing (SW) effluent
- UVB/PDS process is less impacted by the inorganic ions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ )
- UVB/PDS is a promising and sustainable process for real SW effluent treatment

**Figure captions**

**Figure 1.** Degradation of PHE in the presence of TW80 in different systems. Inserts are the corresponding pseudo-first order rate constants. Initial conditions are  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 3.3 \pm 0.1$ .

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**Figure 5.** Influence of  $HCO_3^-$  concentration on the photo-degradation of PHE. A) UVB/ $H_2O_2$ ; B) UVB/PDS. Inserts are the corresponding first-order rate constants. Initial conditions are:  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 8.6 \pm 0.1$ .

**Figure 6.** Influence of  $NO_3^-$  concentration on the photo-degradation of PHE. A) UVB/ $H_2O_2$ ; B) UVB/PDS. Inserts are the corresponding first-order rate constants. Initial conditions are:  $[PHE] = 10 \text{ mg L}^{-1}$ ,  $[TW80] = 0.5 \text{ g L}^{-1}$ ,  $[PDS] = [H_2O_2] = 5 \text{ mM}$ ,  $\text{pH } 3.3 \pm 0.1$ .

**Figure 7.** Degradation of PHE with three real SW effluents in different systems. Initial conditions are  $[PDS] = [H_2O_2] = 5 \text{ mM}$ .