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1 Comparative assessment of a foam-based method for ISCO of coal 2 tar contaminated unsaturated soils

3

4 Iheb Bouzid, Julien Maire, Nicolas Fatin-Rouge*

5 Université de Bourgogne Franche-Comté – Besançon, Institut UTINAM – UMR CNRS 6213, 16,
6 route de Gray, 25030, Besançon, France

7 Corresponding author: Nicolas Fatin-Rouge

8 E-mail: nicolas.fatin-rouge@univ-fcomte.fr

9 Telephone: (+ 33) 03 81 66 20 91

10

11 Abstract:

12 *In situ* delivery of liquid reagents in vadose zone is limited by gravity and soil
13 anisotropy. A new foam-based delivery method of persulfate (PS) solutions in
14 unsaturated soils was previously shown to overcome these limitations. The goal of this
15 paper is to demonstrate the efficiency of this method regarding contaminant removal.
16 Hence, the comparative oxidation of 200 mg.kg⁻¹ coal tar **artificially contaminated soils**
17 with thermally activated PS was carried out after PS-delivery using foam, surfactant
18 solution and pure water. The foam-based method was compared in unfavorable
19 conditions to the reference methods. Especially, in the latter, soil and oxidant solutions
20 were thoroughly mixed to ensure good contact between pollutant and reagent.
21 Degradation kinetics of PS, surfactant and **semi-volatile** hydrocarbons (HCs) were
22 followed. PS-concentration of 9.1 g.kg_{soil}⁻¹, based on the stoichiometric molar ratio
23 between oxidant and HCs, resulted in high HCs oxidation rates (>90%) for the three
24 delivery fluids and degradation rate constants ($k_{obs,HC}$) were calculated. The presence of
25 1%w surfactant led to the decrease of $k_{obs,HC}$ by 10 to 14-times compared to water.
26 However, using the foam-based method, $k_{obs,HC}$ showed intermediate results, being 6 to
27 8-times higher than for the surfactant solution, because of 80% lower surfactant content
28 in soils after PS-injection within foam. This was confirmed through the calculated
29 selectivity of HCs oxidation, which was 38-times higher using foam than for the
30 surfactant solution. Finally, considering the toxicity of leachates from treated soils,
31 lower detrimental effects were observed for the foam-based PS-delivery in contrasts to
32 the reference methods.

33 Keywords:

34 Coal tar contamination; Unsaturated soils; Oxidation selectivity; ISCO; Surfactant foam

35 1. Introduction

36 Soil pollution by petroleum hydrocarbons (HCs) is a worldwide concern, given health
37 and environmental hazards [1]. In France, half of the polluted sites are contaminated by
38 HCs, while PAHs are involved in more than 15% of cases [2]. In particular, the
39 remediation of coal tar contaminated sites is challenging, considering their complex
40 chemical composition, risks associated to hazardous compounds like PAHs and BTEX,
41 and the sticky nature of this dense liquid waste [3,4]. Their presence in contaminated
42 soils and groundwater often result from spillages. Whereas excavation is attractive for
43 the fast remediation of small and heavily contaminated urban areas, it is unsuitable for
44 widespread or low-accessibility contaminations. Hence, *in situ* environmental
45 remediation (ISER) is increasingly used, because of common sense and lower
46 dissemination risks.

47 Existing *in situ* treatment technologies for low to moderately contaminated soils by
48 heavy HCs have limitations. For instance, thermal treatments are limited by high costs
49 due to intense heating [5,6], soil-flushing with extracting agents requires the
50 management and the treatment of large quantities of the recovered effluents [7,8], and
51 biodegradation is often limited by long treatment time, toxicity and the low availability
52 of persistent contaminants like PAHs [9–11]. *In situ* chemical oxidation (ISCO)
53 techniques are promising alternatives to reach high remediation efficiency in relatively
54 short times for an extensive range of contaminants [12–15]. Among the different
55 oxidants used, persulfate (PS) has been increasingly used in recent years [16]. Its
56 advantages are reduced hazards, ease of use, high aqueous solubility, long lasting
57 activity, high selectivity towards aromatic molecules and relatively low cost [17]. It can
58 be activated to generate the powerful sulfate, $\text{SO}_4^{\bullet-}$, and hydroxyl, OH^{\bullet} , radicals (eqs. 1
59 and 2) with standard redox potentials of 2.60 and 2.86 V/SHE, respectively [18].



62 However, ISCO efficiency is limited by the availability in the aqueous phase of heavy HCs
63 strongly **bound** to soil, like PAHs. Hence, coupling treatments that enhance mass transfer
64 in the aqueous phase and destroy HCs, could increase removal efficiencies. For example,
65 coupling ISCO with moderate soil pre-heating (T-ISCO) has already shown promising
66 results [19,20]. Besides, **the use of surfactant** with ISCO (S-ISCO) has shown good results
67 in enhancing the availability and the degradation of contaminants [21–26]. However, the
68 compatibility between surfactants and oxidants must be evaluated to keep surfactant
69 activity, to avoid excessive oxidant consumption by the surfactant, to decrease oxidation
70 selectivity [13,23]. In addition, during the injection of typical water-based solutions,
71 oxidant migration in permeable unsaturated soils is predominantly controlled by gravity
72 [27,28]. This vertical migration leads to low radii of influence and non-uniform
73 distribution of oxidant around the injection points, limiting oxidant contact with the
74 targeted contaminant [29–32]. To overcome challenges associated to non-uniform
75 delivery, high viscosity and shear-thinning fluids can be used. Currently, one of the most
76 promising soil remediation technologies involves the use of surfactant foam [32–38].
77 Surfactant foam in porous media appears as trains of gas bubbles separated by a
78 continuous thin liquid films (lamellae) stabilized by surfactant. The lamellae rest at pore
79 throats and they must stretch to go through pores or break, opposing resistance to gas
80 flow. This gives to the foam an important apparent viscosity and diverts flow from big
81 pores to smaller ones. Because of its high viscosity, foam propagation is less affected by
82 gravity and soil anisotropy conversely to traditional water-based fluids.

83 In our previous works, a novel surfactant foam-based method of active solutions
84 delivery was shown to strongly improve the distribution of PS and its residence time
85 into contaminated unsaturated soils [32]. However, the assessment of the method in
86 terms of treatment efficiency was not reported yet. Hence, in this work, we compared
87 the treatment of a coal tar-contaminated soil by thermally activated PS, whether
88 delivered using the developed foam-based method, water or surfactant solutions.
89 Degradation kinetics of PS, surfactant and HCs were carried out and completed by
90 amounting the selectivity of HCs oxidation and assessing biodegradability of soil
91 leachates after oxidation. Only few studies compared the remedial activity of
92 amendments carried using water, surfactant and foam in contaminated materials,
93 namely nanoscale zero-valent iron for DDT degradation and calcium polysulfide for
94 metals stabilization [30,38,39]. In particular, the comparative oxidation of HCs

95 contaminated soils using PS delivered by water, surfactant and this innovative foam-
96 based method was never reported. This works aims to demonstrate the benefiting
97 effects in terms of controlled reaction of this new technology.

98 2. Materials and Methods

99 2.1. Chemicals

100 The zwitterionic Lauryl betaine surfactant (S) was used, as previously reported
101 [13,32]. The contaminant was a liquid coal tar collected from a former **steelwork**
102 **industrial site in Romania (Hunedoara) whose composition is provided in Table SM.1.**
103 Sodium persulfate (>96%, Fisher Scientific) was used as oxidant. Analytical reagents
104 were dichloromethane (>99%, Fisher), n-hexane (99%, VWR), chloroform (99%, Acros
105 Organics), hydrochloric acid (37%), alizarinesulfonic acid (MERCK), iodide and
106 potassium iodide (99.9%, Fisher). All solutions were prepared with deionized water.
107 Compressed air was provided by Air Liquide.

108 2.2. Contaminated soil

109 Clean sandy soil locally sourced was artificially contaminated. First, it was sieved to
110 collect a fraction having a D₁₀-D₉₀ of 244 and 1113 μm , respectively. D₁₀ and D₉₀
111 correspond to the 10th and 90th percentile of grain size distribution, respectively.
112 **Permeability of the soil was 90 μm^2 . It was measured using the constant head technique**
113 **according to Fireman [40]. The porosity of the soil was 36% as measured by weighing**
114 **the column before and after filling it with water to determine the porous volume (PV) of**
115 **the soil sample. The soil pH was 7.4, it had no organic matter and it was initially dry. The**
116 **preparation of the contaminated soil was as follows: First, 0.46 g of coal tar was**
117 **dissolved in 150 ml dichloromethane. Then, the solution was mixed with 1 kg of dry soil**
118 **in a glass flask for 30 min. After that the soil was layered onto a large Teflon sheet and**
119 **let to dry in the open air under a fuming hood until the soil bulk density was constant.**
120 **The contaminated soil was collected in sealed glass flasks and stored upside-down to**
121 **avoid hydrocarbon volatilization. Finally, the contaminated soil was characterized by its**
122 **C10-C40 total petroleum hydrocarbon index (TPH, $200 \pm 14 \text{ mg.kg}_{\text{soil}}^{-1}$) and the sum of**
123 **the 16 US PAHs concentrations ($43.7 \pm 3.3 \text{ mg.kg}_{\text{soil}}^{-1}$). This lower contamination level**
124 was chosen to not penalize the efficiency of traditional water-based delivery methods,

125 since the contaminated soil remained hydrophilic (measured contact angle at the
126 air/water/soil interface was 0°), and to avoid high oxidant doses. Table SM.2 presents
127 details about the contaminated soil.

128

129 2.3. Experimental set-up

130 PS was delivered in three forms: solubilized in pure water (W-PS), in surfactant
131 solution (S-PS, $C_{S,0} = 10 \text{ g.L}^{-1}$ in water), or as solution in water delivered after foam
132 injection (F-PS). W-PS and S-PS experiments were performed in stirred glass batch
133 reactors with approximately 290 g of dry contaminated soil, to maximize the contact
134 between the oxidizing solution and the contaminated soil. F-PS experiments were
135 carried out in vertical glass columns (length: 18 cm high and i.d.: 3.6 cm, Fig.1). The
136 same mass of soil was put into the column and was compacted using a rubber stick while
137 filling. All column oxidation experiments were started under unsaturated conditions.

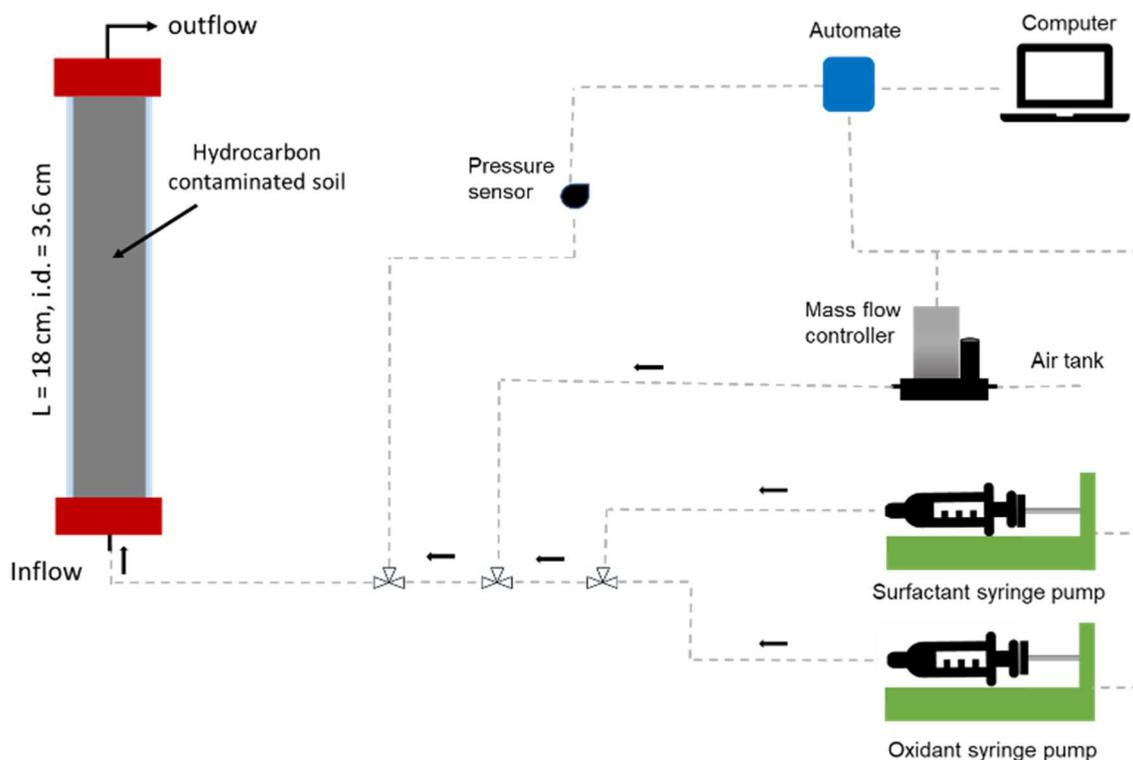


Figure 1. Scheme of the experimental set-up for F-PS experiments in vertical columns.

138 2.4. Injection procedures and treatments

139 For W-PS and S-PS, 1 PV (34 mL) of oxidant solution was mixed thoroughly with the
140 soil in batch reactor. For F-PS experiments, first, foam was injected using the solution
141 alternating gas method (SAG), where slugs of air and surfactant solution were injected in
142 alternation. SAG was selected since it provides injection pressures compatible with field
143 works, considering soils with such permeability [34,35]. Flow rates and volumes per
144 cycle were 70 and 2 ml.min⁻¹ and 5 and 0.2 ml for gas and surfactant solution,
145 respectively. A pressure limit was set at 100 kPa.m⁻¹ for injection to avoid soil fracturing
146 or heaving in field conditions [41]. Then after the foam filled the soil, the PS solution in
147 pure water was injected (0.5 ml.min⁻¹) to replace the surfactant solution in foam
148 lamellae [32]. The volume of PS solution injected was the one necessary to push the
149 surfactant solution from the foam's water network. This volume was estimated to be
150 about 0.3 PV considering that water saturation after foam injection is 30%.

151 In all cases, after PS was injected, the contaminated soil was quickly transferred in
152 glass bottles and let at 60 °C in a thermostated water bath (Polystat, Bioblock Scientific)
153 for PS activation and kinetic measurements.

154 2.5. Persulfate doses

155 Estimating the optimal dose of oxidant is crucial for successful completion of ISCO. The
156 estimated dose is based on the mass of oxidant theoretically required to mineralize the
157 target pollutant [42,43]. Here, the coal tar is a complex mixture of many HCs. Thus, the
158 oxidant dose was estimated from the stoichiometric molar ratio (SMR) between PS and
159 benzene, considering the latter representative of the coal tar, as previously done [44].
160 The mineralization of benzene by PS follows eq. 3:



162 Four doses were assessed: 1 SMR (PS1), 3 SMR (PS3), 8 SMR (PS8) and 13 SMR (PS13).
163 The aqueous PS-concentration required to deliver each dose was calculated using soil
164 mass, density, porosity, and its HCs concentration. PS13 was the maximal concentration
165 that could be delivered by water and surfactant solutions because of PS solubility limit.
166 For F-PS experiments, in order to deliver the same amounts of oxidant into the soil, the
167 final water saturation was considered when calculating aqueous PS-concentrations to be
168 delivered in one dose. Hence, PS-concentrations were higher to deliver the same
169 amount, and only 1 and 3 SMR (PS1 and PS3) could be carried out below solubility limit.

170 Four control experiments without oxidant using water (W), surfactant solution (S), and
 171 foam (F) as fluids were also performed at 60 °C. Table 1 summarizes the conditions of
 172 the experiments.

173 Table 1: Summary of the oxidation experiments carried out on the contaminated soil
 174 using heat-activated PS at 60 °C.

Experiment	Delivery method	PS concentration		Surfactant concentration (g.L ⁻¹)
		g.kg _{soil} ⁻¹	g.L ⁻¹	
W	Water	0	0	0
W-PS1	Water	9.1	41.8	0
W-PS3	Water	27.4	125.3	0
W-PS8	Water	73.1	334.2	0
W-PS13	Water	119.0	544.0	0
S	S solution	0	0	10
S-PS1	S solution	9.1	41.8	10
S-PS3	S solution	27.4	125.3	10
S-PS8	S solution	73.1	334.2	10
S-PS13	S solution	119.0	544.0	10
F	Water in foam	0	0	10
F-PS1	Water in foam	9.1	139.3	10
F-PS3	Water in foam	27.4	417.8	10

175

176 2.6. Analytical measurements

177 2.6.1. Persulfate, surfactant and hydrocarbon analysis

178 PS and surfactant concentrations were measured daily until the oxidant was totally
 179 consumed. Procedure was as follows: 10 g of soil were sampled from each bottle, then
 180 placed in 250 mL flasks with 100 mL deionized water. Flasks were then shaken using an
 181 orbital shaker (300 rpm) for 30 minutes to extract PS and surfactant [45]. Samples were
 182 then filtered, and filtrates were analyzed. Surfactant concentrations were measured as
 183 previously reported [13]. PS-concentrations were determined accordingly to Liang [46].
 184 For TPH index and PAHs measurements, 25 g of soil were extracted three times at room

185 temperature using n-hexane. Measured TPH were obtained according to the NF EN ISO
186 9377-2 analysis as follows: 50 μL of the extracts were analyzed by GC/FID (Thermo
187 Trace 1300, VF Select Mineral Oil 15 m capillary column with 0.32 mm i.d., film diameter
188 0.10 μm) and the quantification was carried out by external calibration using a certified
189 standard. PAHs were determined according to the XPX33-012 method as follows: 1 μL of
190 the extracts were injected at 300°C and analyzed by GC/MS (Perkin Elmer Clarus 580
191 GC, Clarus 580/ SQ8S, Rxi-5Sil MS 30 m capillary column with i.d. 0.25 mm, film
192 diameter 0.25 μm , quantification range: 5–50 ppb) using single ion monitoring.

193 2.6.2. Kinetic analysis

194 PS and surfactant disappearance and HCs loss kinetics followed a pseudo-first-order
195 rate law [47,48]. Pseudo first-order oxidation rate constants (h^{-1}) for PS ($k_{\text{obs,PS}}$),
196 surfactant ($k_{\text{obs,S}}$) and HCs ($k_{\text{obs,HC}}$) at 60 °C were then obtained by linear fitting of
197 concentrations vs. time using eq.4:

$$198 \quad \text{Ln} \frac{C}{C_0} = -k_{\text{obs}} t \quad (4)$$

199 Where C and C_0 are the concentrations of PS, surfactant or HCs at time t and initially,
200 respectively.

201 2.6.3. Selectivity calculation

202 The selectivity of HCs oxidation at 60 °C was calculated as follows [13]:

$$203 \quad \text{Selectivity} = \frac{k_{\text{obs,HC}}}{k_{\text{obs,S}}} \quad (5)$$

204 It illustrates the preferential degradation of HCs over surfactant.

205 2.6.4. Biodegradability assays

206 The biodegradability of soil leachates after oxidation was assessed through the ratio
207 between Chemical Oxidant demand (COD) and Biochemical Oxygen Demand (BOD)
208 measured at 5 days. Those parameters were measured according to standards ISO
209 15705 and NF EN 1899-2, respectively, by an accredited lab. Limits of quantification
210 were 4 and 0.2 ppm for COD and BOD measurements, respectively. The leaching was
211 carried out after 70 h oxidation at 60 °C, as follows: 10 g of soil were sampled from each
212 reactor, then placed in 250 mL flasks with 100 mL deionized water. Flasks were then

213 shaken for 12 h before filtrates (Whatman paper grade 303) were collected and kept at 4
214 °C until rapid determinations.

215

216 3. Results and discussions

217 3.1. Degradation kinetics

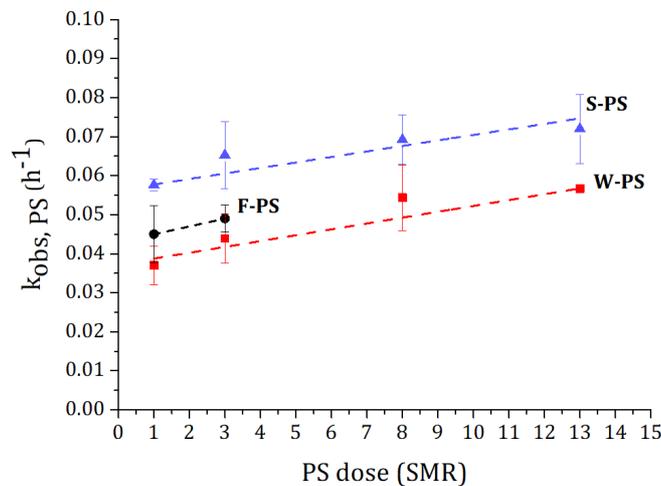
218 All components, namely PS, surfactant and HCs, displayed exponential decrease vs.
219 time after being contacted (see Figs SM.1 to SM.3). For the three methods studied, the
220 oxidant was totally consumed within approximately 70 h. Variations of apparent rate
221 constants for degradation kinetics of PS and surfactant as a function of oxidant doses in
222 W-PS, S-PS and F-PS experiments are presented in Fig.2. When delivering PS in water,
223 $k_{obs,PS}$ were the lowest, since coal tar was the only organic component to be oxidized
224 considering the low content of natural organic matter in soil. The addition of surfactant
225 had a moderate effect on PS loss (Fig.2a). In fact, surfactant increased the oxidant
226 demand and accelerated PS decomposition by an average of 1.4 and 1.1-times for S-PS
227 and F-PS, respectively, as previously reported [13,17,47,49,50]. The slower PS
228 degradation for the foam-based method is explained by the fact that the injection of PS
229 in water after foam injection removed the foaming surfactant solution from the soil as
230 shown in Bouzid [32]. Hence, only about 20% of the initial surfactant concentration used
231 to generate foam was still present in soil after PS injection. Not all surfactant was
232 removed, because of adsorption at interfaces and by-passing phenomena in the porous
233 medium [51,52]. For example, for 1 SMR, apparent rate constants for PS were 0.036,
234 0.043 and 0.057 h⁻¹ for the W-PS, F-PS and S-PS methods, respectively. These values are
235 consistent with previous reports of activated-PS decomposition values in presence of
236 various organic compounds, ranging from 0.02 to 0.1 h⁻¹ [13,17,47,49,50].

237 In absence of oxidant, surfactant concentrations **decreased** slightly due to its sorption
238 onto soil (Fig. SM.2). Increasing PS-concentration slightly increased $k_{obs,PS}$ and $k_{obs,S}$
239 values (Fig. 2), because it promotes more reactive oxygen species generation in solution
240 (*i.e.* S₂O₈²⁻, SO₄^{•-} and HO[•]) as reported [13,17,21,53,54]. However, $k_{obs,PS}$ increased by 1.3-
241 times only for the three systems. PS-degradation rate constants showed a good linear fit
242 with initial PS-concentrations according to:

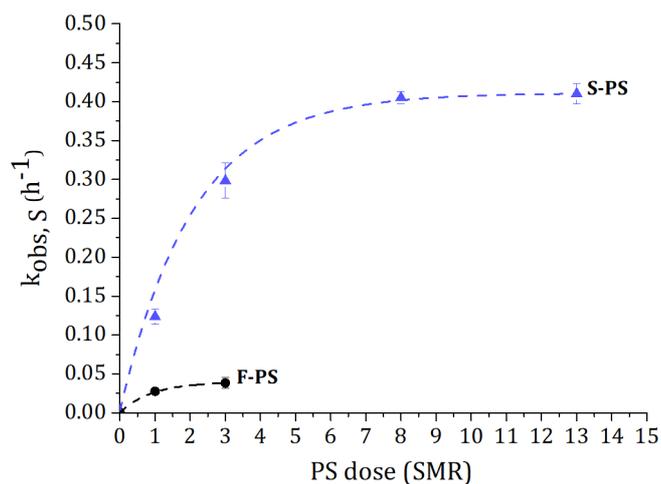
$$243 \quad k_{obs,PS} = 1.4 \times 10^{-4} [PS] + k_{0,PS} \quad (6)$$

244 with the slope being unchanged and independent on PS-delivery method. The slope
 245 increases with temperature as previously reported [55]. The coefficient $k_{0,PS}$ represents
 246 the rate constant for PS self-degradation at 60 °C, and amounted to 0.038 ± 0.002 ,
 247 0.044 ± 0.003 and 0.052 ± 0.008 h⁻¹ for W-PS, F-PS and S-PS methods. Considering that in
 248 the F-PS method, only 20% of the initial amount of surfactant was still present after PS-
 249 injection, a linear correlation was found between $k_{0,PS}$ and the surfactant concentration
 250 in soil pore water. The observations obtained from these experiments suggest that
 251 dissolved organic matter increases self-degradation of PS in agreement with previous
 252 reports [55]. Hence, in the F-PS method, the deleterious presence of surfactant on PS
 253 self-degradation rate constant is much lower than for the usual S-PS method.

254 The decreased value for $k_{obs,S}$ by 5 to 10-times when foam was used is explained by the
 255 lower surfactant concentration in soil, since 80% was removed when PS solution was
 256 injected through foam lamellae [56]. Nevertheless, surfactant degradation rate constants
 257 reached a plateau at 8 SMR. Indeed, a large number of free radicals should be generated,
 258 they might act as scavengers for $S_2O_8^{2-}$ or $SO_4^{\bullet-}$ with high reaction rates [13,57,58].



a



b

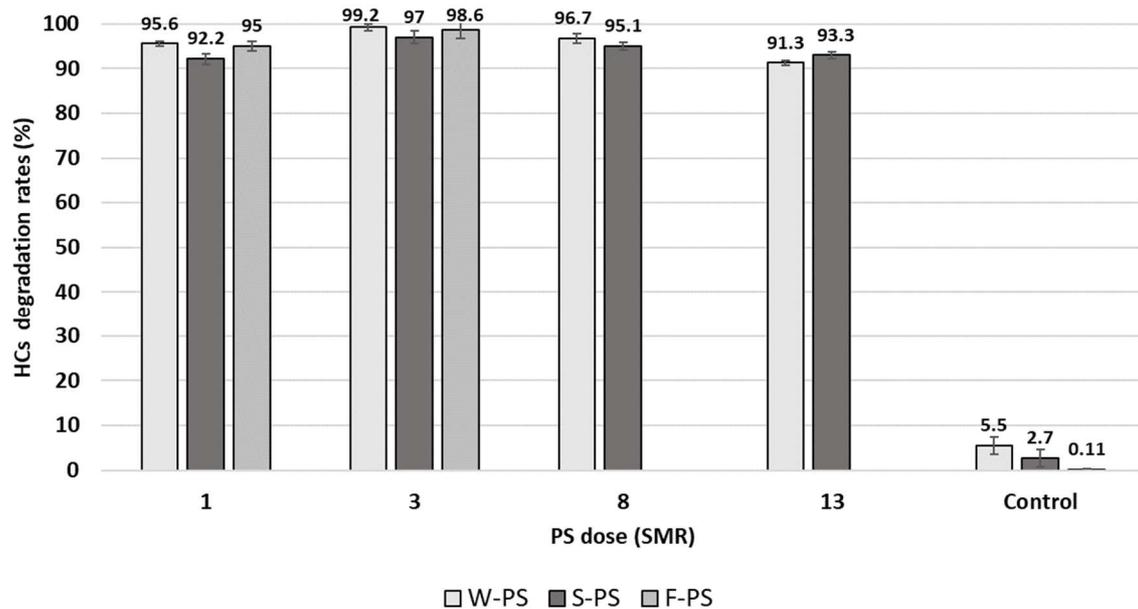
259 Figure 2. Evolution of persulfate (a) and surfactant (b) degradation rate constants
 260 (k_{obs}) at different initial doses of persulfate using W-PS (◻), S-PS (▲) and F-PS (●)
 261 methods of delivery. Experimental conditions: $C_{s,0} = 10 \text{ g.L}^{-1}$, $T: 60 \text{ }^\circ\text{C}$.

262 HCs degradation kinetics conducted using W-PS, S-PS and F-PS methods showed that
 263 only small fractions of HCs were removed in absence of oxidant (Fig. SM.3). HCs
 264 degradation rates for different SMR-values using the different methods are reported in
 265 Fig. 3. Their values in control experiments increased in the order: foam (0.11%) <
 266 surfactant (2.70%) < water (5.50%). This trend is explained as follows: in absence of
 267 surfactant, a bigger fraction of volatile HCs was released in the gas phase. In presence of
 268 surfactant, this volatile HCs were better stabilized by micelles in pore water, decreasing
 269 their volatilization [59]. With foam, the stabilizing effect of surfactant was even stronger,
 270 since gas bubbles trapped into the soil hindered HCs volatilization.

271 **After 70 h of contact** with oxidant, HCs degradation rates were higher than 91% for all
 272 methods and PS doses (Fig.3). For 1 and 3 SMR values, removal rates for HCs were above
 273 92%, showing that SMR estimation was correct; They display the same trend and
 274 followed the order W-PS > F-PS > S-PS. **Considering W-PS and S-PS, the average residual**
 275 **TPH indices after oxidation were low and equal to 8.6 and 11.2 mg.kg⁻¹, respectively. The**
 276 **difference in HCs concentrations at the bottom and the top of the column for F-PS**
 277 **experiments were not significant, since the average HCs degradation rate for the tested**
 278 **PS-concentration was high and equal to 95.9 ± 1.13%, corresponding to an average**
 279 **residual TPH index of 8 mg.kg⁻¹.** The lower HCs removal in presence of highly
 280 concentrated surfactant (10 g.L⁻¹) was explained by its protective effect towards HCs

281 oxidation [13,23,60,61]. This effect hindered the efficient contact between PS and HCs
282 and led to non-productive oxidant consumption. Increasing PS-concentrations above 3
283 SMR decreased HCs oxidation rates by 5 and 3% for W-PS and S-PS methods,
284 respectively. This was explained by the radical scavenging effect mentioned previously
285 (see § 3.1).

286



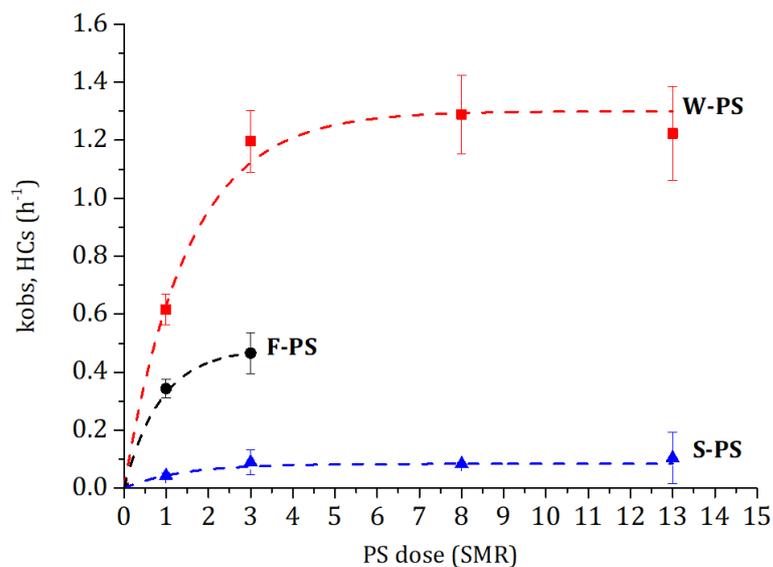
287 Figure 3. HCs degradation rates at different initial dose of persulfate using the
288 compared delivery methods.

289 In this work, the contaminated soil was hydrophilic and mixed before activation for W-
290 PS and S-PS experiments; Hence contact between PS and contaminant was maximal,
291 leading to high oxidation efficiencies even for water. Considering hydrophobic
292 contaminated soil ($\text{coal tar} \geq 1 \text{ g.kg}_{\text{soil}}^{-1}$), the conditions would not be so favorable for
293 the usual methods of delivery [32,38,62]. Hence even though foam delivered in similar
294 proportion than water in those conditions, the gains are expected to be higher in
295 hydrophobic conditions, because oxidation by water-delivered PS is expected to be bad.
296 Indeed, for hydrophobic soils, foam decreases interfacial tension at the solid/liquid
297 interface and inverts the soil wettability due to the presence of surfactant [63,64]. In
298 addition, foam propagates much more homogeneously into soils due to its low density,
299 high viscosity and shear-thinning behavior, leading to uniform contact between the
300 remedial reagent and the contaminated zone [31,32,38,65]. Conversely, the low viscosity

301 water-based solutions tend to migrate vertically especially in vadose, leading to low
302 radii of influence around the injection points and non-uniform propagation of remedial
303 reagents [30–32]. Hence, the most important thing in that experiments is that despite
304 adverse comparative conditions, the foam-based method did not show any detrimental
305 effect regarding the oxidation of HCs. Even more, it showed better efficiency than S-ISCO
306 carried out using thoroughly mixing of soil, surfactant and oxidant solution.

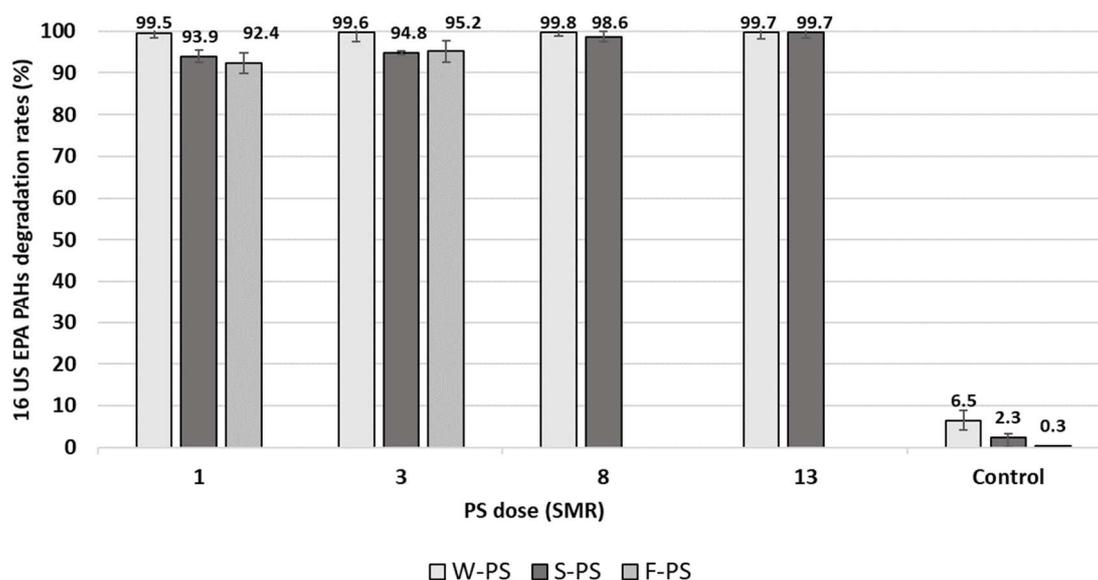
307 Fig.4 illustrates the evolution of $k_{obs,HC}$ for the compared methods at different PS doses.
308 Using the W-PS method, degradation rate constants were the highest, because the
309 availability of HCs in this low contaminated hydrophilic soil and the absence of
310 protective micelles of surfactant. Considering all the injection methods, degradation rate
311 constants increased rapidly with the PS-dose until it reached a plateau at 3 SMR,
312 confirming the radicals scavenging effect discussed earlier. Using the S-PS method,
313 degradation rate constants dropped down significantly compared to the W-PS method.
314 For instance, HCs were degraded 14-times slower for PS-concentrations above 3 SMR,
315 when oxidant was delivered using the S-PS method rather than the W-PS one. The
316 slower HCs degradation rate constants were caused by the protective effect of micelles.
317 Intermediate rate constants were observed using the F-PS method, as observed for PS
318 degradation kinetics (Fig.2a). This behavior is explained by the 80% surfactant removal
319 observed after the injection of aqueous PS through the foam network. Hence, surfactant
320 detrimental effect was not so dramatic, since HCs degradation rate constants using F-PS
321 were only 1.8 and 2.5-times lower than those using the W-PS method for 1 and 3 SMR,
322 respectively.

323



324 Figure 4. Evolution of hydrocarbons degradation rate constants ($k_{obs,HC}$) at different
 325 initial dose of persulfate using W-PS (■), S-PS (▲) and F-PS (●) methods. Experimental
 326 conditions: $C_{s,0} = 10 \text{ g.L}^{-1}$, $T: 60 \text{ }^{\circ}\text{C}$.

327 Considering the sum of the 16 US PAHs, similar results to those of HCs oxidation were
 328 observed. All oxidant doses and delivery methods resulted in removal efficiencies larger
 329 than 92% (Fig.5). All PAHs (rings number from 2 to 6) were strongly removed, showing
 330 no effect of their chemical structure. However, PAHs are known to be tightly bound to
 331 soil matrix, leading to different degradation rates between light and heavy PAHs [66].
 332 Nevertheless, considering the low contamination level of the fresh contamination (1
 333 week), the hydrophilic nature of the contaminated soil and its low content in carbonates
 334 and organic matter, this result is not surprising.



335 Figure 5. Removal rates for the sum of the 16 US PAHs at different initial doses of
 336 persulfate using the delivery methods.

337 Even though degradation rates can be considered very satisfying, a slight difference
 338 was observed between PS delivered using the different methods. However, considering
 339 control samples and standard deviations for measurements, the degradation rates were
 340 the same regardless the injection method (92.3 ± 0.7 and 93.5 ± 1.2 for 1 and 3 SMR-
 341 values, respectively). Overall, for all the oxidation experiments, residual PAHs
 342 concentrations were lower than 4 mg.kg^{-1} . **Table SM.3 summarizes the residual PAHs**
 343 **concentrations in soil after oxidation using the F-PS method.** Control samples show that
 344 a volatile fraction consisting essentially of naphthalene (48%) and phenanthrene (11%)
 345 was removed from the matrix during the experiments. This loss amounted from 6.5 to
 346 0.3% of the overall PAHs content with the order W-PS > S-PS > F-PS. This shows that
 347 matrix disaggregation during mixing for W-PS and S-PS encouraged volatilization in
 348 contrast to the F-PS method. In the latter, the foam prevented the release of HCs in the
 349 gas phase because there was no free running gas in that matrices.

350 3.2. Selectivity of the hydrocarbons oxidation in presence of 351 surfactant

352 Considering the calculated selectivity of the HCs oxidation, increasing PS-
 353 concentrations had no significant effect (0.33 ± 0.02 and 12.31 ± 0.19 for S-PS and F-PS
 354 methods, respectively), in agreement with previous report [13]. However, the sequential

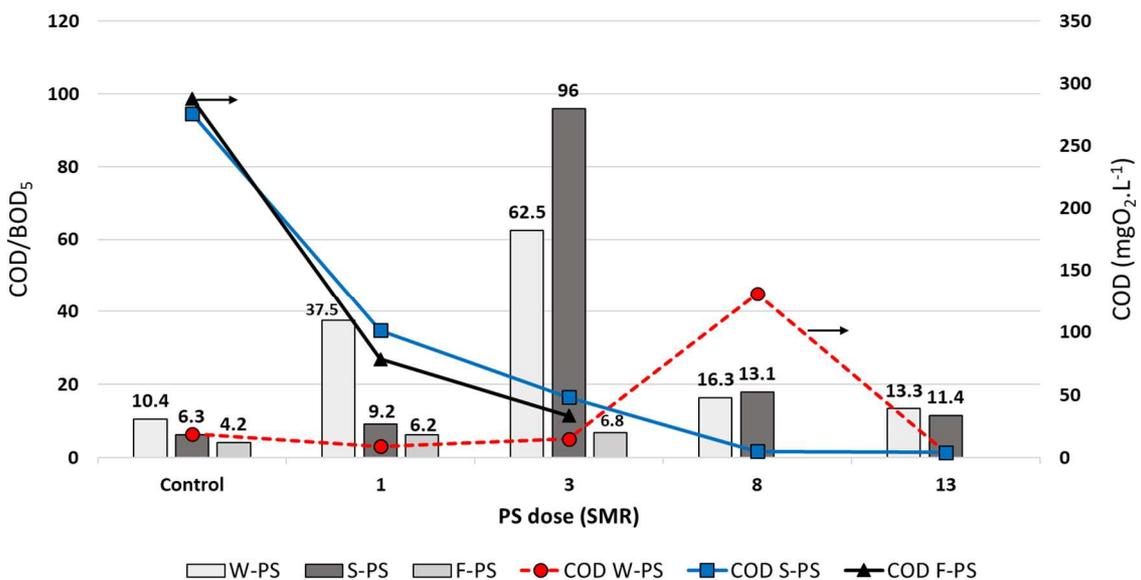
355 delivery of PS using the F-PS method improved the oxidation selectivity by 38-times, as
356 expected by the 80% surfactant removal from soil pores (section 3.1).

357

358 3.3. Biodegradability assays

359 The continuation of the treatment using bioremediation after ISCO is expected to
360 reduce remediation costs and deleterious side effects, since the generation of toxic and
361 stable metabolites during ISCO is an issue [67]. Considering the above-mentioned
362 strategy, *i.e.* HCs pre-oxidation followed by biological treatment of the by-products, the
363 assessment of their biodegradability is essential. Hence, the biodegradability of soil
364 leachates, obtained from the untreated soil or after the use of the compared oxidation
365 methods, were estimated considering COD to BOD ratios (Fig.6 and Table SM.4).

366



367 Figure 6. Biodegradability (bars) and COD values of the soils leachates after the
368 different treatments assessed in this study.

369 The COD/BOD ratio of the untreated soil leachate was approximately 10, showing the
370 well-known strongly recalcitrant nature of these effluents [68]. Adding surfactant
371 **decreased** the COD/BOD ratios to 6.3 and 4.2 for treatments using S-PS and F-PS
372 methods, respectively, since the lauryl betaine is biodegradable and as it may also
373 increase HCs bioavailability.

374 Considering oxidation, the COD profiles vs. PS doses differed strongly depending on the
375 method used. Indeed, for S-PS and F-PS methods, COD decreased exponentially with the
376 initial oxidant concentration, as expected when all the organic matter is available. It is
377 noteworthy the lower amounts of oxidant required using the F-PS method; *e.g.* for 3
378 SMR, the COD was decreased by about 6 and 9-times using S-PS and F-PS methods,
379 respectively. In contrast, a maximum in COD was observed at 8 SMR for the W-PS
380 method, which shows both the recalcitrant nature of HCs metabolites that accumulate in
381 the aqueous phase and their tension-active property that helps for the release of
382 contaminants from soil [69].

383 Considering the biodegradability of leachates, the effect of the PS-dose had a strong
384 influence for W-PS and S-PS methods, unlike for the F-PS one. Indeed, whereas for the F-
385 PS method, COD/BOD ratios gently increased from 4.2 to 6.8 as PS-doses raised to 3
386 SMR, in contrast, maxima were observed for W-PS (62.5) and S-PS (96) at 3 SMR and
387 decreased to about 12 at 13 SMR. The very low biodegradability observed at low PS-
388 doses for W-PS and S-PS methods, is usually explained by the production and the
389 accumulation of very toxic metabolites, such as quinones and ketones, at early stages of
390 HCs oxidation, as shown for PAHs [9,13,66,67,70–72]. At high SMR-values, the
391 metabolites were finally further oxidized to produce smaller and less toxic molecules
392 than their parent compounds, such as carboxylic acids [13,73–75]. The slightly higher
393 biodegradability using S-PS at 1 SMR was probably due to the protective effect of
394 surfactant micelles towards HCs, impeding their conversion; Nevertheless, the maximum
395 observed for the COD/BOD ratio at 3 SMR confirms the preferential oxidation of
396 surfactant observed in the selectivity study.

397 Hence, the unique behaviour observed for the F-PS method about the low release of
398 toxic metabolites is connected to their advanced degradation. For instance, at 3 SMR,
399 biodegradability using the F-PS method was enhanced by 9 and 14-times compared to
400 W-PS and S-PS methods, respectively. This is attributed to a confinement effect arising
401 from the foam structure in soil pores. This observation is a key finding who illustrates
402 another benefit of using foam for the remediation of HCs-contaminated soils, in addition
403 of distributing the oxidant uniformly and increasing the selectivity of oxidation.

404

405 4. Conclusions

406 Previously, we demonstrated the benefit of this new foam-based method to distribute
407 uniformly oxidant solution and enhanced its lateral delivery in permeability or
408 wettability contrasted unsaturated soils. Although very promising, the benefits of the
409 method in homogeneously delivering oxidants rather than on oxidation efficiency were
410 considered. However, the presence of surfactant, that helps for contaminant availability
411 and which is required to make foams, has complex effects on oxidation efficiency. The
412 present work tried to bring a complete final answer about the efficiency of the novel
413 foam-based method developed.

414 Despite assessed in extremely unfavorable conditions, this foam-based method
415 showed very high removal HCs rates and similar efficiency to usual methods. It
416 enhanced by about 40-times the selectivity of the HCs degradation using PS compared to
417 the usual S-ISCO. Moreover, because the improved contact between oxidant and HCs
418 involving confinement effects, the latter were converted to less toxic by-products than
419 for usual ISCO and S-ISCO methods, thanks to their more complete oxidation. Finally, it
420 reduces risks of toxic emanations thanks to the low mobility of contaminants within the
421 foam network.

422 This technology is very promising, and it should allow to reduce drastically the costs
423 and risks associated to ISCO by allowing an optimal delivery and reaction of the oxidant.
424 The field assessment of this new method is in progress.

425

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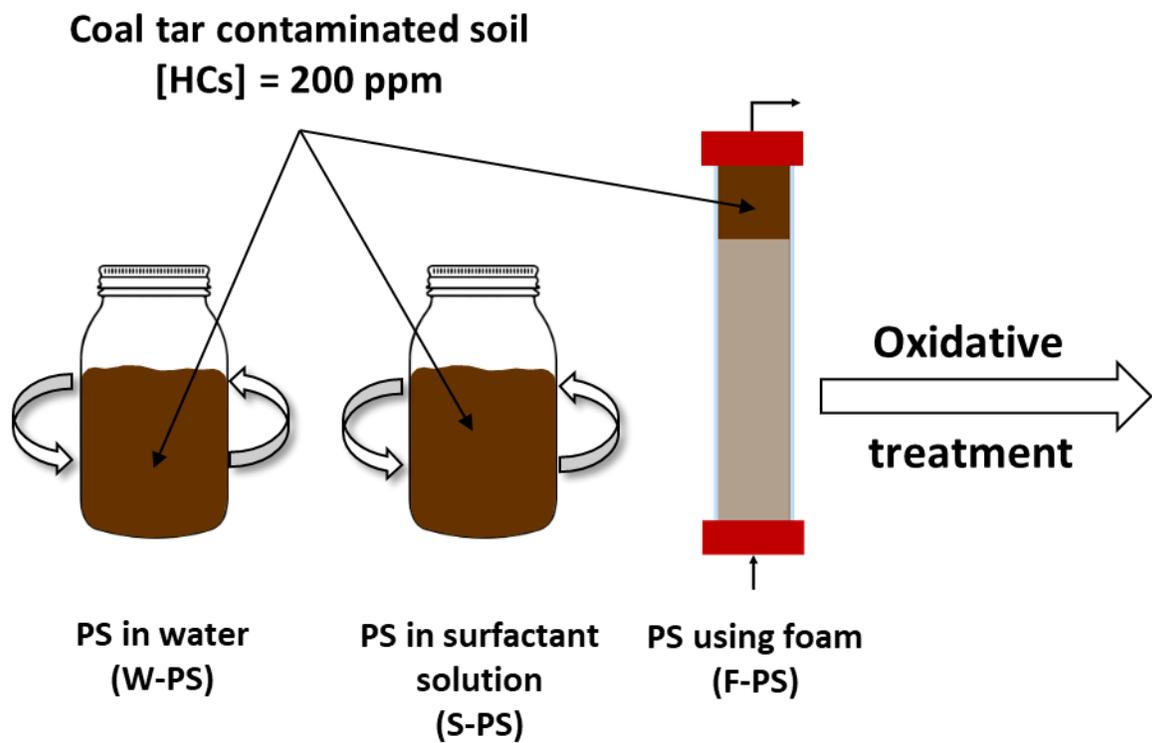
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	HCs elimination	HCs oxidation selectivity	HCs toxic by-products
W-PS	● ● ● ●	/	● ● ● ○
S-PS	● ● ● ○	● ○ ○ ○	● ● ● ●
F-PS	● ● ● ◐	● ● ● ●	● ○ ○ ○