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Remediation of soils contaminated by hydrophobic organic compounds: How to recover extracting agents from soil washing solutions?

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1 **Abbreviations**

2 AOP: advanced oxidation process; BDD: boron-doped diamond; CD: cyclodextrin; CMC:
3 critical micelle concentration; EA: extracting agent; EF: electro-Fenton; HPCD:
4 hydroxypropyl- β -cyclodextrin; HOC: hydrophobic organic compound; K_{CD} : complex stability
5 (or equilibrium) constant between organic compounds and cyclodextrin; K_m : micellar phase /
6 aqueous phase partition coefficient; MEUF: micellar-enhanced ultrafiltration process; NOM:
7 natural organic matter; PAH: polycyclic aromatic hydrocarbon; PHE: phenanthrene; SF soil
8 flushing; SW: soil washing; TX100: Triton X-100; TW80: Tween[®] 80; VOC: volatile organic
9 compound.

10

11 **Abstract**

12 A lot of soil (particularly, former industrial and military sites) has been contaminated by various
13 highly toxic contaminants such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons
14 (PAHs), polychlorobiphenyls (PCBs) or chlorinated solvents. Soil remediation is now required
15 for their promotion into new industrial or real estate activities. Therefore, the soil washing (SW)
16 process enhanced by the use of extracting agents (EAs) such as surfactants or cyclodextrins
17 (CDs) has been developed for the removal of hydrophobic organic compounds (HOCs) from
18 contaminated soils. The use of extracting agents allows improving the transfer of HOCs from
19 the soil-sorbed fraction to the washing solution. However, using large amount of extracting
20 agents is also a critical drawback for cost-effectiveness of the SW process. The aim of this
21 review is to examine how extracting agents might be recovered from SW solutions for reuse.
22 Various separation processes are able to recover large amounts of extracting agents according
23 to the physicochemical characteristics of target pollutants and extracting agents. However, an
24 additional treatment step is required for the degradation of recovered pollutants. SW solutions

25 may also undergo degradation processes such as advanced oxidation processes (AOPs) with *in*
26 *situ* production of oxidants. Partial recovery of extracting agents can be achieved according to
27 operating conditions and reaction kinetics between organic compounds and oxidant species.
28 The suitability of each process is discussed according to the various physicochemical
29 characteristics of SW solutions. A particular attention is paid to the anodic oxidation process,
30 which allows either a selective degradation of the target pollutants or a complete removal of
31 the organic load depending on the operating conditions.

32

33 **Keywords**

34 Soil washing; Reuse; Extracting agent; Separation; Degradation; Hydrophobic organic
35 pollutant

36

37 **Outline**

38 I – Introduction: why should we try to recover extracting agents?

39 II – Separation processes

40 II.1 – Air stripping and related technologies

41 II.2 – Liquid - liquid extraction

42 II.3 – Membrane processes

43 II.4 – Adsorption

44 III – Degradation processes

45 III.1 – Biological processes

46 III.2 – Chemical, photochemical and electrochemical advanced oxidation processes

47 III.2.1 – Removal of target pollutants: generation of oxidant species and reaction
48 mechanisms

49 III.2.2 – Effectiveness for the recovery of extracting agents

50	III.3 - Soil washing solution reuse or total removal of the organic load? A focus on the
51	possibilities offered by the anodic oxidation process
52	IV – Discussion
53	V – Conclusions and Recommendations
54	Acknowledgements
55	References
56	

57 **I – Introduction: why should we try to recover extracting agents?**

58 The development of industrial activities led to the release into the environment of
59 various hydrophobic organic compounds (HOCs) of environmental concern. Particularly,
60 polycyclic aromatic hydrocarbons (PAHs), petroleum hydrocarbons, chlorinated solvents and
61 polychlorobiphenyls (PCBs) are among the most widespread contaminants [1,2]. These
62 pollutants have a severe toxic, carcinogenic and mutagenic potential to higher organisms,
63 including humans [3]. Therefore, implementation of human activities at the vicinity of former
64 industrial sites requires the development of sustainable remediation techniques. This is a major
65 issue for both public authorities (healthcare risk management) and environmental engineering
66 companies (development of environmental-friendly and cost-efficient soil remediation
67 technologies). Conventional remediation techniques all present some major drawbacks such as
68 low effectiveness (bioremediation in case of aged contaminated soils), high costs (thermal
69 treatment or excavation) or selectivity towards target pollutants (e.g. volatile organic
70 compounds (VOCs) for venting) [1,4].

71 Soil is a porous and solid complex matrix made of a mixture of mineral particles and
72 organic matter [5,6]. The presence of various carbonaceous phases in soils can also be
73 associated to the specific history of each contaminated site and can lead to strong HOCs
74 sequestration [7–10]. Using extracting agents (EAs) appeared to be a promising technique in
75 order to improve the transfer of HOCs from the soil-sorbed fraction to the washing solution
76 [11,12]. The pump and treat treatment technique enhanced by the use of extracting agents is
77 named as soil flushing (SF). However, this *in-situ* technique is more difficult to implement and
78 to control because of soil heterogeneities for several critical parameter such as permeability,
79 porosity, nature and concentration of pollutants [13]. Therefore, a preliminary excavation step
80 is often required. A step of granulometric separation is then carried out in order to perform the
81 chemically enhanced soil washing (SW) process on the most contaminated fraction. Compared

82 to SF, homogenization of the soil allows for optimizing the contact between extracting agents
83 and soil pollutants. Thus, treatment efficacy is more easily monitored and the contact time is
84 reduced during SW [1,11].

85 A large range of extracting agents has been tested in the scientific literature. The use of
86 synthetic surfactants above their critical micelle concentration (CMC) constitutes the most
87 widespread technique [12,14]. The accumulation of HOCs in the SW solution originates from
88 the reduction of the interfacial tension between non-aqueous phase liquid (NAPL) and aqueous
89 phase as well as the increase of solubility due to partitioning of HOCs inside the hydrophobic
90 space formed by micelles [15,16]. Synthetic surfactants are divided into four main categories,
91 including anionic (e.g., sodium dodecylsulfate [17,18]), cationic (e.g., quaternary ammonium
92 derivatives [18]), amphoteric (e.g., cocamidopropyl hydroxysulfate [19]) and non-ionic
93 surfactants (e.g., Brij[®] 35 [20,21], Tween[®] 80 (TW80) [22–24], Triton[®] X 100 (TX100) [25]).
94 Surfactant solubilization of organic contaminants can be assessed by a micellar phase / aqueous
95 phase partition coefficient K_m (Eq. 1) [15]. The extraction capacity of extracting agents is not
96 the only parameter to consider for selecting a suitable compound. In fact, some surfactants can
97 have adverse effect on soil according to their chemical structure [26,27].

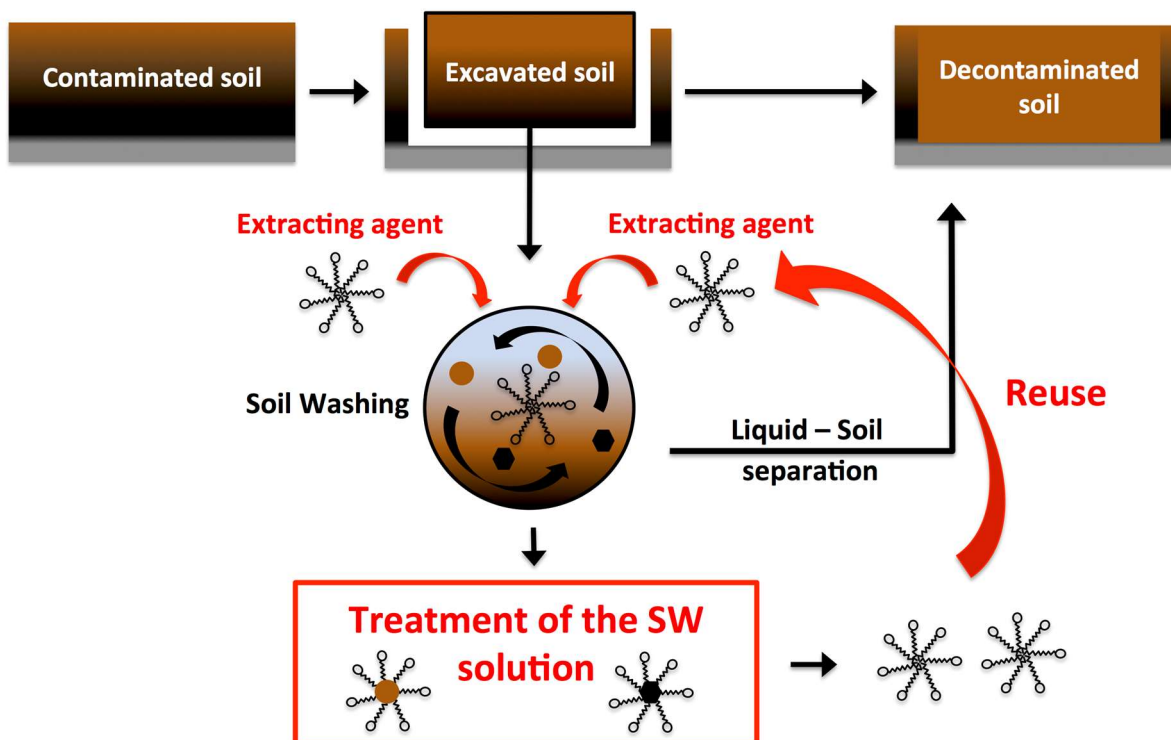
$$K_m = \frac{X_m}{X_a} \quad (\text{Eq. 1})$$

98 where X_m and X_a are the mole fraction of target pollutants in the micellar pseudo-phase and
99 aqueous phase, respectively.

100 There is therefore an important challenge for chemical engineers to develop efficient,
101 low-cost and eco-friendly surfactants. By comparison to synthetic surfactants, biosurfactants
102 (from microbial origin) present several advantages such as high biodegradability, lower
103 toxicity, ecological compatibility and the possibility to be produced *in situ* [28,29]. However,

104 using biosurfactants at industrial scale is still impaired by high production cost and difficulties
105 to stimulate their *in situ* production at large scale [30,31]. Cyclodextrins (CDs) derivatives (with
106 higher solubility than native CDs) have also been tested as extracting agents [11,32]. They
107 allow increasing aqueous solubility of HOCs by forming inclusion complex according to their
108 respective complex stability (or equilibrium) constant (K_{CD}) with organic compounds [11].
109 However, they are considered to be about ten times less effective than synthetic surfactants in
110 terms of pollutant removal from soil [11]. Other promising alternatives currently under
111 development include the use of gemini surfactant (made of two hydrophilic head groups and
112 two hydrophobic tails) [14,33] and surfactant foams [13,34].

113 Efficient removal of HOCs from soil by EA-enhanced SW depends on the nature of
114 target pollutants and soil characteristics [11,12]. This process results in the production of highly
115 concentrated effluents, containing target HOCs at toxic concentrations, natural organic matter
116 (NOM) from the soil as well as large amount of extracting agents [1]. Therefore, a suitable
117 strategy for disposal of the SW solution must be implemented [1]. The ecological footprint and
118 cost-efficiency of the whole process (*i.e.* soil excavation, SW, treatment of the SW solution,
119 Figure 1) depend strongly on both nature and amount of the surfactant consumed. As eco-
120 friendly surfactants are usually more expensive, the use of large amounts constitute a major
121 drawback for further full-scale application of this treatment strategy [1].



122

123 Figure 1– The different steps involved in the treatment of contaminated soils by integrated soil washing
 124 processes.

125

126 Optimizing the SW process is the most direct way to reduce the consumption of
 127 extracting agents. Decontamination of polluted soils by SW has already been widely reviewed
 128 in the literature by using either surfactants [14–16,24] or CDs [11] as extracting agents. The
 129 most important parameters to consider are: (i) the extraction effectiveness of the chosen EA,
 130 (ii) its cost, (iii) its soil sorption capacity (which can lead to important loss of extracting agent
 131 and adverse effects on soil quality) and (iv) the operating parameters, including concentration
 132 of EA, soil/liquid ratio, contact time, mixing conditions and number of successive washing
 133 steps [11]. Usually, optimal parameters are determined through preliminary tests. It is worth
 134 noting that the characteristics of the contaminated soil and pollutants have to be carefully
 135 investigated in order to assess the suitability of the SW process. According to the contamination
 136 history, soil pollution ageing and pollutant sequestration can strongly affect the availability of
 137 target pollutants for extracting agents [8,10,35–38]. Organic matter and clay content might also

138 affect process effectiveness because of competitive solubilization of NOM, mobilization of
139 hardly settling particles or high adsorption of extracting agents on soil [15]. Finally, the
140 horizontal and vertical location of the contaminated soil has also to be carefully studied before
141 soil excavation. Excavation and treatment of non-polluted soil strongly increase the cost of the
142 process.

143 Once the SW has been optimized, it remains another way to further reduce the
144 consumption of extracting agents. Several research articles and one previous review paper
145 focused on the removal of the organic load from SW solutions [1]. However, a large amount of
146 extracting agents can be recovered by implementing a suitable treatment of the SW solution.
147 The objective is to improve the cost-efficiency and ecological footprint of soil remediation by
148 reusing the SW solution. However, it represents an additional treatment step requiring extra-
149 costs [39,40]. For this reason, this article aims at critically reviewing how to recover extracting
150 agents during the treatment of SW solutions, including separation and degradation processes.
151 Different processes are presented and their effectiveness for selective separation or degradation
152 of target pollutants is discussed according to the specific characteristics of SW solutions.

153

154 **II – Separation processes**

155 **II.1 – Air stripping and related technologies**

156 The SW process is usually not applied for the treatment of soil contaminated by VOCs
157 because of the important risk of accidental release. However, surfactant-enhanced SW can be
158 applied to soils contaminated with pollutants such as trichloroethylene, tetrachlorethylene or
159 perchloroethylene. In such case, air stripping and related technologies are relevant for the
160 removal of such compounds from SW solutions [41–44]. Air stripping is based on the formation
161 of a large air-water interfacial area in order to improve the mass transfer of semi-volatile

162 compounds from the aqueous phase to the gas phase. Volatile or semi-volatile pollutants are
163 readily partitioned into the gas phase in contrast to non-volatile extracting agents. However,
164 gas injection in the presence of extracting agents can lead to significant foam formation [45]
165 which is considered as one of the main drawback of this process [46]. The use of hollow fiber
166 membranes instead of usual packed towers and tray air strippers can reduce these foaming
167 issues [47,48]. A lower formation of foam has also been observed with CDs compared to
168 synthetic surfactants. Air stripping was successfully performed at field-scale for recycling
169 hydroxypropyl- β -cyclodextrin (HPCD) for several successive SF steps [32,49]. Then,
170 contaminated air was treated through a granular activated carbon reactor.

171 Solubilization of target pollutants inside surfactant micelles or inclusion complex with
172 CDs has an important impact on the efficiency of the process. While the higher interfacial
173 resistance is often considered to only slightly decrease the global mass transfer [45,50],
174 extracting agents greatly reduce the molar fraction of free organic compounds in the aqueous
175 phase. Extracting agents act as a competing pseudo-phase for partitioning of the organic
176 contaminant in the gas phase [51,52]. This adverse effect increases with the hydrophobicity of
177 target pollutants, solubilization capacity of extracting agents (high K_m/K_{CD}) [45] and
178 concentration of extracting agent [44]. For example, tetrachlorethylene removal rate was 83, 61
179 and 37% when performing air stripping with hexadecylsulfonate as extracting agent at 0, 10
180 and 55 mM, respectively [45]. Thus, Lipe et al. (1996) have developed a surfactant air stripping
181 model (SASM) for assessing the efficiency of air stripping systems by taking into account the
182 effect of surfactants. It is based on the conventional non-equilibrium mass transfer model and
183 has been successfully validated by experiments at both bench and field scale [45,48].

184 Vacuum processes have been investigated in order to improve the effectiveness of air
185 stripping [53]. Vacuum is used as the driving force for the transfer of target compounds from
186 the liquid to the gas phase. The surfactant stream can also be heated in order to increase the

187 vapor pressure of contaminants. The two main advantages of this process are the higher
188 separation effectiveness for contaminants with a lower volatility and the reduction of foaming
189 issues [45].

190 Pervaporation has also been successfully applied to SW solutions [54] containing
191 tetrachlorethylene [55], trichloroethylene [56], 1,1,1-trichloroethane [54,57] and toluene [57].
192 It is based on the vaporization of the SW solution through a selective non-porous polymeric
193 membrane. Field demonstration and pilot-scale experiments demonstrated the high
194 effectiveness of the process for the removal of these target compounds without affecting the
195 performance of the recovered solution [55,57]. Different configurations can be used such as
196 spiral wound modules [57] or hollow fiber membranes [56]. Similarly to previous processes,
197 the use of high concentrations of extracting agents can decrease the performances in terms of
198 selectivity and flux [54,55].

199

200 **II.2 – Liquid - liquid extraction**

201 An organic liquid can be used as the partitioning phase for the extraction of target HOCs
202 from SW solutions [44]. Liquid-liquid extraction is based on the mass transfer of target
203 pollutants from the SW solution to the organic solvent. This process has been successfully
204 applied at both bench and field scale for the removal of semi- and non-volatile organic
205 compounds having high Henry's constants [58,59]. Using surfactants as EA, it has been
206 reported a similar extraction capacity for the treated SW solution compared to the initial
207 solution [58,59]. However, the process can be further complicated by emulsification of the
208 solvent by the surfactant solution and solubilization of solvent molecules into the micellar
209 pseudo-phase. Such phenomenon can be reduced by properly selecting the solvent, particularly
210 by using highly hydrophobic solvents [58–60]. Hollow fiber membranes filled with the
211 extracting solvent have also been used in order to eliminate emulsification and reduce the

212 amount of solvent consumed [61]. Petitgirard et al. [62] developed different methods in order
213 to reduce the amount of solvent used. It was based either on micro-emulsion or impregnation
214 of an organic membrane with oil. Lower amount of solvent allows decreasing the loss of
215 surfactant and facilitating the disposal of the contaminated solvent [44].

216 Hasegawa et al. [58] developed a model for liquid-liquid extraction in order to predict
217 the efficiency of this process for surfactant-containing solutions. The model depends on the
218 solvent / water partition coefficient (K_d), micellar phase / aqueous phase partition coefficient
219 (K_m), solvent-water ratio and hydrodynamic conditions (column height, retention time, water
220 velocity). Particularly, the partition of target pollutants in micelles (K_m) is a crucial parameter.
221 The increase of the surfactant concentration significantly decreases the efficiency of the process
222 due to the micellar pseudo-phase acting as a competing partitioning phase [58]. Moreover, it
223 has been observed that the higher the hydrophobicity of target pollutants (high K_m and K_{CD}),
224 the higher the adverse effects of extracting agents on removal efficiency is [58].

225 This process has also been applied to solutions containing CDs as extracting agents. For
226 example, liquid-liquid extraction with rapeseed oil was used for regeneration of a SF solution
227 containing methyl- β -cyclodextrin [62]. This lab-scale experiment allowed the regeneration of
228 the methyl- β -cyclodextrin solution for continuous SF. After two days of SF, almost complete
229 decontamination of the spiked sandy soil was achieved (96-98% of PAH removal), pollutants
230 were concentrated in the organic phase and the loss of methyl- β -cyclodextrin was negligible.

231 It is worth noting that liquid-liquid extraction leads to the production of highly
232 contaminated solvents, for which the disposal is a real challenge. Moreover, it also involves
233 high risks of handling (leaking storage tanks, exposure of workers via skin contact or inhalation).
234 Distillation systems have been applied for solvent/contaminant separation and reuse of the
235 solvent for further contaminant/EA separation steps [43], but such process represents an
236 important cost.

237

238 **II.3 – Membrane processes**

239 The use of membrane technologies has also been investigated for the treatment of
240 SW/SF solutions. Most of the studies did not report selective surfactant-contaminant separation.
241 However, during SF, are often diluted in recovery wells by groundwater. Therefore, membrane
242 processes can also be used for re-concentration of the SF solution (e.g. after air stripping) before
243 reinjection into the contaminated zone [48]. For example, by using ultrafiltration membranes,
244 it was observed 93-99% of surfactant-contaminant retention from a SW solution containing
245 naphthalene and trichloroethylene as contaminants and linear alkyl diphenyloxide disulfonate
246 as surfactant [45]. The formation of micelles improves the retention of organic compounds [63].
247 Such micellar-enhanced ultrafiltration process (MEUF) is based on the formation of colloid-
248 sized surfactant micelles retained by the ultrafiltration membrane. Only one stud reported a
249 selective removal of target pollutants by ultrafiltration: 67% of the surfactant was recovered in
250 the permeate, while more than 90% of polychlorobiphenyls and 83% of oils were retained [64].
251 This result might be explained by the formation of oil droplets readily rejected by the membrane,
252 thus leading to a selective separation of surfactant monomers and pollutants.

253

254 **II.4 – Adsorption**

255 Adsorption is a widely used technology and has recently received great attention for the
256 treatment of SW solutions because of promising results obtained for the recovery of extracting
257 agents, especially with activated carbon [1,65] (Table 1). Several studies have observed much
258 higher removal rates of target pollutants than extracting agents because of the higher partition
259 coefficient, higher hydrophobicity and lower concentration of target pollutants [66,67].
260 Recently, the use of organo-bentonite and organo-layered double hydroxide has also been
261 investigated [68,69]. The objective of such material is to provide a strong affinity between
262 target pollutants and the organic phase within bentonite or layered double hydroxide. Sorbent
263 materials, pollutants and extracting agents already studied are reported in Table 1.

264 The effectiveness of this process for the recovery of extracting agents can be assessed
 265 in batch experiments by using the selectivity ratio (S) (Eq. 4) [67]. Values reported in the
 266 literature for synthetic SW solutions usually range between 5 and 100, according to operating
 267 conditions (concentration/nature of EAs, target pollutant, sorbent material, dose, etc.). As
 268 regards to the activated carbon dose in batch experiments, low amount (around 2 g L⁻¹) was
 269 reported to be sufficient to achieve 60% removal of 100 mg L⁻¹ of PHE with a selectivity ratio
 270 of 10 (initial concentration of TX100 was 5 g L⁻¹) [67]. Much higher effectiveness was also
 271 reached with lower PHE concentration [67]. However, selectivity ratio measured in synthetic
 272 solutions cannot be used for prediction of the efficiency of the process with real SW solutions,
 273 in which much more competition effects occur.

$$S = \frac{C_{SM,j}}{C_{l,j}} \times \frac{C_{l,SA}}{C_{SM,SA}} \quad (\text{Eq. 4})$$

274 where $C_{SM,j}$ is the concentration of the target pollutant sorbed onto the sorbent material (mg g⁻¹)
 275 ¹), $C_{l,j}$ is the concentration of the target pollutant in the liquid phase (mg L⁻¹), $C_{l,SA}$ is the
 276 concentration of extracting agent in the liquid phase (g L⁻¹), $C_{SM,SA}$ is the concentration of
 277 extracting agent onto the sorbent material (g g⁻¹) and S is the selectivity ratio.

278 By using a configuration with a continuous flow through column, such adsorption
 279 process leads to a much shorter exhausting time of extracting agents compared to breakthrough
 280 time of target pollutants [70].

281
 282 [Table 1 – Adsorption processes for the recovery of extracting agents – an overview of existing studies.](#)

Sorbent	Pollutants	Extracting agents	Configuration	References
Activated carbon	PHE ¹	TX100 ²	Batch	[66]

Activated carbon	PHE ¹ , FLUO ³ , BaA ⁴	TX100 ²	Column	[70]
Activated carbon	Trichloroethylene	HPCD ⁵	Batch	[71]
Activated carbon	Mineral oil	RAMEB ⁶	Column	[72]
Activated carbon	PHE ¹	Mixture SDS ⁷ -TX100 ²	Batch	[73]
Activated carbon	PHE ¹	SDS ⁷	Batch	[67]
Activated carbon	PHE ¹	TX100 ²	Column	[74]
Activated carbon	FLUO ²	TX100 ²	Batch	[75]
Activated carbon	Chlorinated solvents	TX100 ² , TX165 ⁸	Column	[76]
Activated carbon	PHE ¹	TW40 ⁹ , TW80 ¹⁰ , B30 ¹¹ , B35 ¹²	Batch	[77]
Organo-bentonite	Various PAH ¹³	TX114 ¹⁴ , TX100 ² , TX305 ¹⁵	Batch	[68]
Activated carbon	Hexachlorobenzene	Rhamnolipid	Column	[78]
Activated carbon	p-Cresol	TW80 ¹⁰	Batch	[79]
Biochar	PHE ¹ , FLUO ³ , PYR ¹⁶	TX100 ²	Batch	[80]
Activated carbon	PHE ¹	TW80 ¹⁰	Batch	[81]
Activated carbon	Organochlorine pesticide	TX100 ²	Batch	[82]
Macroporous resin SP850	PHE ¹	TX100 ² , SDBS ¹⁷	Batch	[83]
Organo-LDH ¹⁸	PHE ¹ , PYR ¹⁶	SDBS ¹⁷ , B35 ¹²	Batch	[69]

283

284 ¹ Phenanthrene; ^{2,8,14,15} Triton X 100, 165, 114, 305; ³ Fluoranthene; ⁴ Benzo(a)anthracene; ⁵ HPCD ⁶ Randomly

285 methylated β -cyclodextrin; ⁷ Sodium dodecylsulfate; ^{9,10} Tween[®] 40, 80; ^{11,12} Brij[®] 30, 35; ¹³ Polycyclic aromatic

286 hydrocarbon; ¹⁶ Pyrene; ¹⁷ Sodium dodecylbenzene sulfonate; ¹⁸ Layered double hydroxides.

287

288 The selectivity of adsorption processes tightly relies on the reduction of competition
289 phenomena for adsorption of target pollutants. Even if promising results have been obtained,
290 further investigations are necessary [71]. Particularly, it is required to better understand
291 competition mechanisms between partitioning of target pollutants inside micelles or inclusion
292 complex and adsorption on the sorbent material [71]. K_m and K_{CD} are important parameters to
293 take into consideration for the availability of pollutants for adsorption [84]. Besides, other
294 compounds from real SW solutions such as NOM could have strong adverse effects on the
295 selectivity ratio. For example, selectivity ratio was divided by 2 in a fluoranthene/TX100
296 mixture when adding 0.10 g L⁻¹ of fulvic acids because these compounds participate to
297 additional pore blocking [75]. Besides, sand filtration is a required pre-treatment for real SW
298 solutions in order to prevent too much rapid fouling of the activated carbon filter by particulate
299 materials. The influence of the nature of EAs, target pollutants and sorbent materials (particle
300 size, pore size distribution, etc.) should also be further investigated. The extracting agent and
301 the sorbent material have to be carefully chosen in order to limit the phenomenon of pore
302 blocking, which can lead to a reduction of active sites available for target pollutant adsorption.
303 For example, it has been observed that the reduction of surface area of activated carbon after
304 TX100 adsorption was mainly ascribed to the adsorption on micropores [67]. Pore size
305 distribution could therefore be optimized in order to favour adsorption of target pollutants
306 instead of extracting agents.

307 The regeneration of sorbent materials is also a crucial issue for the sustainability of
308 adsorption processes. Thermal processes are currently widely used for activated carbon
309 regeneration. When performing thermal desorption, a large amount of energy is consumed and
310 a post-treatment of the contaminated gas stream is still required. Degradation of target
311 pollutants can be achieved by heating at high temperature under oxidizing conditions, but such
312 treatment usually reduce the potential for AC reuse because of a strong decrease of specific

313 surface area and adsorption capacity [85,86]. Therefore, alternative regeneration processes are
314 currently investigated, such as biological treatments [87,88], microwave irradiation [70,89],
315 ozone [86] or electro-Fenton (EF) processes [85,90,91]. The latter process seems to be a
316 promising technique based on the use of activated carbon as cathode, which allows for both
317 mineralization of organic pollutants and regeneration of the adsorption capacity of the spent
318 activated carbon [91].

319

320 **III – Degradation processes**

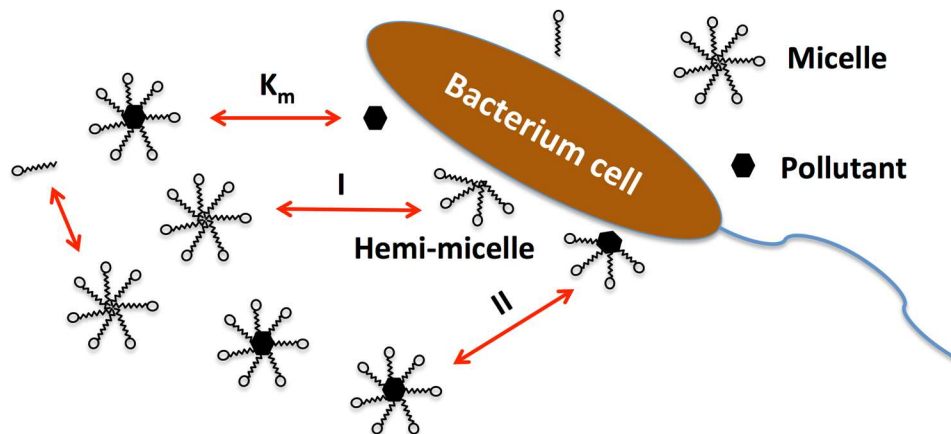
321 **III.1 – Biological processes**

322 Biological treatment (mainly aerobic processes) is one of the most popular processes in
323 water treatment for the removal of biodegradable organic compounds. It is based on the
324 consumption of organic compounds by a large range of microorganisms. Recent progress
325 allows the application of this kind of treatment to various effluents in terms of nature and
326 organic load. For a specific compound, removal rates and pathways depend on several physical,
327 chemical and microbiological aspects [1]. Some organic compounds can be recalcitrant to
328 biodegradation for different reasons such as the absence of microorganism able to use them as
329 substrate, the presence of toxic concentrations of organic compounds or the lower
330 bioavailability due to the physicochemical parameters of the environment [92]. Therefore, the
331 development of an adapted biomass to a specific SW solution and the influence of extracting
332 agents on the bioavailability of target pollutants are two key parameters [93–96].

333 As the uptake of organic compounds by microorganisms occur mainly via the aqueous
334 phase, partition of HOC in the CD inclusion complex or in the surfactant micellar pseudo-phase
335 can strongly influence biodegradation kinetics [97–99]. Different mechanisms are actually
336 involved in the biodegradation of target pollutants in surfactant-containing solutions [92]

337 (Figure 2). First, bacteria can directly utilize aqueous extra-micellar pollutants as substrate.
 338 Then, pollutants diffusing from the micellar (or inclusion complex) to the aqueous phase
 339 (kinetics in the range of microseconds to milliseconds) according to the micellar phase /
 340 aqueous phase partition coefficient (K_m) becomes also bioavailable. Biodegradation of
 341 pollutants solubilized in micelles can also occur due to the formation of a hemi-micellar layer
 342 around the bacteria cells (step I, Figure 2) and transfer of pollutants from the micellar phase to
 343 this hemi-micellar layer (step II, Figure 2) [92]. However, these two steps might be kinetically
 344 limiting for biodegradation [92].

345



346

347 Figure 2 – Organic pollutant uptake by bacteria in soil washing solutions. K_m is the micellar phase /
 348 aqueous phase partition coefficient of the target pollutant. I: equilibrium between the hemi-micellar layer
 349 around the bacteria cells and micelles in the aqueous phase. II: equilibrium between pollutants
 350 solubilized in hemi-micelles around the bacteria cells and micelles in the aqueous phase.

351

352

353 The complexity of such system often led to contradictory results [92]. On the one hand,
 354 the enhancement of HOC biodegradation in solutions containing extracting agents has been
 355 mainly attributed to the increase of the solubility and bioavailability of HOCs [94,95,100,101].
 356 On the other hand, adverse effects have been often ascribed to the inhibition of the direct contact
 357 between microbial cells and target pollutants [97,99,102], toxicity of extracting agents towards

358 microorganisms [102–104] or preferential uptake of extracting agents as substrate
359 [103,105,106]. Overall, the following trend is often observed the presence of low concentration
360 of extracting agent (below or close to the CMC for surfactants) enhances HOC biodegradation,
361 while bioavailability and biodegradability are reduced at high concentration of extracting agent
362 [92,96,98,99].

363 As extracting agents are usually used at high concentration during SW processes, it is
364 very difficult to achieve a selective biodegradation of target pollutants in SW solutions because
365 of the protective environment formed by extracting agents. Therefore, only few authors have
366 investigated SW solution recirculation after biological treatment. Navarro et al. [96] observed
367 a selective biodegradation of PYR from a SW solution containing deoxyribonucleic acid (DNA)
368 as extracting agent. The removal of PYR reached 99% after 1 d, while more than 98% of
369 deoxyribonucleic acid was recovered. This result was explained by the stability of DNA against
370 the aerobic bacteria (*Sphingomonas* sp.) used in this study for degradation of PYR. Thus, the
371 treated solution was re-used for four SW cycles with synthetic contaminated soil, with a high
372 extraction capacity. Recently, it was also reported that the use of a bacterial consortium could
373 allow the reuse of a biologically-treated SW solution containing PHE and TW80 as extracting
374 agent [107].

375

376 **III.2 – Chemical, photochemical and electrochemical advanced oxidation processes**

377

378 **III.2.1 – Removal of target pollutants: generation of oxidant species and reaction**

379 **mechanisms**

380 Advanced oxidation processes (AOPs) have been largely studied for the treatment of
381 SW solutions. AOPs are well-known for the removal of recalcitrant organic pollutants [108].
382 They are based on the *in situ* production of strong oxidants, mainly hydroxyl radicals, the

383 second most powerful oxidizing agent known ($E^\circ(^{\bullet}\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$) [109]. Hydroxyl
384 radicals are characterized by a very short lifetime (in the range of nanoseconds) and a non-
385 selective feature towards organic compounds [110]. There are four main reaction pathways for
386 the reaction of hydroxyl radical with organic compounds, including hydrogen atom abstraction
387 (dehydrogenation), addition to an unsaturated bond (hydroxylation), ipso substitution
388 (hydroxylation with release of halogen ion) and electron transfer (redox reactions) [110,111].
389 Aromatic compounds are the most reactive species with hydroxyl radicals since hydroxylation
390 is typical for these kinds of compounds with rate constants in the range $10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, while
391 lower values are reported ($10^6 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$) for alkanes and alcohols for which reaction occurs
392 through dehydrogenation [110]. Different methods are used for the production of hydroxyl
393 radicals. Mainly photochemical, electrochemical, and Fenton-based processes have been
394 applied to the treatment of SW solutions [1,18,25,112-118].

395 Heterogeneous photocatalysis is based on photoactivation of a semiconductor (e.g.
396 TiO_2), leading to the production of an electron in the conduction band and a positive hole in the
397 valence band [119,120]. These materials have a void energy region avoiding the recombination
398 of electrons and holes. Thus, the reaction of electrons and positive holes with O_2 , H_2O , and OH^-
399 leads to the production of oxidant species on the surface of the photocatalyst and in the bulk,
400 including $^{\bullet}\text{OH}$, H_2O_2 , $\text{O}_2^{\bullet-}$ [121].

401 The production of hydroxyl radicals during Fenton-based processes comes from the
402 catalytic decomposition of hydrogen peroxide by ferrous iron [108,110]. The effectiveness of
403 the process can be enhanced by using UV irradiation (photo-Fenton based processes) [122,123],
404 allowing a better regeneration of ferrous iron and the production of additional hydroxyl radicals
405 from the photolysis of $\text{Fe}(\text{OH})^{2+}$ [124]. The development of iron-containing solids catalysts is
406 also a promising way for reducing the production of iron sludge and allowing the application
407 of the process at circumneutral pH [125,126].

408 Electrochemical processes can lead to the production of hydroxyl radicals from (i)
409 anodic oxidation by water discharge on the surface of anode with high oxygen evolution
410 overpotential (such as boron-doped diamond, BDD) [127,128], (ii) EF process through *in situ*
411 production of the Fenton's reagent [110]: H₂O₂ is produced from the two electron reduction of
412 oxygen at a suitable cathode (such as gas diffusion or three-dimensional electrodes using
413 carbon-based porous materials combined with injection of compressed air in the solution),
414 while only a catalytic amount of ferrous iron is supplied and continuously regenerated by
415 reduction of ferric iron at the cathode [129]. The EF process allows increasing the efficiency of
416 the Fenton's process by avoiding the addition of chemical reagents, reducing waste reactions
417 and avoiding sludge formation [1,130]. Oxidation of inorganic anions in the solution (SO₄²⁻,
418 Cl⁻, etc.) can also lead to the homogeneous production of oxidant species in the bulk such as
419 active chlorine, persulfate, sulphate radical, which also participate to the oxidation of organics
420 ("mediated oxidation") [131,132].

421 Recently, a great attention has also been given to the development of AOPs based on
422 persulfate activation, due to several inherent advantages of sulphate radicals such as (i) the
423 convenience of storage and transportation of solid persulfate, (ii) the different way to activate
424 persulfate (e.g. thermal or electrochemical processes, Fe²⁺) and (iii) the longer lifetime of
425 sulphate radicals compared to hydroxyl radicals [133–137].

426 Total degradation of target pollutants as well as high mineralization rate of SW solutions
427 is usually achieved when using such AOPs. Some examples of degradation kinetic rates are
428 reported in Table 2. When optimized operating conditions are used, the apparent degradation
429 kinetic rates of target pollutants in SW solutions are usually in the range 0.5 – 5 h⁻¹.

430
431 **Table 2 – Degradation kinetic rates of target pollutants in soil washing solution by advanced**
432 **oxidation processes**

Process	Pollutants (mM)	Extracting agent (mM)	Maximum degradation kinetic rate (h ⁻¹)	Reference
Photocatalysis (TiO ₂)	NAP ¹ (0.03)	B35 ² (1.2)	2.04	[138]
Photocatalysis (TiO ₂)	PCP ³ (0.2)	β -CD ⁴ , MCD ⁵ , HPCD ⁶ (0 – 5)	5.3	[139]
Solar-Photocatalysis (TiO ₂)	NAP ¹ (0.2)	TX100 ⁷ (0.04 – 0.13)	4.2	[140]
Photocatalysis (TiO ₂)	Aromatic compounds	B35 ² (25)	0.12 – 3.48	[141]
Photocatalysis (TiO ₂)	PCP ³ (0.018)	TX100 ⁷ (0.023 – 1.01)	3.3	[89]
Solar-Photocatalysis (TiO ₂)	Alkylphenols	B35 ² , C ₁₂ E ₈ , SDS ⁸ , mixtures (1 – 15)	9.3	[20]
Photo-Fenton	TNT ⁹ (0.5)	None (water)	4.86	[142]
		MCD ⁵ (5)	10.05	
EF	PCP ³ (0.1)	HPCD ⁶ (5)	0.546	[143]
EF	PHE ¹⁰ (0.1)	HPCD ⁶ (8.8)	1.56	[144]
		TW80 ¹¹ (0.6)	0.78	
EF	PAHs	HPCD ⁶ (6)	0.83 – 2.61	[145]
		TW80 ¹¹ (5.6)	0.20 – 0.72	
Anodic oxidation	NAP ¹ (0.83)		0.9	[146]
	PYR ¹² (0.27)	CAS ¹³ (9.1)	0.66	

433

434 ¹ Naphthalene; ² Brij[®] 35; ³ Pentachlorophenol; ⁴ β -cyclodextrin; ⁵ Methyl- β -cyclodextrin; ⁶ Hydroxypropyl- β -

435 cyclodextrin; ⁷ Triton X 100; ⁸ Sodium dodecylsulfate; ⁹ Trinitrotoluene; ¹⁰ Phenanthrene; ¹¹ Tween[®] 80; ¹²

436 Pyrene; ¹³ Cocamidopropylhydroxysultaine

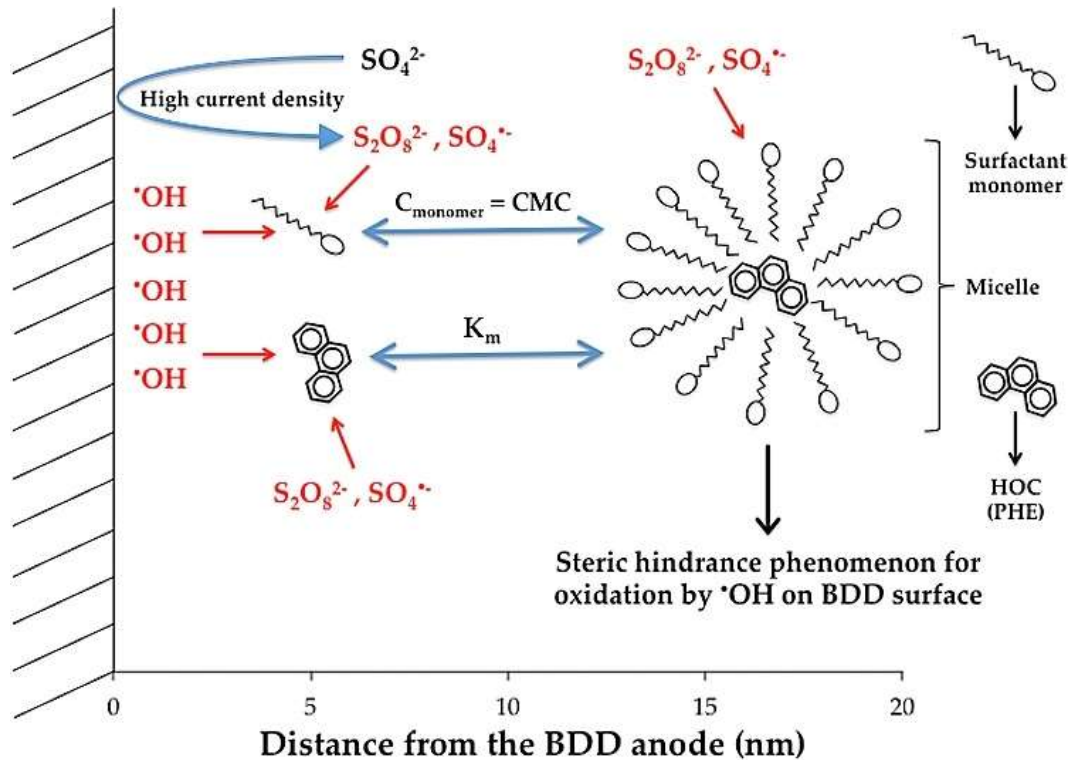
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438 The specificity of SW solutions requires giving a special attention for the understanding
439 of oxidation mechanisms, according to the process used, operating conditions, target pollutant
440 and extracting agent used. Target pollutant removal usually requires high energy and/or reagent
441 consumption, due to the high organic load of SW solutions. Concentrations of extracting agents
442 are usually in the range of 1-100 g L⁻¹ [1,11]. Moreover, a large amount of soil organic matter
443 is also mobilized in the SW solution [1]. Since hydroxyl radicals act in a non-selective way,
444 there is therefore a huge competition for oxidation [112,147–149] and wasting reactions from
445 hydroxyl radical scavengers strongly reduce the kinetics of target pollutant degradation. This
446 high oxidant demand is the main issue for the treatment of SW solution by AOPs. For example,
447 49 g L⁻¹ (using sequential addition) and 30 g L⁻¹ of H₂O₂ was necessary to achieve 95% and
448 96% COD removal from a SW solution [25,146]. As regards to the EF process, the treatment
449 of a SW solution containing PAH and TW80 as EA, required 0.69 kWh per gram of TOC
450 removed [145].

451 Besides, solubilization of target pollutants inside surfactant micelles and inclusion
452 complex with CDs reduces the effectiveness of oxidation processes by decreasing the
453 availability of target pollutants towards oxidant species in the aqueous phase because of
454 formation of a protective environment [132,144,150,151]. However, different mechanisms
455 occur when CDs are used as extracting agents during Fenton-based processes. The formation
456 of a ternary complex CD-pollutant-Fe²⁺ has been observed [152,153]. This phenomenon allows
457 improving the effectiveness of Fenton-based processes thanks to the production of hydroxyl
458 radicals close to target pollutants [142,144,154].

459 As regards to anodic oxidation, hydroxyl radicals are only present in a thin layer (few
460 nm) on the anode surface. Therefore, reaction with organic compounds strongly depends on
461 their mass transport from the bulk to the anode surface [128]. Formation of large size micelles
462 was reported to prevent oxidation on the anode surface, due to a phenomenon of steric hindrance

463 [155]. However, production of oxidant species in the bulk through mediated oxidation
 464 (favoured at high current density) can still participate in the degradation of micelles during
 465 electro-oxidation of SW solutions [132] (Figure 3).



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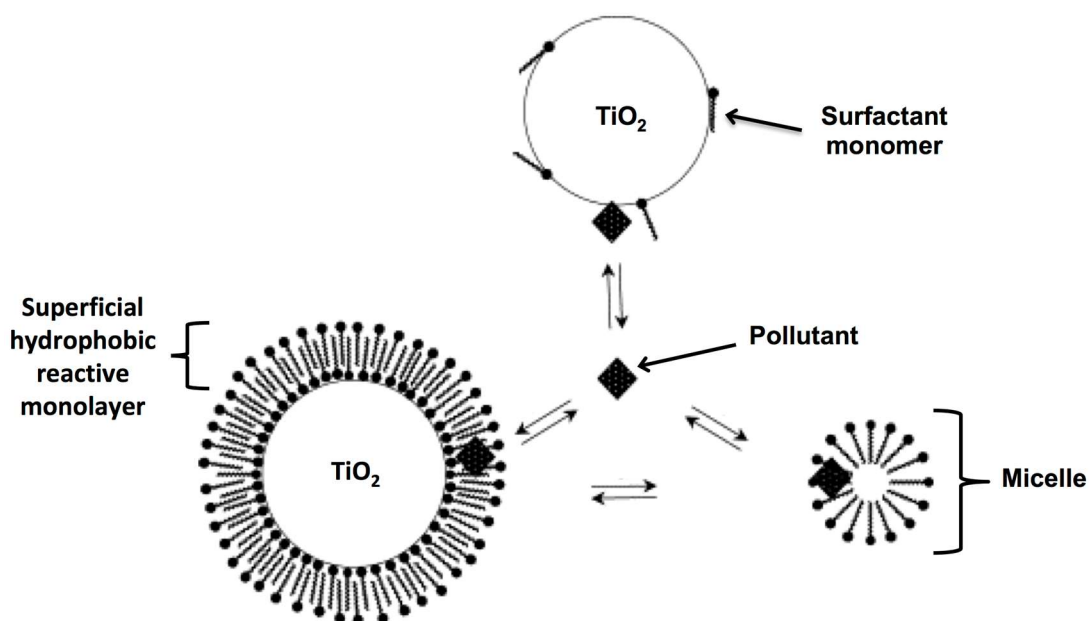
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Figure 3 – Schematic view of oxidation mechanisms occurring during the treatment of a soil washing solution (containing phenanthrene (PHE) as hydrophobic organic compound (HOC)) by anodic oxidation using boron-doped (BDD) anode. Reprinted from [23].

Mechanisms of organic compounds removal from SW solutions during photocatalytic processes also strongly depend on extracting agent characteristics and concentration. Extracting agents influence the adsorption of pollutants onto photocatalysts and thus, the availability of pollutants for oxidant species [1]. Improved photocatalytic degradation of HOCs was observed when using concentrations of surfactant below or close to the CMC [150]. Combination of surfactant monomers with the surface of TiO_2 by hydrophobic (non-ionic surfactants) or electrostatic (cationic surfactants) interactions was reported to form a superficial hydrophobic reactive monolayer in which HOCs have high affinity [150,151,156]. Less favourable effects

479 were observed for photocatalytic degradation of more hydrophilic compounds such as oxidation
480 by-products [151]. It was attributed to the decrease of their availability for oxidant species
481 because of the lower fraction of organic compounds implanted in the superficial hydrophobic
482 reactive monolayer (lower K_m) and/or a different locus of implementation of these organic
483 compounds inside this monolayer (closer to the hydrophilic heads of surfactants) (Figure 4). At
484 high surfactant concentration, photocatalytic degradation of HOCs strongly decreases due to
485 the hydroxyl radical scavengers as well as competitive partition of HOCs within micelles in the
486 bulk (that prevent reaction at the surface of the photocatalyst). Competition between surfactants
487 and HOCs for the occupation of active sites on the catalyst surface may also have strong adverse
488 effects [150,151,157]. Similar effects of concentration-dependant inhibition have been
489 observed when using CDs as extracting agent. Low concentration of CDs promotes the
490 photocatalytic degradation of HOC having high inclusion constant with CDs [158–160], while
491 high CD concentration hinders target pollutant degradation [62,139]. Unfortunately, SW
492 solutions usually contain high concentration of extracting agent. Interestingly, a lower
493 inhibitory effect was observed when using surfactants with bigger hydrated polar head, due to
494 the reduction of surfactant adsorption at the surface of the catalyst [18,112].
495



496

497 [Figure 4 –Partition equilibria of target pollutants during the treatment of a SW solution by a](#)

498 [TiO₂-based photocatalytic process. Reprinted from \[1\].](#)

499

500 Some other non-AOPs chemical oxidation processes have also been applied to the

501 treatment of SW solution, particularly ozone, activated persulfate [\[135,136,161,162\]](#), and

502 electrochemical processes using active electrodes that do not produce hydroxyl radicals

503 [\[128,163\]](#). Lower effectiveness for the removal of target pollutants has been reported because

504 of the generation of weaker oxidant species [\[1\]](#). For example, degradation kinetic rates observed

505 for the removal of PAH from SW solutions by electro-oxidation using graphite electrodes were

506 in the range 0.02-0.2 h⁻¹ [\[21,164\]](#). As regards to ozone, it was observed significant removal of

507 PAH and chlorophenols from SW solutions (45-65% removal) only when using high doses (>

508 500 mg O₃ L⁻¹) [\[165,166\]](#). Besides, it was reported that high concentration of surfactant

509 decreases gas-liquid mass transfer for both (semi)-volatile pollutants and ozone, thus reducing

510 the effectiveness of the ozone process [\[167\]](#).

511

512 **III.2.2 – Effectiveness for the recovery of extracting agents**

513 SW solution reuse by implementing a degradation process means that the aim is to
514 achieve both maximum removal of target pollutants and minimum degradation of extracting
515 agents [1]. Thus, the treated SW solution might keep similar extraction capacity than a fresh
516 SW solution without addition of extracting agents. However, two main issues are involved: (i)
517 the protective environment for target pollutants formed by surfactant micelles and CDs, which
518 usually decreases the availability of target pollutants for degradation (K_m and K_{CD} are crucial
519 parameters), (ii) the degradation of organic compounds in a non-selective way [1].

520 Several authors have also investigated the possibility to recover extracting agents by
521 optimizing operating conditions of AOPs in order to promote the degradation of target
522 pollutants and decrease the degradation rate of extracting agents. Even if hydroxyl radicals are
523 considered as non-selective oxidants, different reaction kinetics with target pollutants and other
524 extracting agents are obtained according to their chemical structure. For example,
525 perfluorinated surfactants present the interesting characteristic to be highly recalcitrant to
526 oxidation by hydroxyl radicals, however, they are considered as toxic persistent organic
527 pollutants and they cannot be used for soil remediation by SW [168]. Aromatic compounds are
528 also considered as highly reactive species [110]. A slower degradation rate of extracting agents
529 compared to aromatic target pollutants can be used for partial recovery of extracting agents. As
530 complete mineralization of target pollutants involves longer treatment time and higher
531 degradation rate of extracting agents [1], only degradation of pollutants is usually considered.
532 Therefore, the toxicity of degradation by-products [169,170] should also be assessed. Mousset
533 et al. [145] observed that a second SW step with a partially oxidized SW solution (containing
534 PAHs and TW80 as EA) by the EF process did not affect negatively the soil microbial activity,
535 compared to the use of a fresh SW solution. This result was ascribed to the production of
536 hydroxylated by-products with higher biodegradability and solubility than initial compounds
537 [145,171].

538 As regards to Fenton-based processes, promising results have been observed by using
539 CDs as extracting agents. The formation of a ternary complex CD-pollutant-Fe²⁺ allows
540 improving the availability of target pollutants towards hydroxyl radicals and higher degradation
541 kinetics of target pollutants were achieved compared to CDs [144,154]. By using the EF process,
542 better selective degradation was also achieved when using HPCD instead of TW80 as extracting
543 agent [144].

544 During photocatalytic processes, the formation of micelles in the bulk reduces the
545 availability of surfactants towards oxidant species generated on the photocatalyst surface
546 [150,151,157] (Figure 4). Even if it might be considered as an interesting behaviour for
547 minimizing the degradation rates of EAs, it was observed to do not improve the selectivity of
548 the process. In fact, much lower degradation kinetic of target pollutants is usually also observed
549 because of the partitioning within micelles. Thus, it was actually reported higher rate of
550 recovery of TX100 after full removal of a target pollutant (pentachlorophenol) when a low
551 concentration of TX100 was used [150].

552 Processes based on the activation of persulfates using iron ions or thermal activation
553 have also been recently developed for the treatment of SW solution. Compared to hydroxyl
554 radicals, sulfate radicals present some more selective features that might be useful for achieving
555 selective degradation of target pollutants [136,172].

556 During anodic oxidation processes, it has been reported that low current density strongly
557 hinders degradation of extracting agents due to a steric hindrance phenomenon for oxidation of
558 micelles on the anode surface. Lower degradation of extracting agents also results from the
559 decrease of mediated oxidation in the bulk at low current density [23,155]. Thus, free extra-
560 micellar target pollutants, continuously released in the solution (according to K_m) can be more
561 selectively degraded [23] (Figure 3).

562

563
564

Table 3 – Promising results reported in the literature on the recovery of extracting agents by using degradation processes

Process	Pollutants (P) (mg L ⁻¹)	Extracting agent (EA) (g L ⁻¹)	Effectiveness	Ref
Photocatalysis	Dibenzothiophene (0.3 – 1.3)	TX100 ¹ (0.14 – 0.25)	Full degradation of P / none degradation of EA	[173]
EF	PHE ² (17.8)	HPCD ³ (10)	Full degradation of P / 10% degradation of EA	[144]
Electro-oxidation (graphite electrodes)	PHE ² (35)	TW80 ⁴ (10)	95% removal of P / Similar extraction capacity of the treated solution	[174]
Electro-oxidation (graphite electrodes)	PHE ²	HPCD ³ (1.0)	Full removal of P / Similar extraction capacity of the treated solution	[164]
Fenton	p-Cresol (20)	TW80 ⁴ (0.86)	Full degradation of P / 10% degradation of EA	[175]
Activated persulfate	Nitrobenzene	SDBS ⁵ (8.2)	Better selective degradation than with the Fenton process	[161]
Anodic oxidation (BDD ⁶ anode)	PAHs from real SW solution (1 – 5)	TW80 ⁴ (6.6)	75-90% removal of P / Similar extraction capacity of the treated solution	[23]
Activated persulfate	PHE ² (10)	TW80 ⁴ (10)	96% removal of P / 20% removal of EA	[176]
Fenton	COCs ⁷ from real SF solution (3700)	E-Mulse 3 [®] (11)	>80% removal of P / Similar extraction capacity of the treated solution	[177]

565 ¹ Triton X 100; ² Phenanthrene; ³ Hydroxypropyl- β -cyclodextrin; ⁴ Tween[®] 80; ⁵ Sodium
566 dodecylbenzenesulfonate; ⁶ Boron-doped diamond; ⁷ Chlorinated organic compounds

567

568 However, contradictory results are also observed and the details of mechanisms leading
569 to the selective removal of pollutants solubilized within micelles are not fully understood.
570 Further development of selective degradation processes depends on the better understanding
571 and control of degradation mechanisms and kinetics, for which the nature and concentration of
572 EAs, target pollutants, and oxidant species have a crucial effect [172].

573 It is also worth noting that the critical parameter is not the amount of extracting agent
574 recovered but the extraction power of the treated solution. Important differences are usually
575 observed because of analysis artefacts of extracting agents, generation of degradation by-
576 products still solubilized in micelles and production of extracting agent by-products with
577 extracting properties [1]. For example, it was observed that a partially oxidized solution (by
578 using the EF process) containing 11% less of HPCD than the initial solution achieved slightly
579 higher PAH removal from soil than a fresh HPCD solution [145]. This result was ascribed to
580 the extraction capacity of hydroxylated HPCD (degradation by-products) with an internal
581 hydrophobic space that remained intact. Interestingly, [Dominguez et al. \[177\]](#) also reported that
582 Fenton oxidation of a SF solution led to >99% degradation of an additive of a commercial
583 extracting agent (E-Mulse 3[®]), however, the equivalent surfactant concentration was only
584 decreased by 40-50%, the interfacial tension of the solution was not altered and the extraction
585 capacity of the solution remained constant. On the contrary, the reduction of 21% of the TW80
586 concentration during the EF treatment of a SW solution strongly decreased the extraction power
587 of the partially oxidized solution compared to a fresh TW80 solution [145]. Such results might
588 be ascribed to the artefacts in analysis of extracting agents (detection of degradation by-
589 products identified as TW80 while they have lower extraction capacity).

590

591 **III.3 - Soil washing solution reuse or total removal of the organic load? The example of** 592 **the anodic oxidation process**

593 Recently, two different treatment strategies have been identified for the treatment of SW
594 solutions by anodic oxidation [22,23]. First, it was observed that treating a real SW solution
595 (with TW80 as EA) by anodic oxidation at low current density (1.8 mA cm⁻²) during a long
596 treatment time (23 h) lead to the selective degradation of PAHs as target pollutants and allow
597 the recovery of the extraction capacity of the treated SW solution [23]. It was also emphasized

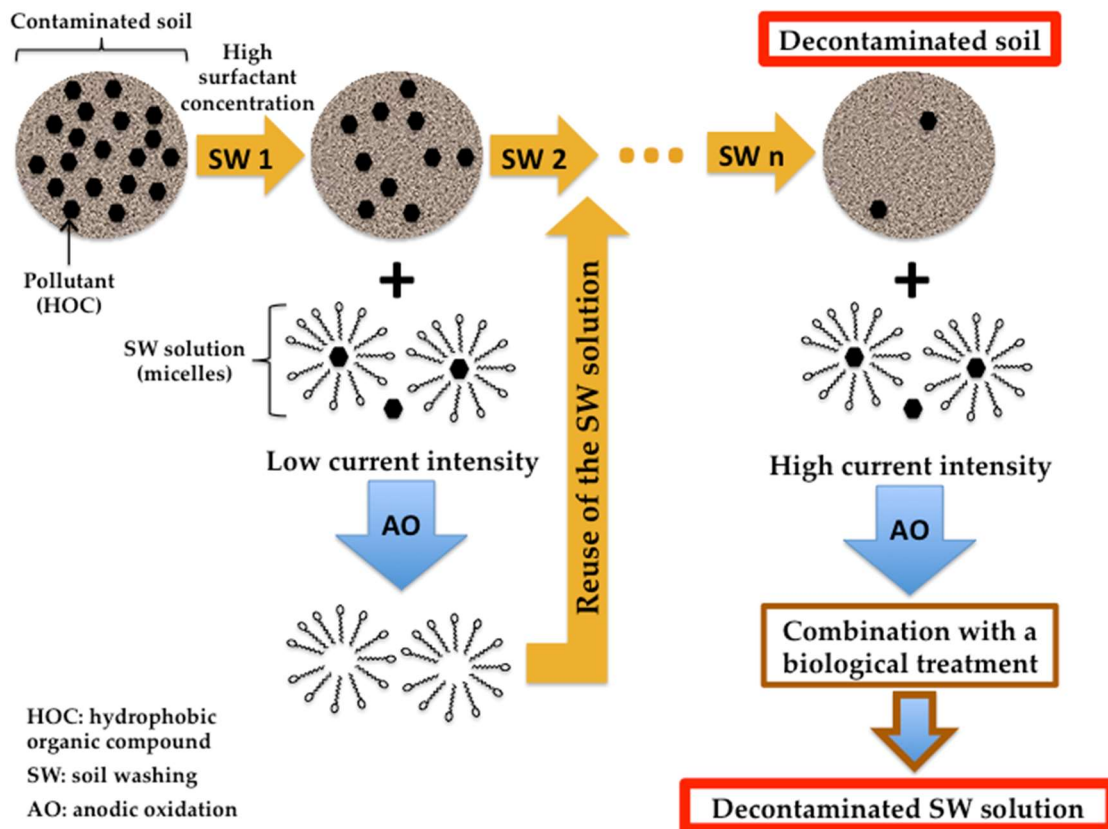
598 that a high surfactant concentration improves the selective degradation of target pollutants with
599 only a slight decrease of degradation kinetics of PAHs. Therefore, high concentration of
600 surfactant might be used in order to increase the transfer of PAHs from the soil-sorbed fraction
601 to the washing solution. In fact, the consumption of an additional amount of surfactant might
602 be compensated by the high rate of recovery of extracting agents during the treatment by anodic
603 oxidation at low current density. A second treatment strategy has been reported for the removal
604 of the organic load of a synthetic SW solution containing PHE as target pollutant and TW80 as
605 extracting agent [22]. It is based on the combination of anodic oxidation with a biological
606 treatment.

607 It might be actually interesting to use these two different treatment strategies in a
608 complementary way. A crucial advantage of anodic oxidation is the possibility to easily manage
609 the operating conditions, particularly the current density [178]. Thus, an anodic oxidation
610 treatment system might be able to implement both strategies (Figure 5). First, low current
611 density might be initially used for the reuse of the SW solution. Then, when sufficient pollutant
612 removal rate from soil would be achieved, the same system might treat the SW solution at high
613 current density in order to remove the organic load with a possible combination with a
614 biological treatment.

615 However, a systematic analysis taking into consideration all the different parameters of
616 such complex environmental engineering issue would be required for concluding on the best
617 treatment strategy (e.g. using life cycle assessment). From data obtained, only a short cost-
618 benefit analysis can be performed on energy consumption, which is a critical parameter during
619 anodic oxidation. It was reported that SW solution treatment at low current density only
620 required 13.2 kWh m^{-3} for the reuse of the treated solution [23]. By considering the price of the
621 electricity as 0.12 € kWh^{-1} (in France), it corresponds to an energy cost of 1.6 € m^{-3} of SW
622 solution treated. Considering a price for TW80 at 4.0 € kg^{-1} , it means that 1 m^3 of a solution at

623 5.0 mM of TW80 (6.6 g L^{-1}) would cost 26 €. Therefore, the saving arising from the reuse of
 624 the SW solution may compensate costs related to energy consumption of anodic oxidation. For
 625 comparison, the energy consumption was 39 kWh per kg of COD removed when using anodic
 626 oxidation at high current density for the removal of the organic load. By considering 3 h of pre-
 627 treatment (29% COD removal of an initial solution at 2.7 g L^{-1}), it corresponds to a consumption
 628 of 30.5 kWh m^{-3} (3.7 € m^{-3}) [22]. This value is much higher than the energy consumption
 629 required for SW solution reuse. Moreover, the energy consumption of the post-biological
 630 treatment are not considered. However, a final step for the removal of the organic load from
 631 SW solutions would be always required prior discharge in order to avoid any contamination of
 632 the aquatic environment.

633



634

635 **Figure 5** - Treatment strategy for soil remediation using soil washing and anodic oxidation processes.

636 Anodic oxidation at low current intensity allows the reuse of the soil washing solution for n soil washing

637 steps. Anodic oxidation at high current intensity combined with a biological treatment allows the removal
638 of the organic load for final disposal of the soil washing solution.

639

640

641 **IV – Discussion**

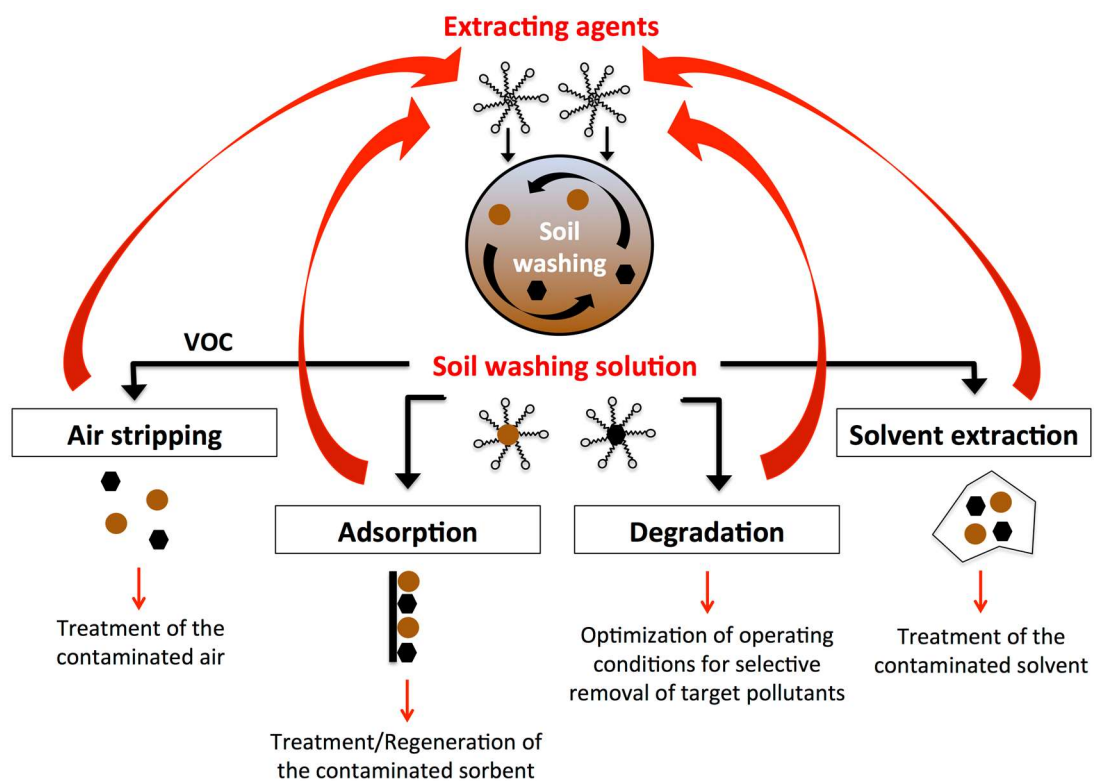
642 Several technologies have been critically reviewed in this article (Figure 6). The choice
643 of the most suitable technique depends strongly on characteristics of the SW solution (Table 3).
644 Air stripping and related technologies (such as vacuum extraction or pervaporation) allows the
645 effective and selective removal of compounds such as trichloroethylene or perchloroethylene
646 from SW solutions. The choice of an adapted organic solvent for a liquid-liquid extraction can
647 lead to an effective extraction of HOCs in the organic phase while a large amount of extracting
648 agents is also recovered. The first drawback is that foaming issues have to be managed. The
649 disposal of the contaminated solvent also represents a critical drawback for the sustainability
650 of the process. Besides, the adsorption process appeared as a promising process for the selective
651 separation of target pollutants from SW solutions. Whatever the separation process used, high
652 concentrations of extracting agent usually reduce separation effectiveness due to the partition
653 of target pollutants in the micellar pseudo-phase or inclusion complex with CDs (K_m or K_{CD} are
654 crucial parameters). Therefore, the optimal conditions for SW (high concentration of extracting
655 agent and high K_m or K_{CD}) have adverse effects on selective separation processes. Furthermore,
656 a post-treatment of the contaminated air/sorbent/solvent is required, thus increasing the global
657 cost of the whole treatment strategy.

658 Optimization of operating parameters for degradation processes can also lead to higher
659 degradation rates of target pollutants compared to extracting agents. These results are mainly
660 ascribed to the different reactivity of target pollutants and extracting agents with oxidant species.

661 The heterogeneous production of hydroxyl radicals at the anode surface during the anodic

662 oxidation process was also reported to promote selective oxidation of target pollutants when
 663 using low current density. Compared to separation process, a lower amount of extracting agents
 664 is usually recovered by using degradation processes but the great advantage lies in the
 665 simultaneous degradation of target pollutants. In case of partial recovery of EAs, periodic re-
 666 injection of fresh extracting agents might be considered for maintaining the extraction capacity
 667 of the reused solution.

668



669

670 Figure 6 – Treatment strategies for the recovery of extracting agents from contaminated soil washing
 671 solutions.

672

673 Table 3 – Important operating conditions, target pollutant and extracting agent characteristics to
 674 consider according to the choice of the process used. CMC: critical micelle concentration; K_m : micellar
 675 phase / aqueous phase partition coefficient; K_{CD} : complex stability (or equilibrium) constant between
 676 organic compounds and cyclodextrins

Process	Important target pollutant characteristics (optimal*)	Important extracting agent characteristics (optimal*)	Important operating conditions
Air stripping	Henry constant (low), saturated vapor pressure (high), K_m/K_{CD} (low)	Henry constant (high), concentration (low), K_m/K_{CD} (low)	Limitation of foaming (hollow fiber membranes, vacuum processes)
Liquid-liquid extraction	Solvent-water partition coefficient (high), K_m/K_{CD} (low)	Solvent-water partition coefficient (low), concentration (low), K_m/K_{CD} (low)	Limitation of emulsification and amount of solvent used (hollow fiber membranes), highly hydrophobic solvent
Membrane processes	Oil-containing mixture (for selective removal), K_m	Concentration, K_m , micelle size, CMC, effect on concentration polarization	Ultrafiltration (for micellar-enhanced ultrafiltration), fouling control (depending on fouling materials)
Adsorption processes	Partition coefficient on the sorbent material (high), K_m/K_{CD} (low)	Partition coefficient on the sorbent material (low), concentration, K_m/K_{CD} (low)	Sorbent material (pore size distribution) and dose
Degradation processes	Reactivity (high), K_m/K_{CD}	Reactivity (low), concentration, nature, K_m/K_{CD}	Optimized for selective degradation of target pollutants

677 * Optimal conditions for the selective removal of target pollutants from SW solutions (different from optimal
678 conditions for the SW step)

679

680 Further studies on real contaminated soils are required in order to assess the efficiency
681 of these processes at real field scale. The complex mixture of compounds in real SW solutions
682 involves strong competition mechanisms, which often reduce separation and degradation
683 effectiveness. Several studies are performed on synthetic SW solutions, without taking into
684 consideration the influence of clay and silt particles. Additional studies would be required in
685 order to a better understand the impact of these compounds on selective separation or
686 degradation processes. The extraction capacity of fresh and recovered SW solutions should also
687 be always assessed with real contaminated soils. The use of artificial or spiked soils usually
688 leads to a strong overestimation of the efficiency due to a lower sequestration of pollutants. For

689 example, it has been observed that ageing and weathering of tar oil-contaminated soil leads to
690 the formation of resinated materials which strongly reduce mass transfer of PAHs from soil to
691 the washing solution [10,189]. Finally, there is an important lack of data in the scientific
692 literature on pilot or field scale applications in this context of most of processes (particularly
693 selective degradation and adsorption processes). These data will be crucial for assessing the
694 real potential of these treatment strategies.

695 Nature and concentration of the extracting agent used during the SW step are also
696 critical parameters for the treatment of SW solutions (Table 3). Thus, the implementation of
697 optimal operating conditions for SW should also take into consideration the impact of the nature
698 and concentration of the extracting agent chosen on the treatment of the SW solution.
699 Particularly, its capacity to be recovered and reused for several SW steps should be assessed in
700 order to improve the sustainability of the whole process. Optimizing the recovery of extracting
701 agents requires taking into consideration all the steps involved in the soil remediation process
702 (Figure 1).

703

704 **V – Conclusions and Recommendations**

705 EA-enhanced SW is an effective treatment strategy for the removal of organic pollutants
706 when it is applied to a suitable contaminated soil. The optimization of operating parameters
707 (nature of the EA, concentration and other operating conditions) is the most direct way to save
708 EAs, improve extraction effectiveness and implement a cost-effective process. However, an
709 appropriate treatment strategy of the SW solution allowing the recovery of extracting agents
710 and the reuse of the SW solution is also a crucial step in order to save large amounts of
711 extracting agents and to improve the sustainability and ecological footprint of the whole
712 remediation process.

713 Promising results have been reported for the recovery of extracting agents from SW
714 solutions but further studies are necessary in order to assess the robustness of each process and
715 the possibility for scaling up. Then, the choice of the most suitable technology (and operating
716 conditions) depends on the physicochemical characteristics of each specific SW solution. It is
717 therefore crucial to adapt the process to the specificity of each kind of SW solution (nature and
718 concentrations of target pollutants, extracting agents and other compounds mobilized during
719 the SW step).

720 Finally, the choice of the most suitable strategy for the treatment of a SW solution
721 should be based on a cost-benefit analysis and life cycle analysis should be performed for
722 selecting the most suitable strategy. Selective separation/degradation of target pollutants
723 involve the implementation of costly processes (in terms of reagents and/or energy
724 consumption). Therefore, these additional costs have to be compared to the savings coming
725 from the reuse of the SW solution. The development of effective processes for recovery of
726 extracting agents could also promote (i) the use of more expensive extracting agents with both
727 higher extraction capacity and lower soil toxicity and (ii) the implementation of several
728 successive SW steps in order to achieve higher removal rates of HOCs from real contaminated
729 soils.

730

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736

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