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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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Abbreviations

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

Abstract

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

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

Keywords

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

II – Separation processes

II.1 – Air stripping and related technologies

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

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

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

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

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

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

II.2 – Liquid - liquid extraction

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

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

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

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

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

II.3 – Membrane processes

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

II.4 – Adsorption

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

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

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

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

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

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]

¹ Phenanthrene; ^{2,8,14,15} Triton X 100, 165, 114, 305; ³ Fluoranthene; ⁴ Benzo(a)anthracene; ⁵ HPCD ⁶ Randomly methylated β -cyclodextrin; ⁷ Sodium dodecylsulfate; ^{9,10} Tween® 40, 80; ^{11,12} Brij® 30, 35; ¹³ Polycyclic aromatic hydrocarbon; ¹⁶ Pyrene; ¹⁷ Sodium dodecylbenzene sulfonate; ¹⁸ Layered double hydroxides.

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

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

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

III – Degradation processes

III.1 – Biological processes

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

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

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

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

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

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

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

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

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

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

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

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

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

Electrochemical processes can lead to the production of hydroxyl radicals from (i) anodic oxidation by water discharge on the surface of anode with high oxygen evolution overpotential (such as boron-doped diamond, BDD) [127,128], (ii) EF process through *in situ* production of the Fenton's reagent [110]: H_2O_2 is produced from the two electron reduction of oxygen at a suitable cathode (such as gas diffusion or three-dimensional electrodes using carbon-based porous materials combined with injection of compressed air in the solution), while only a catalytic amount of ferrous iron is supplied and continuously regenerated by reduction of ferric iron at the cathode [129]. The EF process allows increasing the efficiency of the Fenton's process by avoiding the addition of chemical reagents, reducing waste reactions and avoiding sludge formation [1,130]. Oxidation of inorganic anions in the solution (SO_4^{2-} , Cl^- , etc.) can also lead to the homogeneous production of oxidant species in the bulk such as active chlorine, persulfate, sulphate radical, which also participate to the oxidation of organics ("mediated oxidation") [131,132].

Recently, a great attention has also been given to the development of AOPs based on persulfate activation, due to several inherent advantages of sulphate radicals such as (i) the convenience of storage and transportation of solid persulfate, (ii) the different way to activate persulfate (e.g. thermal or electrochemical processes, Fe^{2+}) and (iii) the longer lifetime of sulphate radicals compared to hydroxyl radicals [133–137].

Total degradation of target pollutants as well as high mineralization rate of SW solutions is usually achieved when using such AOPs. Some examples of degradation kinetic rates are reported in Table 2. When optimized operating conditions are used, the apparent degradation kinetic rates of target pollutants in SW solutions are usually in the range $0.5 - 5 \text{ h}^{-1}$.

Table 2 – Degradation kinetic rates of target pollutants in soil washing solution by advanced 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
437

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

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

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

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

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

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

Figure 4 –Partition equilibria of target pollutants during the treatment of a SW solution by a TiO_2 -based photocatalytic process. Reprinted from [1].

Some other non-AOPs chemical oxidation processes have also been applied to the treatment of SW solution, particularly ozone, activated persulfate [135,136,161,162], and electrochemical processes using active electrodes that do not produce hydroxyl radicals [128,163]. Lower effectiveness for the removal of target pollutants has been reported because of the generation of weaker oxidant species [1]. For example, degradation kinetic rates observed for the removal of PAH from SW solutions by electro-oxidation using graphite electrodes were in the range $0.02\text{-}0.2\text{ h}^{-1}$ [21,164]. As regards to ozone, it was observed significant removal of PAH and chlorophenols from SW solutions (45-65% removal) only when using high doses ($> 500\text{ mg O}_3\text{ L}^{-1}$) [165,166]. Besides, it was reported that high concentration of surfactant decreases gas-liquid mass transfer for both (semi)-volatile pollutants and ozone, thus reducing the effectiveness of the ozone process [167].

III.2.2 – Effectiveness for the recovery of extracting agents

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

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

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

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

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

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

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]

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

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

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

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

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

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

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

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

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

Figure 5 - Treatment strategy for soil remediation using soil washing and anodic oxidation processes. Anodic oxidation at low current intensity allows the reuse of the soil washing solution for n soil washing

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

IV – Discussion

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

Optimization of operating parameters for degradation processes can also lead to higher degradation rates of target pollutants compared to extracting agents. These results are mainly ascribed to the different reactivity of target pollutants and extracting agents with oxidant species. The heterogeneous production of hydroxyl radicals at the anode surface during the anodic

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

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

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

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

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

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

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

V – Conclusions and Recommendations

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

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

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

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