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Electrochemically Assisted Soil Washing for the Remediation of Non-polar and Volatile Pollutants

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Abstract

Purpose of Review This review is focused on the removal of chlorinated hydrocarbons (as representative of persistent pollutants) from soil by soil-washing techniques, paying special attention to the application of electrochemically assisted technologies for the treatment of the liquids and gases produced during this treatment. It considers the degree of maturity of the technologies and suggests challenges for future research.

Recent Findings Electrochemical technologies can help to improve the overall efficiency of soil washing processes in the removal of chlorinated hydrocarbons, contributing to the depletion of these hazardous species from the soil washing liquid and gaseous effluents generated during the treatment of the soil.

Summary Chlorinated hydrocarbons are a good example of persistent organic pollutants which can be found in very high concentrations in polluted soil, especially in industrial sites. Because of its fast action, soil washing can be efficient for preventing the spread of chlorinated hydrocarbons after accidental spills. Recent progress about fundamentals of this process and key parameters involved is discussed at the light of competing technologies, paying special attention to the liquid and gaseous wastes produced during this treatment, in the search of holistic approaches. Among the different alternatives proposed, electrochemical technologies are the focus of attention of many researchers and, because of that, recent progress in electrochemical technologies capable to deplete the pollutants is also discussed, within a comparison context with other competing technologies, indicating the technology readiness level of each electrochemical process and the challenges that must be overcome in order to reach full-scale applicability.

Keywords Soil remediation · Chlorinated hydrocarbons · Ex situ soil washing · Surfactants · Volatile organic compounds (VOCs) · Gaseous streams · Electrochemical technologies

Introduction

Soil is a very complex element, which is continuously interacting with the two other important components of the natural environment: water and air. Because of this interaction, when soil becomes polluted, contaminants may be propagated fastly, affecting ecosystems and human health. Among the large variety of compounds that can be found in soils as pollutants, it is worth to mention chlorinated hydrocarbons (CHCs), chemicals associated to important industrial products such as pesticides, solvents, thermal fluids, metal degreaser, and raw matters of the chemical industry [1]. Because of their anthropogenic nature and negative properties, such as high volatility and strong recalcitrance to degradation, the potentiality of damage that they can cause in the environment is extremely high. Their hazardousness is frequently related with the presence of chlorine atoms which favors the production of many chlorinated intermediates even more dangerous than the parental compound.

Recently, the development of treatment technologies related to the remediation of soils has gained lots of attention because society has started to be conscious of the importance of solving the problem of pollution into soils as soon as it is generated, preventing the spread of the pollutants to avoid low efficient remediations [2, 3•]. The success of technologies developed in the last century does not only depend on the

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technology itself but also on the origin and physical properties of the pollutants (such as water solubility and sorption characteristics) and the structure and soil composition.

Soil treatment technologies have been classified according to the location of the soil during the treatment in (1) in situ techniques that are applied directly in the soil placement where the pollution is originated without implying excavation and (2) ex situ techniques that require the excavation of the polluted soils to be treated in the same place (on-site) or another different place (off-site).

In situ treatments usually involve the movement of air or water (frequently including additives) throughout the polluted soil, which is favored by more permeable media. For soils with low permeability, these technologies are also useful, but applications of electric fields are required to mobilize pollutants. The application of these in situ technologies is recommended for long-term treatments, although some technologies can also be used to prevent the spread of the pollutants.

Ex situ treatments generally offer greater scope for managing conditions such as temperature, humidity, and stirring speed in order to optimize the treatment efficiency and to control fastly the potential spreading of pollutants when accidental spills of hazardous compounds happen. Normally, these processes treat less volume of soils with higher concentration, which normally reduces the overall costs concerning a soil in which pollution has been spread for a long time.

Generally, soil treatments can be classified according to the type of technology as thermal, biological, and physicochemical, although in many cases, not a single but a synergetic combination of the process may offer the most effective remediation strategy for a given case [4••]. Several examples of thermal remediation techniques were applied with heavy metals and organic compounds, but nowadays, these techniques have been applied to increase the volatilization rate of the volatile and semi-volatile target pollutants, promoting their extraction throughout wells, for later treatment of the gaseous polluted streams [5].

Regarding the biological process, most of them are focused on the degradation of organic pollutants under controlled conditions using different microbial communities adapted to each particular type of pollutant (such as petroleum, oil sludge, and CHCs) [6–8]. The long treatment times motivated for significant removals, motivate the necessity of coupling these technologies with other processes such as desorption extraction [9], adsorption onto activated carbon [10], or electrochemical processes [11].

Numerous studies were carried out with persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAH) [12] and pesticides such as lindane or 2,4, dichlorophenoxyacetic acid (2,4-D) [13•], although it is important to consider that the combination with other technologies obtained generally more efficient results than the application of the biological treatments alone [14••, 15].

However, biological treatments are not always successful. There is a large variety of potential anthropogenic pollutants, and it is not always possible to find microorganisms adapted to their degradation cost-effectively [16•]. In this line, physicochemical treatments can be applied to remove pollutants dragged with liquid or gaseous effluents, to transform the pollutants into less hazardous compounds, or to concentrate or isolate them for further treatment.

Thus, applications of in situ electrochemical techniques, such as electrokinetic remediation (EKR) alone [17] or combined with permeable reactive barriers (PRB), have been shown to behave as good alternatives. These technologies require less modification of the environment and less transport; however, the efficiency was sometimes limited, and long-term treatment is required [18, 19••, 20]. Soil properties, such as particle size, stratification, humidity, pH, and organic content, determine the viability of different soil remediation technologies, so a previous analysis would help to apply successful techniques [21]. Anyhow, they are not normally suitable for rapid contention of pollutants after an accidental spill.

In this context, to control main parameters of soil remediation and apply faster treatments to remove pollutants such as heavy metals and CHCs preventing their spread, ex situ, soil washing (SW) emerged as a technology capable of improving the removal of contaminants into soil, especially when accidental acute pollution happens, employing chemical-physical extraction and separation to remove or transfer pollutants to a liquid stream [22]. The study of this technology, their possible improvements, and couplings with other techniques is treated in the next section of this work.

Soil-Washing Remediation Techniques

The use of an extracting solution to recover soil pollutants could be materialized with an in situ process, known as soil flushing (SF), that consists of the movement of the groundwater and/or an aqueous solution with suitable chemicals throughout the soil to drag pollutants up to extraction wells where they are pumped out for further treatment and an ex situ process, known as soil washing (SW), that involves the excavation of the affected land before the treatment in an external extraction tank where the pollutants are transferred from the soil to a liquid solution that later should be further treated.

For the very first moments after acute discharges, ex situ treatments are rather preferred because of the shorter treatment time and the capability to easily combine with other technologies. SW employs chemical-physical extraction and separation process to remove or transfer organic and inorganic contaminants from the soil into a liquid stream, and it operates at a certain solid/liquid ratio frequently between 5 and 40% [23]. Then, after sedimentation, it is required the filtration of effluents to separate from the solid fraction a liquid stream to be further treated. Nowadays, within a context of increasing concern about the total sustainability of processes, it has also to be considered the gaseous fraction that is generated in these processes due to the potential presence of volatile and semi-volatile compounds in soils which are barely mentioned in other related reviews. Related with gaseous treatments, previous studies carried out mainly consider the emission of volatile or semi-volatile pollutants contained in soils, and it reported technologies as thermal desorption, [5], composting [24], advanced oxidation processes, and electrochemical technologies [25, 26], but there is very short information about the generation of gaseous pollutants during the treatment of polluted soil. In these systems, the capture of gaseous effluents must be carried out during the mixing with the extracting solution, so three phases of a very complex product have to be taken into account to understand completely the process in the design of a full remediation treatment (Fig. 1).

The ex situ SW process enhances the contact between the extracting agents and soil pollutants as the mixture can be energetically stirred. However, the transference of pollutants to a liquid solution sometimes requires the use of additives.

Hence, these reagents can reduce the time necessary to treat a polluted site, as compared to the use of water alone, while reducing the necessity of water, leading to more sustainable processes. Nevertheless, the formulation used must be of low ecotoxicity for the soil and, also, of high biodegradability [27].

Surfactants are the most important extractant agents used to improve the solubility of organic pollutants. They consist of amphiphilic molecules, composed of two main components, the hydrophobic tail group and the hydrophilic head group, and are characterized by their chemical structure, hydrophilic-lipophilic balance, and critical micellar concentration (CMC).

Synthetic surfactants are continuously being developed, and their selection is an important feature to reach the final success of SW technology. Among the different types of surfactants available in the market, it is worth to highlight anionics (such as sodium dodecyl sulfate (SDS) or sodium dodecyl benzenesulfonate (SDBS)), cationics (such as quaternary ammonium derivatives), amphoterics, and nonionics (such as Tween 80 or Triton 100) [28]. For ionic surfactants, a high concentration is required to overpower the electrostatic repulsion among ionic head groups, through micellization [29]. Additionally, it had developed new products with higher biodegradability and less affected by the precipitation or sorption onto the soil. Among these compounds, it is worth to mention the biosurfactants, which are amphiphilic compounds able to form micelles and have higher extraction efficiency. As examples, saponin or alkyl polyglycoside was used to enhance the remediation of soil polluted with o-dichlorobenzene (o-DCB) and p-dichlorobenzene (p-DCB) [30], or surfactin and rhamnolipid were applied to remove high quantities of crude oil accidentally spilled in soil [31]. The main advantages of biosurfactants include higher biodegradability, ecological safety, lower toxicity, and the possibility to be produced in situ [4, 32].

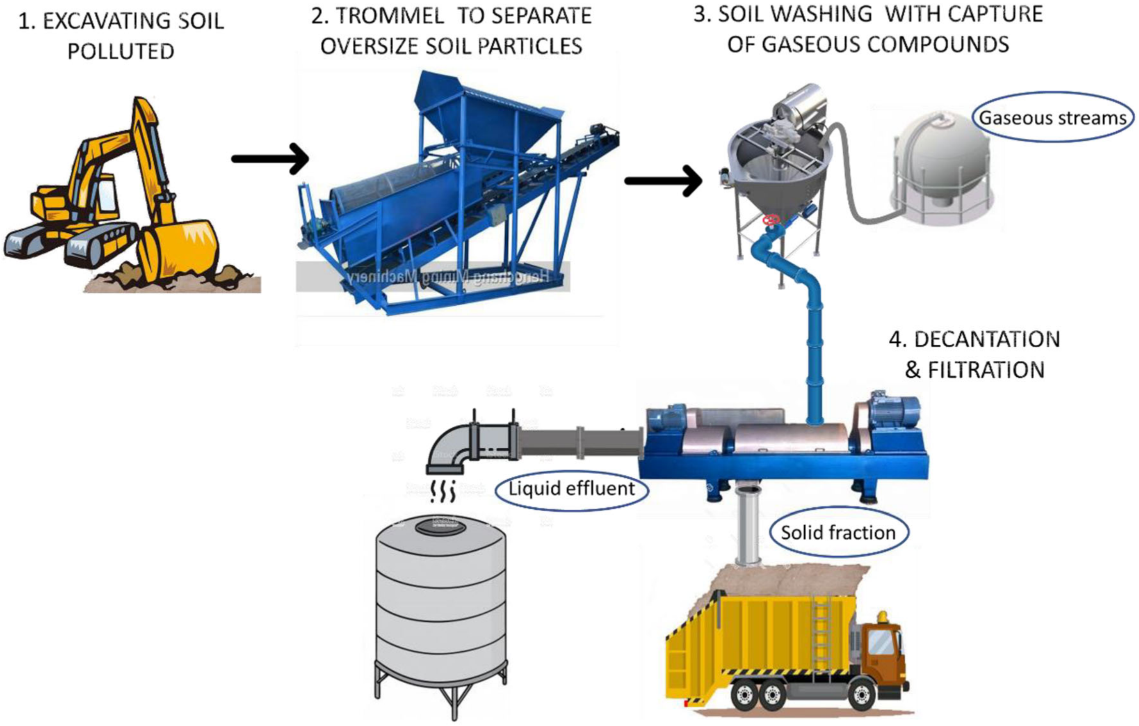

Fig. 1 Scheme of an industrial ex situ soil washing process with the complete recovery of all polluted phases (gaseous stream, liquid effluent, and solid fraction)

Other less common alternatives to be used as extracting agents are the humic acids, which have amphiphilic properties, and their carboxylic groups may bind with several hazardous metals after their deprotonation [33, 34], or the use of organic acids (such as oxalic, citric, and tartaric acids) coupled with and EDTA derivatives which have been proposed for the remediation of vanadium-contaminated soils [35].

Regarding the further treatment of the different SW solutions produced with extracting agents, Trellu et al. [36] summarized in a detailed review the wide variety of extracting agents (synthetic surfactants, biosurfactants, cyclodextrins, organic cosolvents, vegetable oils, and other acidic compounds or polymers), and then, the different options of advanced oxidation process (AOPs) suitable for the treatment of SW wastes generated, including the electrochemical ones.

Recently, the successful treatment evaluations carried out in lab-scale studies have encouraged to scale-up the technology, to develop in a pilot-scale system, and then, even go further in a commercial scale to treat a real portion of soil polluted. In real sample treatment, a pretreatment to remove large objects from the soil is required to obtain a homogeneous soil ready for the washing step. Removal is done through scalping, mechanical screening, jigging, and tabling. The oversized materials may be from construction wastes to large pieces of rock or gravel. These materials are usually not contaminated; however, if treatment is necessary, the size of these pieces must be reduced. Then, different soil-washing systems are designed considering the different remediation conditions as the presence of metallic pieces, larger solid masses, or sands. The most common SW process applied to remove persistent organic matter requires the use of hydrocyclons after control of the size of particles to ensure good mixing. In this step, it is proposed to collect the possible gaseous currents emitted from the SW systems to be further treated [37] which would help to attain a more sustainable process.

The size of industrial extractors for soil polluted depends on the needs of a specific remediation site. As a rule of thumb, the space requirement needed for a typical plant will range from approximately 100 × 200 to 125 × 250 ft for a plant that can process 25 or 50 t h^{-1}, respectively [38]. This area contains the soil and contaminated piles and the equipment for the washing plant. Some treatment facilities that are installed in Glasgow (Scotland) [39] have a maximum capacity of 100 t h^{-1}, and it also can recover the aggregates, sand, clay, and top soil to provide this material back into the construction/agriculture sector. An option to separate the washing solution (liquid phase) from the solid fraction might be the use of a screw decanter centrifuge. This device rotates at high speed (2000–6000 rpm) helping the solids settle further down by centrifugal force, and the solid fastly accumulates onto the inner surface of the tube. Then, an endless screw pushes the solid accumulated, which is moved, dewatered, and discharged by the bottom part. The washing fluid is converted into clarified liquid and discharged from the outlet on the side plate. The liquid obtained can be recovered to reuse in further SW processes, and the solid aggregates, depending on their size, can be used in road construction, building foundations, pavement sand, and as pipe bedding.

Recent Progress in the Ex Situ Soil Washing Treatment

The relevance of SW technologies for the treatment of soil contaminated with organic pollutants has enhanced the publication of relevant works in the last 5 years. It highlighted the use of anionic surfactants as sodium dodecyl sulfate (SDS), not only because of their lower sorption into the soil but also because of their low cost and higher extraction efficiency. In this line, Dos Santos et al. studied the removal of petroleum from low conductivity soils using SDS in a concentration ranged from 500 to 5000 mg L^{-1} with an efficiency higher than 92% [40••]. Removal of several refractory pesticides has been also evaluated, including pendimethalin [41•] or oxyfluorfen [42] aiming to produce SWWs with high organic load that enhances the performance of a further treatment to completely remove these contaminants. To enhance the soil washing process, other authors have proposed the use of different structures to remove organic compounds. Kim et al. [43] applied an ex situ SW process in soil contaminated with large quantities of petroleum using novel core-crosslinked amphiphilic polymer nanoparticles that have low sorption onto the soil particles as compared with the conventional nonionic surfactants as Triton X-100 and Brij 30, obtaining the highest efficiency (96%) with these new nanoaggregates. To remove soil polluted with PAH such as acenaphthene (ACE), phenanthrene (PHE), fluoranthene (FLA), or pyrene (PYR), it was coupled the extraction effect of a non-ionic surfactant as Tween 80 with a CD as hydroxypropyl-beta-cyclodextrin showing extraction efficiency higher than 80% [44]. However, high loads of soil polluted with diesel were extracted using a different concentration of a single non-ionic surfactant (Tween 80) obtaining an efficiency close to 90%, which confirms the strong influence of physical properties of hazardous hydrocarbons in the viability of the process [45••]. In recent years, these surfactants have been applied in the treatment of heavy metal-polluted soils because of their potential risk to human health due to their detection in abandoned industrial soils. Eco-friendly washing agents are very in demand for practical applications of SW to remediate these contaminated sites. As an example, there are different artificial chelating agents, such as EDTA, which can bind multiple heavy metals to form soluble and stable complexes and generate large molecules with the pollutants that are easily further removed.

Recently, the combined utilization of multiple SW reagents has become a clear objective to improve the process.

However, sometimes, it required different sequential extraction with alternative washing reagents that increase the total costs. Thereby, new formulations with the capacity of treating high concentrations of heavy metals and a reduction of toxicity and mobility were required. As an example, it mentioned the removal of Cu, Ni, and Zn from an industrial soil that was recovered with a low concentration of EDTA and three organic acids (citric, oxalic, and tartaric acid) with an efficiency higher than 80% [46].

Also, a new and interesting concept called "technology readiness level" (TRL) firstly applied by NASA in 1974 has appeared to evaluate the level of maturity that a technology has reached. Thus, during the last quarter of the last century, the TRL applied to soil washing technology for the remediation of soils polluted with hazardous organic compounds increased from very low values (3–4) to almost levels 7–9, with all elements of the required value chain in full operation for the simpler technologies and, even, companies that are selling key-on-hand solutions to real problems. However, there is still a lot of work to be done regarding the optimization in the combination of processes and the effect of the formulation of the washing fluids, with many studies whose TRL that still need to be largely improved [47•] to reduce the big gap in their development and scale-up which has to be considered in future research.

Ex Situ Soil Washing Treatment for the Removal of CHCs

Many technologies have been developed to remediate polluted soils with CHCs using SW techniques, being differentiated in terms of the different strategies faced and/or the combination with other processes. Thus, the identification of the type of surfactants and the most useful concentration according to the target pollutants has been studied. Laha et al. [48] described the selection of the appropriate surfactant concentration with different CHCs and the influence of surfactant sorption onto soils that appears with the increasing surfactant concentration until the onset of micellization. It was provided a discussion of equilibrium partitioning theory to account for the distribution of CHCs between soil, aqueous phase, sorbed surfactant, and micellar surfactant phases. In this line, more studies were reported using different surfactants, types of soils, and pollutants. Zhang et al. [49] applied a coupled process with non-ionic surfactant (Triton X-100) and powdered activated carbon (PAC) to remove chlorine pesticides such as chlordene, chlordane, and mirex, with the aim to extract the maximum quantity from polluted soil and later retain in the PAC for a further treatment.

Among typical surfactants used, anionic surfactants, such as sodium dodecyl sulfate (SDS), or non-ionic, such as Tween 80 and Triton X-100, are less likely to be adsorbed onto the soil, and initially, they were used in works to confirm the efficiency to extract the pollutants from soils [50••]. CHCs such as lindane [51], clopyralid [52], and trichloroethylene [53] have been removed from low permeability soils with good results in a concentration that ranged from 1 to 100 mg kg^{-1} soil. However, later, it was necessary to enhance the treatment to remove contaminants from the soil washing wastes (SWW) generated. The aim of these studies was not only the study of the remediation of soils but also the study of properties of the resulting SWWs, such as their regeneration capacity to create an environmentally friendly process, the degree of sorption onto soil, and the evaluation of biological parameters of washing solutions as biodegradability, enzyme activity, or toxicity to avoid the use of large amount of surfactants that can cause possible harms to the soil ecosystem.

Thus, many technologies are still being developed to extract pollutants in a cost-efficient way. In this line, the coupling of SW with other processes and technologies seems to be the most valuable alternative to face the problem of spiked soils, not only with CHCs compounds but also with other non-chlorinated hazardous hydrocarbons and other toxic inorganic compounds such as heavy metals. Therefore, new perspectives of the ex situ treatment of spiked soils would be focused on the following:

1) The improvements of extracting agents applied to be more environmentally friendly for soils, to increase their final recovery and
2) To determine an efficient coupling with Electrochemical Advanced Oxidation Processes (EAOPs) technologies to remove the more refractory and hazardous compounds.

The alternatives could be biological processes which would be focused on the reduction of their final toxicity and the removal of a biodegradable fraction or with processes that consist of a separation step that enhance a previous recovery of the extracting agent and further complete removal of pollutants, but these processes should be applied as a coupled treatment. Table 1 summarizes most relevant works published in the last 5years and, with informative purposes, the approximate TRL of these works.

Treatment of Liquid Soil-Washing Wastes by Improved Degradation Processes

Oxidation technologies are very important for the removal of CHCs from liquid wastes. Several recent reviews show that these technologies produce outstanding results [54••, 55], although the operating conditions must be carefully evaluated to obtain high efficiencies and to avoid the formation of byproducts that can be even more dangerous than the original pesticides, from a viewpoint of potential toxicity, mutagenicity, and carcinogenicity.

Table 1 Soil-washing experiments conducted for remediation of different hazardous hydrocarbon-polluted soils

Pollutant/concentration	Remediation technology	Experimental conditions	Main results	Technology readiness level (TRL)	Reference
Petroleum/100 mg kg^{-1} soil	Soil washing enhanced with sodium dodecyl sulfate (SDS)	0.8 L of washing agent (SDS); 1 g kg^{-1} petroleum soil; 100–5000 mg L^{-1} SDS Kaolinite, low permeability soil	92% of total removal from soil	5 (tested in intended environment)	[45]
Herbicide oxyfluorfen/100 mg kg^{-1}	Soil washing enhanced with sodium dodecyl sulfate (SDS)	0.8 L of washing agent (SDS); 100–10,000 mg pollutant kg^{-1} soil; 100–5000 mg L^{-1} SDS: low permeability soil	99% total removal from soil	5 (tested in intended environment)	[52]
Diesel 50 g kg^{-1} soil	Soil washing enhanced with Tween-80	10 g of synthetic soil, 100 ml of Tween 80 (5, 7.5, 10 g/L); 180 min; 20 °C 320 rpm	Removal efficiency Tween 80, 5 g L^{-1}, 75.2%; 7.5 g L^{-1}, 80%; 10 g L^{-1}, 87.9%	6 (tested in intended environment close to expected performance)	[50]
Pendimethalin 100 mg kg^{-1} soil	Soil washing enhanced with surfactants (SDS)	Spiked soils 0.1–0.5 kg, SDS 5–50 g L^{-1} Soil washing 12 h 150 rpm; 25 °C	100% extraction at 10 L/kg of SDS at 20 g/L	5 (tested in intended environment)	[46]
Petroleum oil with heavy metals Pb and Zn (0.035–0.142 mg dm^{-3})	Soil washing enhanced with surfactant (TritÓn X-100 Brij 30) and core-crosslinked amphiphilic polymer (CCAP)	60 g of soil sample 250 rpm; 3–8 h mixing 1000 mg L^{-1} surfactants 1 L of washing solution	Removal of 96% petroleum oils	6 (tested in intended environment close to expected performance)	[48]
Diesel-polluted soil (20 g Diesel/100 g soil)	Soil washing enhanced with surfactants (SDS, SDBS, TX-100, Tw-80, Saponin, Tannin)	2 g of soil; 20 mL 10:1 ratio water-soil 340 rpm; T^{a} =20 to 45 °C Surfactants 0.2 g L^{-1} to CMC	Removals higher than 60%	6 (tested in intended environment close to expected performance)	[53]
Crude oil-contaminated soil (32 g kg^{-1} of soil)	Soil washing under mixed biosurfactant (surfactin + rhamnolipid)	Soil water ratio—10–30 g mL^{-1}; biosurfactants (0–1 g L^{-1}); temperature 20–40 °C; mixing time 4–24 h; 200 rpm	86% of total petroleum hydrocarbons was removed from the oil-contaminated soil	6 (tested in intended environment close to expected performance)	[32]
Polyaromatic hydrocarbon (PAH)-polluted soil: acenaphthene (ACE), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR).	Soil washing under mixed hydroxypropyl-beta--cyclodextrin (HPCD) or Tween 80)	500 mL 10 rpm 24 h soil/water ratio 10:1 Hydroxypropyl-beta-cyclodextrin (HPCD) and Tween 80 (7.5± 0.2 g L^{-1}) Settling 12 h	Extraction efficiency ACE (89%), PHE (100%), FLA (95%), PYR (91%)	5 (tested in intended environment)	[49]

Technologies that are related with the generation of hydroxyl radicals are called advanced oxidation processes (AOPs), and they can be classified depending on the mechanism that promotes the formation of these radicals. Thus, technologies based on the production of hydrogen peroxide [56••] or other species have attracted considerable attention due to their simplicity, high efficiency, and easy application. As an example, Fenton process was used to treat high load of non-aqueous liquids produced in the treatment of soils polluted with lindane and other CHCs using novel formulations of surfactants as E-mulse 3 (a mixture of non-ionic surfactants and citrus terpenes) [57]. To increase efficiency, instead of using AOPs as a single treatment, it is preferred to combine them with other processes. In this line, the light irradiation coupled with the addition of a photocatalyst increases the efficiency in the production of hydroxyl radicals, and many works have reviewed the application of this process for the treatment of hazardous organic compounds in effluents [58]. Titanium dioxide was the most used semiconductor photocatalyst, due to its good properties as cost-effectiveness, inert nature, photostability, and the efficiency of this process, which mainly depends on the adsorption capacity of target pollutants onto the photocatalyst because their oxidation is promoted by hydroxyl radicals formed on the surface of the photocatalyst. Thus, higher doses of surfactants may generate the production of micelles that cannot react or adhere at the surface of catalysts, pointing out a paramount influence on the process of the concentration and type of extracting agent used [59].

To treat SW effluents, technologies that use Fenton reaction have been widely reviewed. This process consists of the catalytic decomposition of H_2O_2 in acidic media to generate the hydroxyl radicals using ferrous salts. It can be enhanced by its combination with heterogeneous photocatalysis [60], dehalogenation processes [61, 62], or irradiation using sono- [63] and photoenergies [64, 65]. These approaches can be used to achieve complete or almost complete removal of organics in the treatment of polluted solutions.

Some of the drawbacks of chemical Fenton processes, in which the H_2O_2 and the iron salts are added externally, arise from the cost, storage, transport, and environmental impact of decentralized H_2O_2 production, as well as the use of high amounts of iron salts with further sludge formation [66••].

Electrochemical Advanced Oxidation Processes (EAOPs)

In last decades, electrochemical advanced oxidation processes have emerged as a new class of AOPs to treat polluted effluents [55, 67]. The main feature of those processes is the use of the electron as an efficient, versatile, cost-effective, and clean reagent. However, today the market share of EAOPs for the treatment of polluted effluents on an industrial scale is relatively small, and most of their applications remain on a bench/pilot plant scale [68•]. Some of the main drawbacks that prevent the widespread application of those technologies are the electrode lifetime, the costs associated to energy supply [69•], or the reaction rate limited by the heterogeneous nature of charge transference processes.

The simplest and, probably, most popular EAOP is anodic oxidation (AO). In the 1970s, studies demonstrated that the reactions occurring during AO could be used for the degradation of organic pollutants in wastewater [70, 71]. During an AO treatment, pollutants can be removed by two different mechanisms, direct and mediated oxidation explained in many research works [68•]. Innovations over the last decades lead to the discovery of more efficient and stable coatings, such as boron-doped diamond [72] and sub-stoichiometric titanium oxide [73], which paved the way for the development of robust AO reactors for wastewater treatment [74, 75, 76•]. Particularly, for the treatment of SWW, the high carbon content (extracting agent, target pollutant, and soil organic matter) leads to a competition for the oxidation of pollutants and extracting agents, and the behavior and efficiencies depend on the nature of all these organics, pollutants, and extracting agents used.

To remove persistent hydrocarbons from SW effluents using EAOPs, the coupling of electrooxidation was carried out with alternative processes to overcome one of the significant drawbacks of this technology, which are related to the mass transfer limitations of pollutants to the electrode surface where most of the generated hydroxyls are concentrated (they have a low lifetime to be transported to the bulk). In this line, the coupling with ultrasounds or UV-light irradiation, trying to promote the production of large amounts of oxidants and free radicals in the bulk, favors the removal of organic pollutants by mediated oxidation mechanisms and reduces the competition effect of soil organic matter and target pollutants [77, 78•].

Synthetic SWWs polluted with pendimethalin were treated, using sono- and photoelectrolysis processes and SDS as a surfactant, obtaining removal percentages higher than 75% [41•]. Likewise, effluents polluted with phenanthrene were studied using different coupled processes as the addition of persulfate to the photoelectrolysis using active electrodes as mixed metal oxide anodes [79] or also with the addition of an easily biodegradable complex as Fe (III) -EDDS (ethylenediamine-N-N-disuccinic acid) using simulated solar light irradiation [80]. In all studies evaluated, the aim was the development of coupled processes to improve the EAOPs and to reduce the reagents and energy consumption.

CHCs are another specific group of hydrocarbons that should be considered in the development of efficient EAOPs technologies to remove these refractory compounds. BDD electrooxidation is a well-known technology that promotes suitable reactive conditions to remove these compounds and also their intermediates, but it is necessary for the transport of CHCs to a liquid phase. In the case of an extended herbicide as atrazine that has polluted many groundwaters, it was studied that their removal from a SW fluid using a single electrooxidation process with different electrode material as BDD, mixed metal oxide with Ir and Ru and carbon felt to confirm the full removal only using BDD [81] 2,4-dichlorophenoxyacetic acid was removed from aqueous solutions using a hybrid process based on the combination of electrooxidation and ozone for the integration of hydroxyl and sulfate radicals. 2,4-D was removed in 90 min, and 68.9% of total organic matter was removed within 3 h [82]. Table 2 summarizes some of the most relevant treatments carried out in SWW polluted with CHCs using EAOPs technologies.

Table 2 Treatment of SW effluents polluted with CHCs compounds using coupled processes with EAOP technologies

Pollutant/concentration	Removal technology	Experimental conditions	Main results	Technology readiness level (TRL)	Reference
Non-aqueous viscous black-brown liquid from Bailius landfill (Sabiñanigo) of CHCs	Fenton process with a surfactant E-Mulse3 (non-ionic surfactants and citrus terpenes)	Volume 4.2 L, Fenton process with 50–100 and 200% of H_2O_2 theoretical; 15 g L^{-1} E-MULES3; duration 144–48 h	Removal of 28 organochlorinated pollutants; 80% of efficiency	5 (tested in intended environment)	[79]
Soil washing effluent of groundwater with 70 mg lindane L^{-1} solution and SDS	Electrooxidation (EO) with 4 electrodes of the soil washing fluid	BDD, MMO-Ir, MMO-Ru, and carbon felt as anode and a stainless steel cathode. 15–30 mA cm^{-2}; 5 g L^{-1} SDS; 5 L of solution	Lindane is degraded in all anodes evaluated. BDD and CF anodes increase the biodegradability of the solutions	5 (tested in intended environment)	[81]
40 mg L^{-1} of 2,4 dichlorophenoxyacetic acid	Coupling of electrooxidation (EO) with PbO_2 anode, oxone, and transition metals (Co and Fe)	10 mM Na_2SO_4 as supporting electrolyte. 3 cm between the anode and the cathode; current density 10–30 mA cm^{-2} and 1–3 mM of oxone. Duration 1.5–3 h	Total removal of 2,4-D in 90 min and 68.9% of TOC removal at 3 h	5 (tested in intended environment)	[80]
100 mg kg^{-1} of PCE mixed with oily fluids in a non-permeable soil	Electrooxidation with BDD anodes using SDS in the soil-washing fluids	BDD and stainless steel as electrodes 50 mA cm^{-2} 5–20 g L^{-1} of SDS 100 ml of oil/kg^{-1} of soil 6 h	Higher PCE recovery when soil/SWF increases, total removal with 30 Ah dm^{-3}	6 (tested in intended environment close to extend performance)	[82]

Treatment of Gaseous Emissions from Soil-Washing Wastes

To end up, it should be considered the development of novel technologies related with the efficient treatments of gaseous compounds generated during soil treatments. In this context, recent studies of VOCs using advanced oxidation process coupled with other technologies have reached relevant results.

Processes such as thermal oxidation and photocatalytic oxidation (PCO) are promising technologies after VOCs are captured because the pollutants can be oxidized to H_2O and CO_2. However, thermally catalytic oxidation requires temperatures higher than 200 °C and a relatively high concentration of pollutants for an efficient operation, and, hence, it is not always economically feasible when combined with soil washing [83]. Thus, integrated removal processes have been proposed which combine the mediated electrochemical oxidation (MEO) and an absorption column into an electrochemically assisted scrubbing process [84••]. In these processes, the pollutants are oxidized through the mediation of some electrochemically generated redox reagents (Eqs. 1 and 2), which act as mediators for electron transfer between the electrode and organics [85]. These mediators can be metallic redox couples, such as Ag(II/I), Ce(IV/III), Co(III/II), Fe(III/II), and Mn(III/II), or strong oxidizing chemicals, such as active chlorine species, ozone, hydrogen peroxide, persulfate, percarbonate, and perphosphate. The optimum temperature and pH depend on the metallic redox pair used $(M(^{n+})/M(^{n}))$. Additionally, the role of efficient TiO_2 or BDD electrodes and electrolytes is key to promote the production of these mediators from precursors.

$$M^{x+} - 1e^{-} \rightarrow M^{(1+x)+} \tag{1}$$

$$C_xCl_y + n\,e^{-} \rightarrow C_xCl_{y-n} + n\,Cl^{-} \tag{2}$$

Thus, Muthuraman et al. studied the removal of some gaseous pollutants as carbon tetrafluoride [86•] and nitrous oxide [87], both very recalcitrant greenhouse gases, using wet scrubbing methods with an in situ electrogenerated Co and Ni mediators in a highly alkaline medium.

Lately, novel studies applied coupled technologies with EAOPs also to treat VOCs. In this line, Chen et al. [88] removed gaseous pollutants, such as ethyl acetate or toluene, using a novel continuous system integrating UV-assisted photo-electrochemical catalysis with a microbial fuel cell. In the cathode, it was used as a metallic catalyst of CeO_2 and TiO_2 loaded on the activated carbon fiber felt substrate, obtaining high elimination capacities for both pollutants.

All these previous studies were related to the direct treatment of gases, but it is worth to take in mind that very few studies about gaseous compounds emitted during SW processes were carried out. Most of them aimed to quantify the gaseous emissions, but they are not focused on the capture and treatment of these pollutants. These processes are characterized by a low TRL, commonly in level 2 or 3 with manuscripts related to the technology formulation or experimental proofs of concepts. Chao et al. [89] reported in 2006 the high influence of parameters as soil organic matter, water solubility, and surfactant concentration in the volatilization of VOCs with low solubility after applying SW technologies.

Then, because of their particularity, chlorinated VOCs have been considered as a specific group of toxic gaseous compounds that are removed using catalytic oxidation with temperatures ranged from 200 to 500 °C. In these processes, it is more important, the complete oxidation pathways without generating byproducts than the oxidation efficiency of the target compound. In a very recent document, Lin et al. [90•] explained some critical aspects related to the formation routes of chlorinated byproducts in gaseous treatments to achieve their complete destruction including some strategies focused on the inhibition of chlorinated intermediates and the improvements of further oxidation to final products. Regarding the treatment of specific gaseous compounds produced from

Table 3 Studies related with the Cl-VOCs promoted from SW treatments of spiked soils with CHCs

Pollutant/concentration	Removal technology	Experimental conditions	Main result	Technology readiness level (TRL)	Reference
10 mg L^{-1} of aliphatic compounds (*n*-hexane and *n*-heptane), aromatic compounds (benzene and toluene), and chlorinated organic compounds (1,1,2-trichloroethane and tetrachloroethene)	Study of changes in the volatilization amounts of organic compounds using alcohols and two types of soil with low and high organic matter	Alcohols at 2, 6, and 10 mg L^{-1}were mixed with the target organic compound at 10 mg L^{-1}; soil and solution are separated by a partition baffle; aeration of 50 mL min^{-1} was used to purge the solution at 25 °C for 3 h	Alcohols can attract the organic compounds to aggregate in interface between air and water, and they generate volatilization enhancement rates	2, technology formulation	[82]
100 mg dm^{-3} of tetrachloroethylene	Electro-absorption in an aqueous solution using a column scrubber and BDD electrochemical cell coupled with an UV-lamp	Column Scrubber 0.5 m of length and 50 mm of diameter. Aqueous solution of 5000 g/l of Na_2SO_4 in aqueous solution UV-light 9 W j= 50 mA cm^{-2}	Efficient removal of PCE was obtained with different removal pathway as function of the use of an electrochemical cell coupled with or without UV light. Lower current density promotes CCl_4 and higher trichloroacetic acid	5, tested in intended environment	[91•]
100 mg dm^{-3} of tetrachloroethylene	Electro-absorption in an aqueous solution and methanol solution using a jet aerator and BDD electrochemical cell	Jet Aerator based on Venturi effect, electrochemical cell with electrolyte of 3000 mg L^{-1} of $NaSO_4$ and NaCl in aqueous solution and methanol. J= 50 mA/cm^{-3}	Efficient removal of PCE was obtained but high reactivity with the detection of by-products as trichloroacetic acid and carbon tetrachloride. The size of bubbles generated has high influence in the overall process	5, tested in intended environment	[92]
1000 mg dm^{-3} of CCl_4	Mediated electrochemical reduction reaction with Ni (I) catalysts using a divided electrolytic flow cell with a scrubber column in a closed loop	Electrochemical cell with an electrolyte volume of 500 mL, a scrubber column (40-cm high and 5.5 cm (i.d)) packed with 1 cm^2 of Teflon tube; 10–50 mA cm^{-2}; anode area of 50 cm^2	Complete degradation of gaseous CCl_4 was carried out using metal-complex mediator ion (Ni(I)) in highly alkaline medium until inlet concentration of 50 mg dm^{-3}	3, environmental proof concept	[93]
1000 mg dm^{-3} of trichloroethylene	Mediated electrochemical reduction reaction with Co (I) catalysts using a divided electrolytic flow cell with a scrubber column in a closed loop	Electrochemical cell with (500 mL) a scrubber column (40 cm high and 5.5 cm (i.d)) packed with 1 cm^2 of Teflon tube; 10–50 mA cm^{-2}; anode area of 50 cm^2; Optimal L/G ratio was 15	Efficient removal of TCE in highly alkaline medium was carried out up to 30 ppm in the inlet. No chloro compound was identified.	3, environmental proof concept	[94••]

CHCs, some recent works removed perchloroethylene in gaseous streams to evaluate the capacity of different electro-absorbers to remove it obtaining a surprising reactivity with different reaction pathways depending of the system and experimental conditions applied [91•, 92]. Likewise, carbon tetrachloride and trichloroethylene [93, 94••] were removed from a synthetic gas current using in situ electrogenerated Co mediators from an electrode of Co(OH)$_2$ in a divided cell using an electrolyzer. Other efficient redox pairs are Ce(IV/III) that were applied to remove CHCs such as chlordane, Ambush, and 2,4 D with an efficiency higher than 85% [95, 96]. Some examples with the main parameters of the removal of chlorinated VOCs are summarized in Table 3, but the authors have not found any real studies of these compounds with high TRL produced during the SW treatments yet. Thus, there is still slot for the improvement to be carried out in terms of the capture and treatment of VOCs generated during treatment processes using electrooxidation. Therefore, future works related with a whole treatment of polluted soil have to be focused on developing a cost-efficient technology to combine the recovery and removal of all gaseous currents generated in SW processes and the treatment of solid and liquid effluents generated.

Conclusions

This review identifies the key aspects carried out in the soil treatments using ex situ techniques coupled with electrochemical processes and remarks a very important treatment technology for the remediation of soils, especially when this treatment is faced immediately after an acute discharge of pollutants occurs because it may help to prevent diffusion of the pollutants. A suitable formulation of the soil-washing fluid has a paramount influence to obtain an efficient transfer of the pollutants from the soil to the selected washing fluid, which can be further treated by different efficient technologies including very efficient electrochemically assisted processes. This type of process can also be used for the treatment of the gases emitted during the soil washing and the treatment of the liquid SWFs, being especially important the use of homogenous catalyst salts to promote the efficiency in the removal of the volatile and semi-volatile pollutants. In this work, it has reviewed the most recent and important works in all these topics, allowing to shed light on the future perspectives of application of all these technologies.

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Declarations

Conflict of Interest The authors declare that they have no conflicts of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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