1 **Advanced technologies for the remediation of pesticide-**
2 **contaminated soils**

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13 **ABSTRACT**

14 The occurrence of pesticides in soil has become a highly significant environmental
15 problem, which has been increased by the vast use of pesticides worldwide and the
16 absence of remediation technologies that have been tested at full-scale. The aim of this
17 review is to give an overview on technologies really studied and/or developed during
18 the last years for remediation of soils contaminated by pesticides. Depending on the
19 nature of the decontamination process, these techniques have been included into three
20 categories: containment and immobilization, separation or destruction. The review
21 includes some considerations about the status of emerging technologies as well as their
22 advantages, limitations, and pesticides treated. In most cases, emerging technologies,
23 such as those based on oxidation-reduction or bioremediation, may be incorporated into
24 existing technologies to improve their performance or overcome limitations. Research
25 and development actions are still needed for emerging technologies to bring them for
26 full-scale implementation.

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1. FUNDAMENTALS, HISTORY AND GENERAL OVERVIEW

Agricultural production has increased dramatically during the last decades to ensure the food supply of a population that is growing at a vertiginous rate. Greatly enhanced agricultural production has been made possible due to an increase in the use of pesticides, which have become an important part of modern agriculture. Although pesticides use is an old practice, their development and use increased dramatically after the Second World War (Gavrilescu, 2005). According to the EPA definition a pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (insects, mice and other animals, unwanted plants (weeds), or microorganisms). Although pesticides constitute an important aspect of modern agriculture, their excessive and persistent use results in damage farmland and causes serious soil pollution and deteriorated soil quality and environment. A large percentage of pesticides applied in agriculture never reach their target organisms (Niti et al., 2013). They are dispersed through soil, water and air, and detected in food for human consumption. In the case of soil-applied pesticides, their residues and metabolites can accumulate in the soil at unacceptable high levels. The potential impacts of pesticides on the environment and human health have been now recognized by governments and the public. Remediating contaminated soils to protect human health and to achieve sustainable development has become a desirable goal (Cheng et al., 2016).

In 1995, the United Nations Environment Programme Governing Council recognized only 12 Persistent Organic Pollutants (POPs) due to their adverse effects on the environment and human health. A global ban on these toxic compounds was placed, requiring taking measures to eliminate or reduce the release in the environment of these POPs. Eight of these POPs were insecticides (endrin, heptachlor, mirex, toxaphene, aldrin, chlordane, dieldrin and DDT), one of them was a fungicide (hexachlorobenzene, HCB), and the rest were dioxins (some of them by-products in pesticide production), PCBs and PCDFs. As POPs, these pesticides persist in the environment for long periods of time, are toxic and biomagnify in the food chain (Ali et al., 2014). The signing of the Stockholm Convention on Persistent Organic Pollutants took effect in May 2004. In this convention the previous list was expanded in 2009 to include new POPs, being five of them other organochlorine insecticides: chlordecone, lindane, α - and β -hexachlorocyclohexane and pentachlorobenzene. Endosulfans were included in 2011.

This gives an idea of the importance of developing technologies to remediate pesticide contaminated sites such as soil, groundwater and aquifers, although the present review will be focused only in soils.

2 TECHNOLOGIES FOR SOIL PESTICIDE REMEDIATION

As most of pesticide-contaminated soils contain complex mixtures of different compounds rather than one single contaminant, their remediation can be a complicated process. The majority of pesticides applied in agriculture are organic compounds, therefore, only their remediation will be treated in this chapter. As for the rest of organic contaminants, technologies to treat pesticide-contaminated soils fall into two categories: containment-immobilization or treatment, and treatment technologies fall into two different categories: separation and destruction.

To reduce, eliminate, isolate or stabilize a pesticide, soil remediation technologies use physical, chemical, or biological processes. The selection of appropriate technologies depends on several factors, such as site characteristics and contamination (punctual or diffuse), concentration and type of pesticides to be removed, and the end use of the contaminated media (Gavrilescu, 2009).

Depending on the technology used, techniques for soil remediation can be applied in three ways (Caliman et al., 2011): (I) *In situ*, the remediation method is applied without excavating the soil and the contaminants are treated on the place the contamination occurred; (II) *on site*, contaminated soil is excavated, treated on site and returned to the original location; (III) *ex situ*, contaminated soil is excavated and transported to another location for its treatment.

Remediation of organic pesticides can be done using any of the techniques developed for other organic pollutants with similar characteristics; however, in fact, only some specific techniques are really studied and/or developed for pesticides remediation due to the particular circumstances involved in soils contaminated by these compounds. Their contamination in the majority of soils is due to diffuse pollution, and has to be treated in a different manner than in soils with point-source contamination. On the other hand, agricultural soil properties have to be maintained, and aggressive technologies used to remediate industrial polluted soils cannot be used for agricultural soils. For this reason,

the aim of the present manuscript is the actualization of literature about remediation of pesticide contaminated soils in the last years, and, therefore, the majority of references collected are from the last decade, and almost all referred exclusively to pesticides.

2.1 Containment-immobilization technologies

2.1.1. Containment technologies

Pesticide contamination of soils may result not only from agricultural processes, but also from manufacturing, handling, improper storage, and disposal of pesticides and wastes. In particular, environmental contamination with organochlorine pesticides (OCPs) is widespread worldwide because, with the signing of the Stockholm Convention, many OCP production factories close to cities were abandoned (Galuszka et al., 2011). Most of these contaminated sites pose a threat to the environment and face urgent land use conversion (Li et al., 2008; Yang, et al., 2010; Ye et al., 2013). Due to specific properties of such pesticides, remediation efforts at macroscale in those soils where OCPs were manufactured or their waste disposed are based on containment-immobilization technologies. Such techniques comprehend excavation and landfilling both inside and outside the site, capping to limit infiltration and leaching, as well as subgrade barriers to limit lateral plume migration, and include engineering techniques to remove or isolate the source of contamination. Barriers used to be amended with sorbents such as carbonaceous materials or organic-rich soils which additionally binds the contaminant (Younas et al., 2013).

This is the case of soils contaminated with the pesticides lindane and DDT and their metabolites and isomers. Hexachlorocyclohexane (HCH) and its γ isomer (lindane) were among the most extensively used organochlorine pesticides, generating the world's largest POP stockpile, estimated at between four and seven million tons of wastes (Vijgen et al. 2011, Fernández et al., 2013). Although a containment cement or concrete wall is constructed to prevent the release of the pollutants (Weber and Varbelow, 2013), in many cases traces of the contaminants were detected in the groundwater and the surrounding soil (Usman et al., 2014). For example, a multilayered landfill cover system was deposited on top of a HCH/lindane landfill in Hamburg, Germany, to cover and “immobilize” the hazardous wastes (Götz et al., 2013), but

leaching from the landfill continues to be a threat to the groundwater. Such disposal practices are unsustainable due to the risks of contamination of the food chain and ecosystems. These POPs will persist in landfills for many decades and possibly centuries due to their very slow or absent degradability. Over these extended time periods landfill systems are likely to degrade, thus posing a risk of releasing large contaminant loads to the environment. When this occurs, excavation of the waste and associated contaminated soil and remediation of the site are carried out, and the final destruction of the contaminant waste is frequently carried out in well-regulated incinerators (Lysychenko et al., 2015), which is only possible in highly industrialized countries.

These containment processes are considered as a type of waste disposal, because not a real remediation of the polluted site is reached, constituting only a provisional solution. In spite of this, they have been of great applicability because they appeared as the only possibility for such highly polluted soils. None of the containment-encapsulation technologies are entirely satisfactory (Bini, 2009), and there is a need for continuous monitoring and careful supervision of these waste disposals stockpiles. Nowadays, even in industrial countries, the regulatory framework for the management and control of POPs stockpiles, in general, and pesticides stockpiles in particular, is not always effective and appropriately implemented, and this is still a much wider problem in developing countries (Weber et al., 2015).

2.1.2. Immobilization technologies

Current remediation methods for removing contamination from soil which involve removing and processing a large amount of contaminated soil are costly and time-consuming. These methods are not generally applicable in agricultural fields because they can lead to problems such as soil erosion, fertility loss or nutrient leaching. Therefore, for large areas of contamination economical remediation approaches to reduce risks and meet the requirements to protect human and ecological health are needed. Such risks can be mitigated by reducing the bioavailability of the contaminant and, thereby, a higher contaminant mass could be left in place, reducing the need for more expensive remediation actions (Centofanti et al., 2016). The *in situ* application of

an adsorbent amendment in contaminated soils is a new and cost-effective alternative for remediation of pesticide-contaminated soils.

Adsorption is the first process that takes place when pesticides are into contact with soil, affecting other processes such as leaching, bioavailability or toxicity against non-target organisms (Villaverde et al., 2009). Organic amendments are usually used as an immobilization technology. According to Khorram et al. (2016), the use of organic amendments reduce bioavailabiliy due not only to binding of pesticides to reduce their ~~potential~~ mobility into water resources and living organisms, but also due to the provided nutrients which stimulate plant growth and promote ecological restoration. Generally, carbonaceous materials (CM) originated from biological matter are used because they require minimal treatments before application to the soil.

Carbonaceous materials, often referred to as “black carbon”, are produced by incomplete combustion of fossil fuels and vegetation and constitute an important carbon sink due to their stability to microbial and chemical degradation. When produced from biological sources and are added to soil, CM is often termed “biochar” (Kupryianchyk et al., 2016). The addition of biochar and other CM to soils and sediments enhances the sorption of hydrophobic organic compounds (HOC), playing an important role in controlling transport and bioavailability of organic contaminants. Pollutant sequestration depends upon CM molecular (carbonized and non-carbonized fractions) and structural (surface, pore, and bulk properties) characteristics, which in turn depend on the CM starting material and on pyrolytic conditions (Khorram et al., 2016).

Biochar is a carbon-rich solid made from agricultural crop residues, wood or waste via pyrolysis in the absence of oxygen. Although biochar was primarily introduced as a soil amendment for carbon sequestration, reductions of greenhouse gas emissions, and improvement of soil fertility (Díez et al., 2013a), it has attracted attention for its ability to reduce the bioavailability of pesticides (Martin et al., 2012; Mukherjee et al., 2016). Research dealing with this issue has increased in recent years (Table 1). The impact of biochar in sorption and dissipation of pesticides such as atrazine, terbutylazine, pyrimethanil or bentazone has been studied (Cao et al., 2009; Wang et al., 2010; Yu et al., 2009; Cabrera et al., 2014). The irreversible adsorption of pesticides to soils has been demonstrated when using biochar as amendment (Yu et al., 2011) due to

entrapment into biochar micropores, surface-specific adsorption and partitioning into condensed structures.

Sopeña et al. (2012) reported that the adsorption capacity for isoproturon on a soil amended with biochar was 5 times higher than for the non-amended. Cabrera et al. (2011) observed a drastic increase in the adsorption of fluometuron and MCPA in soil amended with 2% (W/W) of some biochars made from different feedstocks. Adsorption was particularly increased using wood pellets (about 30 times higher for fluometuron and up to 50 times for MCPA). However, the authors observed an enhanced leaching of both herbicides after amendment with biochars containing soluble organic compounds. Martin et al. (2012) also observed that ageing of biochars in the soil reduced their sorption capacity. The soil containing aged biochars over a 32 month period exhibited sorption-desorption properties similar to the control soil, while soils freshly amended showed an increase in herbicide sorption, and desorption hysteresis was high.

The land management using organic green wastes and compost from various origins as soil amendment to retain pesticides has also increased. This practice is accepted as an ecological method to increase soil fertility and organic matter, preventing losses of pesticides from runoff or leaching due to increased pesticide immobilization by sorption, while allows the disposal of such wastes.

Additionally, beneficial effects on soil biochemical properties and microbiological parameters are reached, accelerating the dissipation of pesticides in soil (García-Jaramillo et al., 2016). López-Piñeiro et al. (2013) studied the sorption and degradation of MCPA in soils amended with fresh composted and aged olive mill waste, observing that the greater the amount and maturity of wastes applied, the greater the retention of MCPA. However, they also observed that MCPA could be easily desorbed if the amendment was not aged or composted.

Also different organic residues from olive oil production were used by García-Jaramillo et al. (2014) to evaluate their effect on the leaching and immobilization of tricyclazole and bentazone. Tricyclazole was not detected in any of the leachates in the amended soil. The authors concluded that the sorption of dissolved organic matter from the amendments changed the physicochemical properties of the soil surface. Centofanti et al. (2016) used biosolids compost and aged dairy manure amendments for risk mitigation of aged DDT, DDE and dieldrin residues in an old orchard soil. The addition

of waste material “spent mushroom substrate” (SMS) is also a promising strategy to optimize pesticide immobilization and mitigate water pollution (Marín-Benito et al. 2009, 2013; Álvarez-Martín et al., 2016).

Biochar and organic green wastes and compost from various origins have demonstrated to be good physicochemical methods to immobilize pesticides, but they could act as a new source of pollution. Taking into account that they can be altered due to aging, the environmental fate of retained pesticides should be tested over the years. In the case of biochar, its characteristics vary widely with the use of different biomass materials and pyrolysis conditions, and it is important to check previously if any specific biochar could be suitable for remediation purposes and its application rate and frequency of biochar amendments to reach an optimal remediation. To date, as it can be observed in Table 1, the applications of biochar and organic green wastes for the remediation of contaminated soil have mainly been conducted in the laboratory, greenhouses or small plot experiments. Large-scale field trials are needed before operational scale remediation projects are implemented.

2.2 Separation technologies

Remediation of many pesticide-contaminated soils is often limited by their persistence and recalcitrance, decreasing their availability to be treated by different destruction methods. In those cases the contaminant has to be removed from the host medium.

2.2.1. Soil washing

Soil washing is an *ex-situ* remediation technique that uses liquids, usually aqueous solutions of different kinds of extractants (organic compounds, acids, tensioactives, etc.), to remove chemical pollutants from soils. The excavated contaminated soil is mixed with the water containing extractants in an extractive unit and agitated. After washing, soil particles are allowed to settle out, and the washing solutions can be separated and regenerated or sent to landfill. The extraction of pesticides from soils has been studied in a wide variety of papers, but few studies have focused on the regeneration of the washing solution. Soil washing is most appropriate for soils that contain at least 50% sand and gravel. Table 2 shows some results obtained by using soil washing technologies for remediation of pesticide-contaminated soils.

2.2.1.1. Solvents

The solvent used is chosen depending on the type of pollutant to be extracted. Ye et al. (2013) applied several organic solvents as a remediation technique for OCP-contaminated soils and studied the effect of factors such as solvent concentration, contact time and temperature, mixing speed, or solution to soil ratio. The use of thermal desorption techniques and solvent washing approaches using n-alcohols and surfactants have been studied by Gao et al. (2013) to remediate OCPs-contaminated soils. More than 90% of ethanol used could be recovered. However, there are several factors that limit the applicability of this extraction process, such as the extraction of organically bound metals together with pesticides, the low effectivity of the solvent extraction on very high molecular weight pesticides, or the toxicity of the solvent to the soil microbial population (Pavel and Gavrilescu, 2008). These are perhaps the reasons for the few studies using solvents as extractants in the last years, particularly in the case of pesticide polluted soils.

2.2.1.2. Synthetic surfactants

Surfactants are compounds that lower the surface tension (or interfacial tension) in aqueous solutions, enhancing the solubilisation of persistent environmental pollutants in the soil. Industrially synthesized surfactants include chemically ethoxylated alcohols, sulphonates, Triton, Brij 35 and sodium dodecyl benzene sulphonate (SDBS), among others (Mao et al., 2015).

Villa et al. (2010) chose the non-ionic surfactant TX-100 for remediation of a soil contaminated by DDT and DDE, and the wastewaters obtained from the washing experiments were treated using a solar photo-Fenton processes. Bandala et al. (2013) also used Fenton and Fenton-like processes for treating wastewater from washing with sodium dodecylsulfate (SDS) a soil artificially contaminated by 2,4-D, scaling-up parameters for site restoration process. Dos Santos et al. (2015) used the surfactant SDS for atrazine removal from soil, and the resulting washing waste was treated by electrolysis with a boron-doped diamond electrode. Surfactants are also used to increase the bioavailability of pesticides to be degraded by soil microorganisms. In the paper from Torres et al. (2012) the removal of methyl parathion using anionic, non-ionic, cationic and natural surfactants was studied, and wastewater was biologically treated. However, surfactants present the disadvantage that they could be used as a substrate for

microorganisms or have toxic effects when using at high concentrations (Laha et al., 2009). Betancurt-Corredor et al. (2015) observed reduced DDT biodegradation when using Tween 80 plus biostimulation than when only biostimulation was used.

Organic solvents and many synthetic surfactants have the disadvantage of being toxic to resident microbial population. In the case of surfactants, they use to form high-viscosity emulsions difficult to remove from soil due to their low water-solubility, and sometimes the adsorption of surfactants onto soils is high. Due to the environmental risk posed by solvents and chemosynthetic surfactants, an alternative is the use of biogenic compounds such as biosurfactants.

2.2.1.3. Biosurfactants

Biosurfactants are biocompatible and favorable to the subsequent utilization of soils and, therefore, more ecologically acceptable in the bioremediation of pesticide-contaminated soils (Mulligan, 2009). A wide range of bacteria capable of producing biosurfactants have been proposed. The biosurfactants commonly used for soil remediation include glycolipid (e.g., rhamnolipids, fructose lipids, sophorolipids) and lipopeptide (e.g., surfactin, polymyxin) compounds. In particular, the feasibility of rhamnolipid biosurfactants, mostly produced by *Pseudomonas aeruginosa*, to remove pesticides from soil has been studied. Wan et al. (2015) used rhamnolipids combined with citric acid to remove simultaneously lindane, lead and cadmium from soils. Biosurfactants not only have the capability of desorbing and dissolving contaminants, but also facilitate the biodegradation of contaminants. The effect of several biosurfactants (rhamnolipid, sophorolipid and trehalose-containing lipid) on solubilization and biodegradation of HCH and their isomers in soil was studied by Manickam et al. (2012), indicating that sophorolipid offered highest degradation and enhanced solubilization. Odukkathil and Vasudevan (2015) observed an enhanced bioavailability of endosulfan and its metabolite when using biosurfactant-producing bacterial strains. Even though further research regarding the behavior of biosurfactant in the fate and transport of soil contaminants is still required, biosurfactant appears as an attractive choice for surfactant-based soil remediation technology.

2.2.1.4. Cyclodextrins

Cyclodextrins (CDs) have been proposed also as an alternative to organic solvents and synthetic surfactants for the removal of hydrophobic contaminants from soils (Fenyvesi et al., 2009). The advantage of using CDs as extractants is their low environmental impact. CDs have been approved as non-toxic compounds that do not harm resident microbial populations. In addition, due to their glucose-based composition, CDs are considered biodegradable, although some CDs are resistant at least a few months (Fenyvesi et al., 2005).

CDs are widely used in pharmaceutical science, but, due to the low production cost of some of them, they have gained considerable attention in many other fields, such as nanocomposite technologies, chromatography, biotechnology, and agriculture (Morillo, 2006). Recently, CDs have been used to improve the remediation efficiency of contaminated soil, because they can increase the apparent water solubility of low-polarity organic compounds (Morillo et al., 2012), reducing their sorption to soil (Sánchez-Trujillo et al., 2013, 2014). This transfer of the contaminants into the soil solution is an important way of increasing the subsequent efficiency of soil remediation by chemical oxidation or biodegradation (Gruiz et al., 2011; Morillo et al., 2014).

CDs used as pesticide complexation agents have gained much attention in recent years. Many of these studies have only determined the increasing solubility and complexation constants between specific pesticides with a variety of CDs (Orgoványi et al., 2009; Yáñez et al., 2012), but increasingly more studies can be found indicating the capacity of CDs for soil remediation based on their extractant ability and subsequent soil washing of a wide variety of pesticides, such as the herbicide norflurazon (Villaverde et al., 2005, 2006), hexachlorobenzenes (Wan et al., 2009), other organochlorine pesticides (Wong and Bidleman, 2010; Mao et al., 2013; Ye et al., 2014a), 2,4-D, alachlor, metolachlor, acetochlor, dimethenamid, dicamba, and propanil (Flaherty et al., 2013). The enhanced extraction from soils facilitates subsequent phytoremediation (Ye et al., 2014b), oxidation (Villaverde et al., 2007) or biodegradation (Villaverde et al., 2012; Gao et al., 2015; Zhao et al., 2015).

Although research studies using CDs to extract pesticides by soil washing are mainly carried out at a laboratory scale, high desorption yields with very low CD concentrations can be obtained with those pesticides which form strong inclusion

complexes. However, in those soils that present an extremely high pesticide adsorption, higher amounts of CDs should be used. The results obtained indicate the potential use of CDs for in situ remediation of pesticide-contaminated soils.

2.2.2. *Soil flushing*

In-situ soil flushing using extractant eluents with additives that enhances contaminant solubility is another strategy for soil remediation. Flushing solutions are injected into the area of contamination via injection wells. The soil contaminants are mobilized by solubilization or chemical interactions. Surfactants or solvents are frequently used as additives. After passing through the contamination zone, the contaminant-bearing fluid is collected and brought to the surface for disposal, recirculation, or on-site treatment and reinjection. The effectiveness of this process is dependent on hydrogeologic variables (e.g., type of soil, soil moisture) and the type of contaminant. This technique has been scarcely used for pesticides remediation in the traditional pump-and-treat type technology, such as that used in the remediation of phosalone (Di Palma, 2003) and atrazine (Di Palma et al., 2003) (Table 3). This technique is not in use at present for remediation of pesticide-contaminated soils, but, nevertheless, electrokinetic soil flushing (EKSF) is one of the most promising technologies for pesticides soil remediation, especially when the pesticides are ionic species.

In electrokinetic soil flushing a current electric field is applied across the soil using electrodes located in the subsurface. This current simultaneously initiates many physical processes (heating, changes in viscosity, etc.), electrochemical processes (water oxidation and reduction, etc.), chemical processes (ion exchange, dissolution of precipitates, etc.) and electrokinetic transport processes (electro-osmosis, electromigration, electrophoresis, etc.), which significantly change the soil (Rodrigo et al., 2014). Such processes favour the transport and removal of pollutants from soils. This technology is particularly useful for fine-grained soils with low hydraulic conductivities and large specific surface areas, and it is capable of treating fine and low-permeability materials.

As a model ionic pollutant, the removal of the anionic herbicide 2,4-D has been widely studied. Souza et al. (2016) observed 90% removal of 2,4-D using electrokinetic soil

flushing, and Risco et al. (2016) studied the influence of the arrangement of electrodes in the soil to obtain increasing amounts of 2,4-D removal. Ribeiro et al. (2011) observed that electrokinetic processes could efficiently remove molinate and bentazone from soils, and it was related to the differential pH values between both electrodes. Vieira dos Santos et al. (2016) used EKSF to remediate a soil spiked with four herbicides, demonstrating that efficiency depended on the chemical characteristic of the pesticide.

In a study with kaolinite and humic acid-kaolinite complexes spiked with diuron, results showed that the electrokinetic removal efficiency of diuron decreased from 90 to 35% in the presence of humic acids (Polcaro et al., 2007). These results have important implications for the application in real soils, where most of pesticides tend to be strongly adsorbed on the soil organic matter. In such cases, their extraction has to be carried out using enhanced electrokinetic techniques (Karagunduz, 2009; Gomes et al., 2012). The integration of EKSF with chemical oxidation, especially Fenton's process, is a widely accepted technique to increase the degradation of organic compounds in soil. Bocos et al. (2015) used the electrokinetic-Fenton treatment to remediate a soil polluted with the pesticide pyrimethanil and PAHs, evaluating also the effect of several complexing agents. Surfactants have been used to bring DDT into soil solution (Karagunduz et al., 2007). Li et al. (2011) used permeable reactive barriers (PRB) filled with Pd/Fe particles installed between anode and cathode to reach the dechlorination of PCP during its EKSF movement. Its distance from anode and decreased pHs were important factors to increase removed PCP. Also Wan et al. (2010) used EKSF coupled with Pd/Fe particles to remediate hexachlorobenzene-contaminated soil using a surfactant as solubility-enhancing agent. Volatilization presents a major significance in the application of electrokinetic techniques to polluted soils (Risco et al., 2016; Vieira dos Santos et al., 2016; López-Vizcaíno et al., 2017).

Most of the EKSF research works analysed is based on spiked soils and the successful results obtained cannot always be transferred directly to soils sampled at polluted sites. The relative rareness of data available for real contaminated soils may reflect the challenges involved in transferring this technology into the field. Further research is needed since technical and environmental issues will require a careful evaluation for further full-scale implementation. These include controlling side effects during treatment (such as anodic precipitation, oxidation of the conditioning agent and

generation of toxic gases), as well as evaluating the potential ecotoxicological effects of the surfactants, co-solvents, oxidants or reductants used.

2.3. Destruction technologies

2.3.1. Chemical remediation

A variety of reactions, such as ionization, hydrolysis or oxidation-reduction, usually related to the pH value, take place when chemical degradation or abiotic degradation occurs. In general, the technologies based on chemical reactions use to take place *ex situ*, but the application of some of them can be *in situ* or on site. Table 4 shows some results obtained by using chemical technologies for remediation of pesticide-contaminated soils.

2.3.1.1. Chemical reduction

In redox reactions one reactant loses electrons (is oxidized) and the other gains electrons (is reduced). Reducing conditions used to be more favorable for degradation of pesticides persistent in aerobic environments. Nano-scale zero-valent iron (nZVI) is usually used as a chemical reductant for a cost-efficient degradation of chlorinated pollutants in soil. Treatment with nZVI promotes a rapid abiotic degradation of such contaminants via reductive dechlorination and can be used to remediate soils contaminated with OCPs (Shea et al. 2004; Cong et al., 2010; Yang et al., 2010; Han et al., 2016). In one study, metolachlor degradation was enhanced by adding $\text{Al}_2(\text{SO}_4)_3$ to the Fe^0 , increasing acidity and promoting the formation of green rust [mixed Fe(II)/Fe(III) double hydroxides], which facilitated the pesticide dechlorination (Satapanajaru et al. 2003).

The combination of chemical treatment using nZVI with biodegradation can maximize the remediation of pesticide-polluted soils. Boparai et al. (2008) reduced the concentration of metolachlor in a contaminated soil after chemical treatment with nZVI and aluminum sulfate, but atrazine and nitrate remained. After adding sucrose, a decrease in atrazine and nitrate concentrations were observed. The presence of readily available carbon gave as result an enhanced microbial activity. Amendments such as nZVI improved the reductive dechlorination process of DDT because it serves as an

electron donor under anaerobic conditions, thereby stimulating biological dechlorination (Sudharshan et al., 2012).

However, properties such as the small size and high redox reactivity of nZVI, which are useful for environmental remediation, also make them harmful to microbial populations, plants or earthworms (El-Temsah et al., 2016). Moreover, as a certain percentage of nZVI is lost due to its reaction with dissolved oxygen, oxide minerals and organic matter of soils, it has to be compensated with increasing amounts of applied nZVI.

2.3.1.2. Chemical oxidation. Advanced oxidation processes.

The purpose of chemical oxidation in contaminated soils is to mineralize the pollutants to CO₂, water and inorganics, or transform them into biodegradable or harmless products. The most commonly used oxidizing agents are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide (Pavel and Gavrilescu, 2008). However, these traditional chemical oxidation methods are not effective enough to degrade pesticides, but these oxidants can be combined with iron salts, semiconductors (such as TiO₂) and/or ultraviolet-visible light irradiation to yield better results. Such remediation processes are called “advanced oxidation processes” (AOPs), a promising technology for the remediation of soils contaminated with highly refractory organic chemical such as pesticides (Cheng et al., 2016).

Fenton processes, TiO₂ photocatalysis, plasma oxidation, ozonation and electrochemical oxidation processes are the most common AOPs techniques (Rodrigo et al., 2014). However, their application to soil remediation is very scarce, being Fenton oxidation and TiO₂ photocatalysis the most typical techniques. AOPs neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge. Strong oxidizing intermediates (mainly OH[•] radicals) are formed and their reaction with organic contaminants not only leads to their destruction, but also provides optimal conditions for their complete mineralization (John and Shaik, 2015).

The Fenton process, initially investigated in the 1990s by Watts et al. (1990), is the most commonly used AOP in the remediation of pesticides in soil. Hydroxyl radicals (OH[•]) are generated by the catalytic decomposition of hydrogen peroxide (H₂O₂) due to soluble iron (II) in acidic medium. Fenton process has the possibility to be used for *in*

491 *situ* remediation, allowing the rapid treatment of non-easily removable without having
492 to excavate the contaminated soils. DDT, diuron, 2,4-dichlorophenol (2,4-DCP),
493 pentachlorophenol (PCP), and other pesticides in soils can be degraded by
494 Fenton/Fenton-like processes (Usman et al., 2014; Rosas et al., 2014). However, there
495 are collateral effects of the Fenton process. Villa et al. (2008) observed that, although a
496 high percentage of DDT was degraded in soil, an increase of dissolved organic carbon
497 (from 80 to 880 mg l⁻¹) occurred, and 80% of the natural organic matter was degraded;
498 also an increase in metal concentrations was observed in the slurry filtrate. Direct
499 application of the Fenton process is very aggressive to the soil and can be also a disaster
500 to the microbes (Brillas et al., 2009).

501 In photocatalysis technique, hydrogen peroxide molecule is separated into two hydroxyl
502 radicals by UV/vis photolysis, increasing the rate of photolysis with alkaline conditions.
503 As catalyst, it uses the semiconductor metal oxide, and TiO₂ in the anatase form is the
504 most appropriate due to its characteristics: high photoactivity, non-toxic, low cost,
505 chemical inertness, and easy to obtain. Different pesticides have been successfully
506 decomposed in soils using TiO₂ under solar light or UV-irradiation. Xu et al. (2011) and
507 Sharma et al. (2015) observed for glyphosate and imidacloprid that the photocatalytic
508 reaction mainly occurs in the surface part of the soil and the degradation efficiency
509 decreases as the soil layer increases. It was observed by Xu et al. (2011) that only a
510 small amount of catalyst (0.5%) was needed to remediate a soil with low glyphosate
511 content. Similar results were observed for diuron (Higarashi and Jardim, 2002).

512 Although Fenton processes and TiO₂ photocatalysis are the two typical AOPs,
513 ozonation has to be also considered because it is one of the most promising techniques
514 which can be applied *in situ* or *on site*. The pesticide can be directly decomposed by O₃
515 or can react with OH[•] radical which has been generated by the O₃ decomposition on
516 active surfaces of soil, such as metal oxides or organic matter. As ozonation is a
517 relatively new technique for pesticides remediation, the majority of the studies have
518 been performed in aqueous medium.

519 However, there are strong limitations for using the ozonation technique to degrade
520 organic contaminants in soil due to the difficulty of the diffusion process through this
521 heterogeneous matrix. Ozone can only penetrate the upper 15-45 mm of the soil.
522 Balawejder et al. (2014, 2016) developed an effective remediation method for DDT-

contaminated soil based on the utilization of hydroxyl radicals that were generated from water aerosol and ozone in a fluidized bed reactor. Soil contamination was reduced by 90%. The total organic carbon was preserved and no degradation products were detected.

An alternative to using AOPs as single treatment technologies is to combine AOPs with other technologies to minimize cost or enhance efficiency by exploiting complementarities or synergies between technologies. Innovations such as the use of chelating agents or surfactants on the traditional AOPs and the combined utilization with bioremediation or soil washing are also documented.

In studies evaluating the difference in efficacies between Fenton and photo-Fenton processes for treating pesticide-contaminated wastewater, laboratory data showed that 99% degradation for chlorimuron-ethyl was achieved in 10 min by using photo-Fenton oxidation, however, only 68% degradation was observed after 30 min Fenton oxidation (Gozzi et al., 2012). Villa et al. (2010) observed that 99% of DDT could be removed by Fenton oxidation after soil washing using a Triton X-100 solution and subsequent treatment of wastewater using photo-Fenton oxidation.

Research in advanced oxidation processes is still at an early stage. Most studies to date have been conducted at the lab-scale and many improvements are required before the technology can be scaled up to bench and pilot plant levels in terms of assessing cost and operation conditions. According to Rodrigo et al. (2014), most of the studies published in the literature have focused on pollutant removal at concentrations that are significantly higher than typical pollutant concentrations in a soil, and which are only found in industrial wastes. However, these studies are the only way of determining the efficiency of the technology.

2.3.2. *Biological remediation*

The conventional techniques used for remediation of organic pollutants in soil such as landfilling, high temperature incineration or chemical decomposition can be effective. However, they are also associated with many drawbacks such as complexity and high costs, and some may pose environmental risks; consequently, public acceptance is often low. There is a significant risk in the excavation, handling, and transportation of

hazardous materials, apart from the cost of removal of contaminated soil. In addition, these traditional techniques are not always sufficient and therefore alternative 'greener' remediation approaches, low cost and easy methods are needed to completely destroy the pesticides, if possible, or at least to transform them to innocuous substances, reducing risk for both the environment and human health.

Bioremediation, i.e. the use of living organisms to remediate pesticide-polluted sites, is an emerging technology (Chawla et al., 2013). Bioremediation of contaminants includes different techniques such as biodegradation using soil microorganisms, phytoremediation using plants, or vermiremediation using earthworms. One of the most important reasons for using bioremediation to eliminate organic pollutants is that it is a cost-effective and environmentally friendly technique and offers the possibility to destroy or render harmless organic contaminants using natural biological activity. Bioremediation is well accepted by the general public and can often be carried out on site. Although any procedure for removing or destroying pollutants is expensive, biological procedures tend to be the least expensive ones (Alexander, 2000).

2.3.2.1. Bioremediation by microorganisms

The main biological agents used in bioremediation are bacteria and fungi which use the contaminants as nutrient or energy source. The microbial diversity of the site is one of the most important parameters for bioremediation, together with the nature of the pollutants, and some properties of the soil (pH, moisture content, nutritional state, temperature, oxidation-reduction potential) (Niti et al., 2013). Table 5 shows some results obtained by using biodegradation by soil microorganisms for remediation of pesticide-contaminated soils.

In situ bioremediation

These techniques have the advantage of avoiding excavation and transport of contaminants. In natural soil bioremediation, the existing native microflora already present in the polluted soil is used to degrade the target contaminants. Bioremediation of soils contaminated with pesticides has drawn considerable research interest, mainly because pesticide pollution is constantly increasing and most chemicals are persistent in the environment. However, in situations in which microbial populations are not large or diverse enough to efficiently degrade the target pollutants, inoculation of

enriched/acclimated consortia or single pollutant degrading strains is carried out; this procedure is called *bioaugmentation*. Lopes et al. (2012) assessed the potential capacity of natural attenuation or bioaugmentation to degrade molinate in an agricultural soil, as well as the impact of these bioremediation technologies on the composition of indigenous microbiota. A molinate mineralizing consortium was used as inoculum in the bioaugmentation assays, and a significantly higher removal of molinate was observed in bioaugmentation than in a natural attenuation system. The strains can be obtained from the indigenous soil flora isolating strains from the polluted site and selecting them under laboratory conditions according to the pollutant (enrichment cultures); after growth, microorganisms are inoculated on site in the polluted area. Salunkhe et al. (2015) report the *in vitro* and *in vivo* biodegradation of three triazole fungicides by isolated *Bacillus* strains. Chen et al. (2014) observed that *Bacillus* sp. DG-02, previously isolated from a pyrethroid-manufacturing wastewater, was capable to degrade fenpropathrin, and a wide range of synthetic pyrethroids. Dai et al. (2015) investigated the bioremediation potential of a novel degrader for 2,4-D-polluted soil and its bioaugmentation impact on the microbial soil community. Farhan et al., (2014) isolated microbial strains from cotton-growing agricultural soils which were managed with chlorpyrifos.

Although microbial biodegradation of pesticides has mostly been studied using bacteria, a number of fungal strains belonging to different genera have also been isolated and characterized to be used for biodegradation of different pesticides (Maqbool et al., 2016). Peng et al. (2012) isolated from a contaminated soil a fungal strain (BP-H-02) able to rapidly degrade bensulphuron-methyl. This strain could be used to bioremediate sulphonylurea herbicide contamination. Biodegradation of chlorpyrifos was studied in mineral medium and soil with the novel fungal strain JAS1 isolated from a paddy field soil (Silambarasan and Abraham, 2013). However, and because environmental microbiologists estimate that less than 2% of bacteria have been cultured in the laboratory, molecular approaches to study microorganisms for bioremediation have become important tools for assessing potential natural attenuation, and hence, the need to apply a bioremediation technique (Chakraborty and Das, 2016).

On the other side, *bioestimulation* consists in the addition of appropriate nutrients (nitrogen, phosphorus, trace elements) to provide the microorganisms with an environment which favors the development of metabolic pathways for contaminant

biodegradation. Islas-García et al., (2015) studied different parameters such as concentrations of hydrocarbons and organochlorine pesticides (OCPs), nutrients and tolerant microorganisms in an agricultural soil to define its feasibility for bioremediation. The decreasing in the pollutant concentration and the increasing in microbial activity indicated that the use of bio-stimulation of native microorganisms was feasible in a soil contaminated with hydrocarbons and pesticides. In a similar study, Ortiz et al., (2013) proved that stimulation of indigenous microbial soil flora by the addition of small amounts of secondary carbon sources enhanced the biodegradation/mineralization of DDT and its main metabolites. Chen et al. (2012) explored biostimulation mechanisms with an electron donor and a shuttle for accelerating pentachlorophenol (PCP) degradation in iron-rich soils. Bioestimulation of indigenous microbial soil communities by the addition of lactate and anthraquinone-2,6-disulfonate increased the rates of pentachlorophenol dechlorination. Silva et al. (2004) developed a joint bioaugmentation and biostimulation approach for the clean-up of soil contaminated with high concentrations of the herbicide atrazine. The *Pseudomonas sp.* strain ADP was used for bioaugmentation and citrate and succinate for biostimulation. They also concluded that the studied soil had indigenous potential for atrazine mineralization, but a significant mineralization rate only took place after a acclimation phase.

As mentioned previously, bioavailability of pesticides and other organic contaminants is a major limitation to complete bioremediation of contaminated soils (US EPA, 1999). It affects the clean-up time, cost, and the end-point of the process (Pignatello et al., 2010). From a biodegradation point of view, bioavailability was defined as the accessibility of a chemical for assimilation by microorganisms (Alexander, 1995). The term “bioaccessibility” encompasses what is immediately available plus that which may become available, whereas bioavailability refers to what is available immediately. In this sense, a number of pollutant soil risk assessments based on bioaccessibility studies have been published. For this purpose, non-exhaustive extractions have been used to determine the bioaccessible fraction of the contaminant after different aging periods. Recently, Villaverde et al. (2013) have used different non-exhaustive extraction techniques to determine whether their extraction abilities correlated with the bioaccessible diuron fraction in an aged contaminated soil. Diuron bioaccessibility was evaluated through correlations between the biodegraded diuron after different aging

periods (diuron biodegrader microbial consortium) and the diuron extracted by a biomimetic extraction using a 50 mM hydroxypropyl- β -cyclodextrin (HPBCD) solution, 10 mM CaCl_2 , hexane, or butanol. The authors concluded that the aqueous HPBCD extraction technique has potential to become a valuable tool for estimating the bioaccessible fraction of soil-associated diuron at different aging times, and this could be applicable in the assessment of risk and contaminated land bioremediation potential.

Nagy et al., (2013) investigated reliable methods for assessing the soil microflora and its activity as a prerequisite for successful technology planning and sustainable bioremediation of different contaminated sites. The contaminant concentrations were measured by using a harsh extraction and by a biomimetic extraction using a cyclodextrin solution. Most of the applied biological and chemical methods were reliable indicators of chlorophenol biodegradation in soil. Baczynski et al. (2012) obtained results of desorption kinetics using Tenax solid phase extraction (SPE) as predictors after 3 weeks of anaerobic soil biodegradation effectiveness for chlorinated pesticides gamma-HCH, DDT, and methoxychlor. Fenlon et al., (2011) performed a study on the formation of bound residues and mineralization of the insecticide cypermethrin in four organically managed soils. The potential bound residues formed were measured using three different non-exhaustive extractions employing, 0.01 M CaCl_2 and 0.05 M HPBCD solutions and acetonitrile solvent; biodegradation was assessed by mineralization bioassays of cypermethrin. The bound residues formation assessment varied according to the mild extraction tested, soil type and the aging period.

On the other side, surfactants can be used as bioremediation promoters accelerating pesticide mineralization through increasing the amount of the pollutant present in the soil solution. Singh et al., (2016) used a crude rhamnolipid biosurfactant produced by ChlD, which improved the aqueous phase solubility of chlorpyrifos by 2–15 folds. Singh and Cameotra (2014), studied the effect of different surfactants (rhamnolipids and triton X-100) on biodegradation of atrazine herbicide by a degrader strain A6, belonging to the genus *Acinetobacter*. Bacterial cell surface hydrophobicity as well as atrazine solubility increased in the presence of surfactant. Villaverde et al., (2012) developed a cyclodextrin-based bioremediation technology which showed for the first time an almost complete diuron mineralization in soil, using a diuron biodegrader consortium. Ye et al. (2014a) performed a study to investigate the anaerobic biodegradation

potential of biostimulation by nitrate (KNO_3) and the application of methyl- β -cyclodextrin on an aged organochlorine pesticide-contaminated paddy soil. Gao et al., (2015) carried out a study to verify the feasibility of the HPBCD biomimetic extraction for assessing the bioavailability of DDT and their metabolites in soils. The effect of HPBCD on their biodegradation in different soils was also investigated. However, HPBCD affected negatively to DDT soil biodegradation when was applied as a bioestimulant.

The use of microbial processes have been broadly used for the elimination of chemicals from household or industry effluents as waste-treatment systems. However, many compounds are not always completely degraded, not necessarily because of the absence of a biodegradative microflora, but rather because the technique have not been optimized which highlights the need for new or modified bioremediation techniques. A number of novel and promising methods have been developed, where biostimulation combined with bioaugmentation and bioavailability improvements have yielded promising results. *In situ* treatments, in which soil is not removed from the contaminated land, have several advantages, such as the relatively low costs, but the disadvantage of diminished rigorous control.

Composting

Composting is a conventional treatment technology employed in remediation of agricultural and municipal solid wastes and sewage sludge, but the application of composting in soil as an *in situ* bioremediation is somewhat more recent. The principle of operation consists of mixing the contaminated soil with non-hazardous organic amendments, generally other solid wastes (i.e., manure, agricultural wastes) suitable for composting applications, to encourage the development of bacterial populations or other organisms, such as fungi, earthworms, etc., which are able to degrade the pollutants in the soil via cometabolic pathways. Moorman et al. (2001) employed several organic amendments, including compost, corn fermentation byproduct, corn stalks, manure, peat and sawdust to improve the removal of the herbicides atrazine, trifluralin and metolachlor from contaminated soils. On the contrary, Delgado-Moreno and Peña (2009) observed that the addition of vermicompost and olive cake in soils did not increase the removal of different pesticides, simazine, cyanazine, terbutylazine and prometryn. Kadian et al. (2008) investigated the effects of different organic

amendments on the removal of atrazine in contaminated soils. The addition biogas slurry showed the highest atrazine removal, and the study on synergistic effect of sodium citrate with farmyard manure showed initially a negative effect, increasing dissipation gradually. Diuron desorption and mineralization were studied on an amended and artificially contaminated soil by Rubio-Bellido et al. (2015). Two different composted organic residues, sewage sludge mixed with pruning wastes, and urban solid residues, and two different solutions (micronutrients and cyclodextrin) were used, concluding that the joint application of all treatments investigated at the best concentration studied showed the best diuron mineralization results.

The addition of particulate organic matter from composts has important effects especially when the contaminant is present in relatively low concentrations in soils. Marín-Benito et al. (2014) studied the dissipation kinetics of three different pesticides, linuron, diazinon and myclobutanil, in an un-amended agricultural soil and in soil amended with three different organic residues. DT50 values decreased in both the unamended and amended soils for linuron, but increased for the unamended and amended soil for diazinon and myclobutanil, due to the formation of non-extractable residues formation in amended soils. The results obtained revealed that the simultaneous use of amendments and pesticides in soils requires a preliminary study in order to evaluate the environmental specific persistence of these compounds and the effectiveness of amended soils to enhance pesticide biodegradation.

The presence of water-soluble compounds such as humic or fulvic acids as well as small biomolecules such as peptides and fatty acids (natural surfactants) may cause desorption, solubilization and complexation of organic pollutants. Rubio-Bellido et al. (2015) concluded that the dissolved organic matter from the organic amendments, used for soil diuron bioremediation, acted as a natural surfactant provoking an increase of the bioavailable fraction of the herbicide, and hence improving its mineralisation rate. Therefore, compost may be used for the balance between sorption to soil particles and biodegradation in contaminated sites (Kästner and Mitner, 2016). The success of composting in the bioremediation of contaminated soils depends on a number of physical, chemical and biological characteristics of the reaction environment. A key factor is the microbial bioaccessibility to the pollutants, which is determined both by the mechanical conditions (mixing, moisture contents, soil composition), and by the properties of the applied amendment.

In many cases, it is necessary to move the contaminated soil to a site where a suitable treatment system can be applied (*ex situ* bioremediation). If the economic and technical analysis favors *ex situ* bioremediation, it can be concluded that such treatment is the optimal approach. There are a variety of technologies available which can be considered and they could be classified into two generic technologies: i) landfarming and biopiles; ii) slurry bioreactors. Landfarming and biopiles dominate the *ex situ* bioremediation of contaminated soils, although however, bioreactors offer advantages in the level of process monitoring and the modifications of the operation.

Land farming and biopiles

Landfarming is an *ex-situ* treatment procedure that is performed in the upper soil close to the contaminated soil zone or in biotreatment cells. Contaminated soils are transported to the landfarming site, incorporated into the soil surface over large areas with a thickness of a few ten centimeters and periodically tilled to aerate the mixture. This technique is easy to implement, does not require heavy infrastructure, and is cost-efficient. However, operations last a long time (years or decade) and are likely to produce odors and visual nuisances. In addition, pesticides may leach from the site contaminating groundwater, and volatile emissions may pose hazards in the vicinity of the site. Therefore, leaching or volatilization of toxic compounds (original compound and metabolites) must be controlled or prevented. To avoid any risk of infiltration, a waterproof cover must be in place before the start of the treatment.

Land farming requires a significant period of time, since slow kinetic microbial degradation takes place; its applicability is therefore limited to superficially contaminated soil. Landfarming has been successfully employed for the treatment of contaminated soils by different organic pollutants, aliphatic and aromatic hydrocarbons, pesticides, etc., and it is still a valid technology when remediation times are not a critical concern, or the degree of contamination is not high enough to expect a strong inhibitory effect on the endogenous bacterial community.

An application of landfarming in the bioremediation of soils heavily contaminated (>5 g/kg) with hexachlorocyclohexane (HCH) isomers was reported by Rubinos et al., (2007). They found different behaviours of the four investigated isomers: two of them, α and γ , could be significantly removed (89% and 82%, respectively) while for the others (β and δ) a negligible decrease was observed. This finding is a good example of the high

specificity of the microbial bioremediation. Felsot and Dzantor (1997) suggested landfarming as an efficient method for soil pesticide remediation, which could be made more efficient by amendments with different organic nutrients, mixing contaminated with uncontaminated soil, with the result that the dissipation of several herbicides (alachlor, atrazine, metolachlor, and trifluralin) was stimulated. Rodríguez-Vázquez and Acosta-Ramírez (2015) performed a biological technology, based on “Solid Cultivation On-site”, (Mexican Patent No. 291975), using coffee grain and straws, as well as low humidity and aeration, for the removal of the organochloride pesticide DDT and its metabolites.

A somewhat more sophisticated approach is associated with soil piles, which are also called biopiles, where a piping system is placed in the pile, and air or O₂ is introduced to enhance aerobic decomposition of the pollutant. In addition, a solution containing nutrients is applied to the soil surface to stimulate microbial activity, and the leachate may be collected through the pile. In biopiles, the sample, after excavation, is scraped up in a waterproof slab. A biopile can reach a height of 3-4 m, with a volume of several hundred m³ (Bertrand et al., 2015). In this technology, more engineering controls can be included, such as systems to provide irrigation water and nutrients, a liner at the bottom of the soil (clay or a synthetic material), and a means to collect the generated leachate. Hence, the level of sophistication, and consequently the cost, will vary enormously.

Slurry Bioreactors.

Slurry bioreactors (SB) are considered as the most engineered treatment for soil bioremediation. The main advantage of this approach would be the accurate control of the bioremediation process, which can be optimized by setting and monitoring the most critical parameters. The main disadvantage is the high cost, which has to be justified for each particular application, and hence, slurry bioreactors need a good record of medium- and full-scale success prior to the large investments.

In slurry bioreactors contaminated soil is mixed with wastewater residue to obtain slurry of a predetermined consistency, an aqueous suspensions in the range of 10–30% w/v. The system can work under aerobic or anaerobic conditions and in different feed modes: continuous, semicontinuous, and batch. Slurry bioreactors have been applied to the bioremediation of persistent or recalcitrant contaminants such as herbicides, pesticides and explosives. An interesting emerging area is the use of slurry bioreactors with

simultaneous electron acceptors, which has demonstrated to work for the bioremediation of PAHs in soils and some organochlorinated compounds (Robles-González et al., 2008). Varo-Arguello et al., (2012) performed a study with two main objectives: to evaluate the effect of co-substrate supplementation and possible synergistic effects of the indigenous population and a lindane-acclimated inoculum on the removal of lindane in three-phase, aerobic slurry bioreactors; they also evaluated the effect of a final electron acceptor and supplementation with carbon source on the removal of lindane in triphasic laboratory scale slurry bioreactors. In both cases, under aerobic and anaerobic conditions, pesticide biodegradation was enhanced.

Biodegradation of pendimethalin, a pre-emergence herbicide, was carried out by Ramakrishnan et al. (2011) in a bioslurry reactor operated with native microflora and amended with sewage, reaching 91% removal efficiency. The bioreactor operated as an anoxic-aerobic-anoxic at different soil-water ratios and substrate loads. The effect of different operating conditions, electron acceptors, and additional carbon sources were studied by Robles-Gonzalez et al. (2008) in the bioremediation of a clay soil with a high organic matter content contaminated with 2,4-D. They studied two parallel slurry bioreactors inoculated with aerobic a degrader strain, and with sulfate-reducing anaerobic bacteria. The aerobic system showed better results in terms of overall removal extent, while the sulfate-reducing bacteria showed better specific removal rates. Batch slurry bioreactors were used by Quintero et al. (2006) for the remediation of a soil contaminated with lindane, one of the most widely used pesticides in agriculture. Fuentes et al. (2014) observed an increase of about 10% in methoxychlor removal in stimulated slurry bioreactors. Znad et al. (2010) conducted biodegradation assays for the herbicide 2,4-D in a net draft tube airlift bioreactor at different concentrations and air flow rates, using activated sludge. Characterization of microbial communities of SB is still in the early stages, despite their significance for improving reactor operation and optimization.

Soil contamination prevention. Biobeds

Biobeds (BB) are simple and inexpensive systems for bioremediation designed to collect and biodegrade pesticide spills. The original design consists of a hole in the ground in which a layer of clay is placed on the bottom. A mixture of straw, peat and

soil is added, followed by a layer of grass. Straw is the main component used for fungi growth, the soil is used for the contaminant adsorption and improves the microbial activity, and the peat contributes to moisture control. An efficient mix of materials for a BB must include wide surfaces for the retention of pesticides, which will reduce leaching, and at the same time provide an active soil microbial flora. The principal component is straw due to its positive effects on biological activity and hence, pesticide biodegradation. However, access to straw can be limited in some regions, and must be replaced by other more readily available residues. In this sense, recent works are focused on the improvement of the biomixtures employing novel materials for BB replace. Mukherjee et al. (2016) assessed the sorption-desorption potential of three pesticides with different properties on novel biomixture materials based on bioenergy residues (biochar) in laboratory batch equilibrium experiments, determining that desorption was hysteretic for all pesticides on the materials used, and concluding that these biomixtures can be used as effective and alternative adsorbents for removing pesticides from percolating water in different biofilters. Chin-Pampillo et al. (2015) prepared five novel biomixtures using different lignocellulosic materials mixed with either compost or peat and soil to evaluate the dissipation of the insecticide carbofuran. Detoxification capacity of the matrices was high, and compost-based biomixtures showed better performance than peat-based biomixtures. Gao et al. (2015) investigated the effect of replacing peat by spent mushroom substrate (SMS), a locally available material. The pesticides, chlorothalonil and imidacloprid were used in this research. They were selected based on the different physico-chemical properties, biological activity and preliminary results on pesticide degradation. The authors concluded that SMS is suitable and can therefore be used as a substitute for peat. Díez et al. (2013a) studied the effect of biochar as a partial replacement of peat in pesticide-degrading biomixtures for BBs. In general, pesticide degradation was higher in the control (conventional biomixtures) than in biomixtures prepared with biochar, except in the case of the herbicide iprodione, which presented a significant biodegradation when biochar was included in the biomixture. Díez et al. (2013b) used two lignocellulosic materials (barley husks and pine sawdust) as substitutes for straw. The degradation of the six pesticides was enhanced for mixtures containing the new tested materials, concluding that straw in the traditional biomixture can be replaced by other lignocellulosic materials to efficiently degrade different pesticides.

A combination of BBs and bioaugmentation (previously commented technique) is used to accelerate the efficiency of biodegradation in the BB. Castillo-Díaz et al. (2016) used 6 bacteria and 4 fungus strains from different mixtures incubated during one month to increase the mineralization rates of different herbicides. Madrigal-Zúñiga et al. (2016) used ligninolytic fungus *Trametes versicolor* as bioaugmentation agents in a compost- and peat-based biomixtures for obtaining a rapid biodegradation of the pesticide carbofuran.

It is generally agreed that less than 1% of prokaryote species can be cultivated. The extent of genomic diversity is unknown, but comparative genomic analysis suggests that the genetic diversity in microorganisms is greater than expected. This suggests that there is much catalytic diversity yet to be discovered. From this basis, more information on microbial genomic will be necessary to translate a DNA sequence into knowledge of the specific reaction encoded by that gene. On the other side, the range of possible organic structure of pesticides is enormous and hence, more challenges will be posed for microbial metabolism, and it will be necessary to continually discover new microbial microorganisms to match the discovery of new organic pesticide compounds.

2.3.2.2. Phytoremediation

The use of plants to remediate contaminants in the environment is called phytoremediation. The term phytoremediation was first used in the 1980s, but its rapid expansion in organic contaminants remediation began at the end of the last century (Gerhardt et al., 2009). Low molecular weight compounds such as some pesticides can be transported across plant membranes and removed from the soil. They can be released through leaves via evapotranspiration processes (phytovolatilization). Non-volatile compounds can be degraded (phytodegradation) or become non-toxic via enzymatic modification and sequestration *in planta* (phytoextraction), or are degraded by microorganisms present in the rhizosphere (rhizodegradation). Compounds sequestered in the plants can be removed with the biomass for incineration (Gerhardt et al., 2009). The plant activity depends on the medium to be remediated, the type of plant used, and also on the properties of the contaminant (Newman & Reinolds, 2004). Till date, the majority of phytoremediation research has focused on PAHs, PCBs, explosives,

antibiotics, etc., and very few studies are reported on the phytoremediation of pesticides (Lunney et al., 2004).

Phytoremediation presents numerous advantages: reduced costs in comparison to other remediation technologies, reduction of erosion rate, improvement of chemical, physical and biological soil properties; land esthetic improvement and high population consensus. But it also presents some disadvantages such as the prolonger duration of land restoration, and its strong dependence upon: climatic conditions, contaminant concentration and bioavailability, plant tolerance to contaminants, contamination area extent and depth (limited by the rhizosphere or the root zone) or the disposal of plant wastes. This technique is particularly suitable at sites where contamination is low and diffused over large areas, and when there are no temporal limits to the intervention (Bini, 2009). Table 6 shows some results obtained by using phytoremediation technologies in pesticide-contaminated soils.

There are significant differences in the tolerance of plants to pesticides. Karthikeyan et al. (2004) gave exhaustive information regarding the potential use of non-target plants such as trees, shrubs and grasses in remediating pesticide-contaminated soil. White (2002) and White et al. (2003a) reported that the uptake of DDE was specific for certain subspecies. Cultivars such as those from Cucurbitaceae family show significant higher uptake. The difference was the result of higher exudation rates of low molecular weight organic acids. Also Murano et al. (2010) observed that cucurbits have uptake mechanisms for dieldrin. Mitton et al. (2016) observed that sunflower presented the highest phytoextraction capacity of endosulfan in comparison to tomato, soybean or alfalfa. However, in the case of DDT polluted soils, tomato plants seem to be the most suitable phytoremediator candidates (Mitton et al., 2014).

Phytoextraction of pesticides has mainly focused on food crops e.g. members of the genus *Cucurbita* known to extract from soil chlordane and DDT (Whitfield Aslund et al., 2010) or dieldrin and endrin (Otani & Seike, 2006). Therefore, it would be very interesting to screen non-food crops and other wild species for phytoremediation. As the selection of a plant for phytoremediation purposes must be tailored for each environment to be treated, a good candidate should be naturally growing vegetation in the pesticide-contaminated area or able to grow in the specific polluted soil. In both

cases, plants should be able to decrease pollutant concentration (Ramírez-Sandoval et al., 2011; Nurzhanova et al., 2013; Singh and Singh, 2014).

The effects of phytoremediation and microbial bioremediation strategies have led to a more successful approach to remediation of organic compounds. Rhizodegradation is a specific type of phytoremediation that involves both plants and their associate rhizosphere microbes, whose growth is enhanced by the release of root exudates (Agnello et al., 2014). Sun et al. (2004) observed that the enhanced removal of aldicarb in plant-grown soil was mainly due to plant-promoted degradation in the rhizosphere. The same was observed by Abhilash et al. (2013) in the phytoremediation of lindane and by Dubey and Fulekar (2013) for cypermethrin. Microbe-assisted phytoremediation can be also carried out by stimulation via inoculation with pesticides degrading microorganisms (Dam et al., 2007; Mitton et al., 2012).

Phytoremediation of pesticides is affected by a number of factors. Their low bioavailability in soils may restrict the success of this technology. In order to increase the ability of pesticides to be transferred from the soil to the degrader microorganisms, some of the natural low molecular weight organic acids excreted by roots were used to enhance phytoremediation. White and Kottler (2002) and White et al. (2003b) showed that several organic acids increased the desorption of DDE. Similarly Mitton et al. (2012) studied the effects of citric and oxalic acids and plant root exudates on the desorption of DDTs in soils. These natural organic acids alter the organomineral linkages disrupting the soil structure, and resulting in the release of metals and organic carbon in the aqueous phase. Pesticides are usually complexed with this fraction of organic carbon, and, therefore, their desorption was enhanced. Also surfactants can enhance the desorption of pesticides from the soil to be phytodegraded (Wu et al., 2008; Mitton et al., 2012).

As a recent advance in phytoremediation, in the last decade transgenic plants expressing specific pesticide-degrading enzymes have been developed (Doty, 2008; Hussain et al., 2009). The overexpression of genes involved in metabolism, uptake or transport of specific pollutants in transgenic plants enable to overcome some of the disadvantages of phytoremediation, such as high concentrations of pesticides or the disposal of plants that accumulate organic pollutants (Kawahigashi et al., 2006; Viktorova et al., 2014). Once pesticides are degraded by specific transgenic plants to non-toxic metabolites or

completely mineralized, the plants can be disposed of safely. Although their field applications have not yet been regulated due to their possible impacts on the environment and biodiversity, in the near future this strategy may receive an increasing attention.

As mentioned above, in the last decade there have been a growing number of papers dealing with phytoremediation of pesticides under laboratory and greenhouse conditions, but efforts to translate phytoremediation research to the field have proven challenging (Gerhardt et al., 2009), and there have been numerous inconclusive and unsuccessful attempts, due to the multitude of variables: plant stress factor, uneven distribution of contaminants, moisture content, spatial variability of microbial activity, changing climatic conditions, different soil properties, nutrient contents, aeration of the soil, etc. Although the limits of this remedial strategy need to be acknowledged, phytoremediation, and particularly rhizoremediation, have more potential than ever before, for becoming cost-efficient and effective ways of removing organic contaminants from the environment.

2.3.2.3. Vermiremediation

The term vermiremediation has been introduced recently to indicate the use of earthworms in the removal of contaminants from soils or when earthworms help to degrade non-recyclable compounds (Rodríguez-Campos et al., 2014). Several studies have reported on the accelerated removal of pesticides when earthworms were added to a contaminated soil, but there are other studies that demonstrated the contrary (Hickman and Reid, 2008). Earthworm gut transit can greatly modify the structure of the soil, destroying and forming organomineral complexes. The ability of earthworms to change the structure, biomass, and functioning of soil microbial communities may indirectly stimulate POPs biodegradation, which depends predominantly on microbial activity (Natal-Da-Luz et al., 2012). Earthworm activity is generally known to increase nutrient availability (water-soluble C and carbohydrate concentrations, and extractable mineral N and P) that can be used by soil microorganisms as co-metabolites, leading to an increase in the biodegradation rate of pesticides (Meharg, 1996).

A number of studies have investigated the use of earthworms within bioremediation to enhance losses of pesticides in soil (Table 7). Gevaio et al. (2001) observed a higher removal of atrazine, isoproturon and dicamba when the earthworm *A. longa* was added to soil, and concluded that earthworms not only limit the formation of the soil-bound fraction, but they also promoted the release and mineralization of bound residues. Other authors have also observed increased pesticide degradation in soils in the presence of earthworms (Fahrenhorst et al., 2000; Schreck et al., 2008; Lin et al. 2012). Kelsey et al. (2011) observed a decrease in hydrophobicity of humic acids in soil in the presence of plants and earthworms, and suggested that bioavailability of organic contaminants could increase.

Lin et al., (2016) used two earthworm species and revealed that only one of them could enhance pentachlorophenol removal from soil due to stimulation of indigenous PCP bacterial degraders; Li et al. (2015) also investigated the effect of two earthworm species on the soil microbial degradation of PCP, and observed that earthworms introduced new functional bacteria into soils for PCP biodegradation.

Previous findings are in conflict with those of Binet et al. (2006) and Kersanté et al. (2006) who observed an increased pesticide sorption due to earthworm activity. Alekseeva et al. (2006) observed that the transit of OM through the earthworm gut leads to changes in its composition (greater C, HA/FA ratio and degree of humification). All these changes in the OM can also modify the pesticide-solid matrix (bioavailability), and it can be more important the OM composition than its content that contributes to the enhancement of pesticide retention in soil.

Until today, all experiments with vermiremediation have been done in the laboratory or in outdoors mesocosms, but it is clear that earthworms can help to remediate pesticide-contaminated soils. However, they need rather well defined conditions to survive, such as enough food to be active, adequate climatic conditions and soil water content. On the other hand, the costs might be too high to remediate large contaminated areas. However, their contribution to soil quality should be taken into account when calculating the cost of remediating a contaminated soil with earthworms. More knowledge and research is required in the field so that the practical application of vermiremediation can be demonstrated on a large scale.

2.4. Economic analysis

Cost assessment and comparative cost evaluation of the potential technological alternatives may be some of the most important considerations in the decision-making process. However, no reports have been found in the literature about the costs of remediation techniques applied to pesticide-contaminated soils. As remediation of organic pesticides in soil can be done using any of the techniques developed for other organic pollutants with similar characteristics, the economic costs should be also similar. Costs associated with soil remediation are highly variable and depend on the contaminant, soil properties, site conditions and the volume of material to be remediated. Techniques that remediate a soil in site are less expensive than those that require excavation. According to Gruiz et al. (2009), cost-benefit assessment is part of spatial planning and complex land management, and has economic and social implications both for the owner and for local authorities. The cost-benefit ratio depends on the future land use, and does not always agree with the needs of nature and people.

The most expensive remediation technology is excavation of contaminated soil and final disposal on landfills. Policies regarding the remediation of such landfills vary considerably among different countries, but all remediation projects are enormously expensive (US\$ 2200-2400 ton⁻¹, Weber et al., 2011).

With respect to soil washing/flushing technologies, Bini et al. (2009) estimated a cost of \$50-\$80/m³ for *in situ* treatments, and \$150-\$200/m³ if the treatment is performed *ex situ*. For *in situ* flushing of contaminated soils with alternate periods of water and water/surfactant was estimated a total cost of \$104/m³ (Iturbe et al., 2004).

The data currently available indicate that the cost of production for biosurfactants is between 1 and 60 USD/kg, depending on the degree of purity and product specifications required by the desired application (Mao et al., 2015). Considering the huge production of synthetic surfactants and their lower average price (1-2 USD/kg surfactant), biosurfactant is currently not a cost-competitive substitute in the marketplace. Therefore, a massive and cost-effective production of biosurfactant is very crucial to promoting its extensive use. There is no information about costs of technologies such as EKSF because they need to be scaled up to be able to calculate their real cost.

Although in situ technologies based on natural biological processes are particularly mistrusted due to lack of information, objective evaluation and transparent verification, what we can know is the approximate cost for the different remediation processes. Conventional ex situ methods, such as excavation and incineration, off-site storage, soil washing, and in situ capping for stabilization are generally much more expensive than in situ bioremediation.

In phytoremediation protocols are relatively easy to implement, and after initial site preparation and planting, the maintenance costs for phytoremediation are minimal (Gerhardt et al., 2009). The estimated cost of phytoremediation is between \$10–\$50/ton - \$12–\$60/m³ if we consider that 1 m³ of soil is about 1.2 ton- (Pilon-Smits and Freeman, 2006), similar to the cost proposed by Gavrilesu (2005) (\$60/m³).

For bioremediation using microorganisms, Gavrilesu (2005) estimated a cost of \$6.4–\$150/m³, and Bini (2009), \$50–\$100/m³ if the treatment is *in situ* or \$150–\$500/m³ if it is performed *ex situ*. The feasibility of cyclodextrins use concerning the price of bulk material is frequently argued for not selecting them as remediation technology. Gruiz et al. (2009) compared the use of cyclodextrin (RAMEB) as bioavailability enhancer for in situ bioremediation with various realistic alternative technologies (monitored natural attenuation, excavation and disposal on landfills, on-site bioventing, soil flushing with water (pump-and-treat)). They demonstrated that the cost-efficiency was similar or even lower than in the others technologies, proving their efficiency and competitiveness. The estimated cost of this bioremediation technology using CDs was \$220/ton, and the duration of the treatment was only 1.5 years (for monitored natural attenuation the cost was \$218/ton, but the duration was 15 years). One of the strengths is that CDs technologies are less time consuming than other alternative ones (40–70% lower than the other treatments), and it compensates the price of the bulk material.

In the case of vermiremediation, the most important limitation for its use in contaminated soils is its cost, which might be too high to remediate large contaminated areas. Rodríguez-Campos et al. (2014) calculated that for each ha of soil they would need 33800 kg earthworms, and each kg costs about 40 USD.

Conclusions

Pesticide occurrence in soils is a highly significant environmental issue on which the attention of the scientific community is currently focused. This review gives an overview on the technologies used for pesticide-contaminated soils remediation. The fundamentals, advantages and disadvantages, progress and limitations of the technologies are summarized and analyzed. For the different technologies, perspectives are proposed for future research, and their limitations for application are also discussed.

A number of techniques have been developed to remediate soils contaminated by pesticides, traditionally either by treating or isolating the soil *in situ*, or by removing it for disposal or removal of the contaminant, both by extraction or degradation. However, the selection of a technique depends on its suitability for the extension of the contamination (point-source or diffuse pollution), type and concentration of the pesticide to be removed as well as the type of soil, climatic conditions and the presence of other potential contaminants. Social and economic factors must also be taken into account, and the range of application can be limited by energy and cost considerations.

In relation to biological processes, the innate capability of many soil microbes to degrade pesticides has been explored a lot but still the use of these organisms in the field remains a big issue for the bioremediation process. Composting and landfarming may be the most practical of the biological methods because they are immediately ready for implementation at low cost. Some disadvantages of biological technologies is that the process requires more time, and also the fact that during the bioremediation process some pesticides may be broken down into more toxic by-products. Also the introduction of enriched microbes to the contaminated soil can be problematic due to variations in the environmental factors (temperature, pH, moisture content, nutrients) or because of competitive inhibition caused by other microbes.

Experiments with vermiremediation have been done only in the laboratory or in greenhouse, and more research is required in the field to define conditions for earthworms to survive and reduce costs. Also efforts to translate phytoremediation research to the field have proven challenging, and there have been numerous unsuccessful attempts, due to the multitude of variables involved. Despite such difficulties, this technique is rapidly developing due to its high population consensus and reduced costs in comparison to other remediation technologies.

Chemical treatments of pesticide-contaminated soils can be completed in short time periods in comparison with biological treatments. The disadvantage is that treatment residuals from separation techniques require treatment or disposal, which adds cost to the project. Chemical treatments are very aggressive to the soil and can negatively impact microbes and other soil properties, restricting future land use of these soils.

Soil washing is a very effective technology for extracting pesticides from soil, but, as an ex-situ remediation technique, is highly costly. The increasing use of more ecologically acceptable extractants, such as biosurfactants and cyclodextrins, allows maintaining soil properties. Electrokinetic soil flushing has become one of the most promising technologies for pesticides soil remediation, especially when the pesticide consists of ionic species. However, further research is needed for full-scale implementation and controlling side effects during treatment.

Physical treatments of containment (excavation and storing in a landfill, or isolating with one of the different types of barriers) have been the most common solutions for specific areas of soils contaminated with banned pesticides, or when concentrations are high. It was the solution for soil remediation in industrial countries into the 1970s or even 1980s. However, landfilling may not be viable because of space limitations and its highly possible environmental concerns. According to the Stockholm Convention such highly polluted soils are not allowed to be landfilled but need to be managed in an environmentally sound manner and pesticides destroyed without the generation of other POPs.

The majority of scientific studies published in the literature to date are still at the lab scale stage and were conducted using artificially contaminated soils. In the present review a lack of studies exploring naturally (field) pesticide-contaminated soils and field scale scenarios have been highlighted. Within the next few years a significant effort should be done to scaling up these remediation technologies to be able to know their real cost and the possible operation problems at full-scale. But, according with López-Vizcaíno et al. (2017), here a problem arises: financial support for doing large-scale studies is not easy to be obtained without the participation of companies, and in this case, they are interested in keeping the information to get a benefit and non-disclosure agreements prevent a good diffusion of results.

1164

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Table 1. Selected reports on the use of immobilization technologies for remediation of pesticide-contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	Reagent used/ Operation conditions	Results/Pesticide removal	Reference
DDT, DDE, Dieldrin	Organochlorine insecticides	Laboratory	Old orchard soil (aged>50years)	Dairy manure compost (5%) Biosolids compost (5%) Pine chip Biochar (5%)	Dairy manure and Biosolids composts lowered bioavailability by 18-39%. Biochar was ineffective.	Centofanti et al. (2016)
Terbuthylazine	Triazine herbicide	Laboratory	Artificially contaminated	Biosolids (1%) Sawdust and charcoal Biochars (1%)	Biosolids: limited effect on adsorption Sawdust Biochar: 63 times higher adsorption Charcoal Biochar: 3 times higher adsorption	Wang et al. (2010)
Acetamiprid	Neonicotinoid insecticide	Laboratory	Artificially contaminated	Eucalyptus wood chips biochar (0.5%)	Dissipation decreased up to 31.5% in the soil with the lower OM content	Yu et al. (2011)
Carbofuran chlorpyrifos	Carbamate and Organophosphate insecticides	Laboratory	Artificially contaminated	Eucalyptus wood chips biochar (0.1-1%)	Chlorpyrifos and carbofuran bioavailability decreased about 89% and 75% using biochar at 1%.	Yu et al. (2009)
Aminocyclopyrachlor bentazone	Unclassified and Benzothiazinone herbicides	Laboratory	Artificially contaminated	Three biochars (10%)	Increased retention up to 240% of Aminocyclopyrachlor and up to 40% of bentazone with one of the biochars	Cabrera et al. (2014)
Isoproturon	Urea herbicide	Laboratory	Artificially contaminated	Eucalyptus wood chips biochar (0.1-2%)	Mineralization reduced by 13, 40 and 50% at 0.1%, 1% and 2% of biochar	Sopeña et al. (2012)
Diuron Atrazine	Phenylurea and triazine herbicides	Laboratory	Artificially contaminated	Poultry litter (PL) and paper mill sludge (PM) biochars (1%)	2-5 fold increase in sorption. Ageing of biochars over 32 months reduced the sorption by 47% (PM) to 68% (PL) for diuron.	Martin et al. (2012)
Bentazone Tricyclazole	Benzothiazinone herbicide and Triazolobenzothiazole fungicide	Laboratory	Artificially contaminated	Composted alperujo (CA) and biochar from CA (BA) (2%)	3 fold increase in sorption for soil + BA. CA was ineffective for increased sorption	García-Jaramillo et al. (2014)
MCPA	Aryloxyalkanoic acid herbicide	Laboratory	Artificially contaminated	Composted and field-aged olive mill waste (COW, AOW) (5%)	Leaching losses of MCPA reduced by up 39% and 53% in the COW- and AOW-amended soils	López-Piñeiro et al. (2013)
Tebuconazol Triadimenol Cymoxanil Pirimicarb	2 Triazol fungicides, Cyanoacetamide oxime fungicide, Carbamate insecticide	Laboratory	Artificially contaminated	Spent mushroom substrate (SMS) (2-75%)	Adsorption increased 1.40-23.1, 1.08-23.7, 1.31-42.1, and 0.55-23.8 times for tebuconazole, triadimenol, cymoxanil and pirimicarb for soils amended with biosorbent.	Álvarez-Martín et al. (2016)
Linuron Diazinon Myclobutanil	Urea herbicide Organophosphate insecticide Triazole fungicide	Laboratory	Artificially contaminated	Sewage sludge (SS), grape marc (GM) and spent mushroom substrate (SMS) (5%)	Leaching reduced up to 65.6% for amendment incubated 1 month, and up to 53.5% after 1 year ageing.	Marín-Benito et al. (2013)
Penconazole Metalaxyl	Triazole and Phenylamide fungicides	Pilot (undisturbed soil cores)	Artificially contaminated	Fresh and composted spent mushroom substrate (SMS) added to agricultural soils (25 tons ha ⁻¹)	Enhanced adsorption of both fungicides (up to 24-fold). Increased degradation of metalaxyl after 77 d incubation, but not of penconazole.	Marín-Benito et al. (2009)

Table 2. Selected reports on the use of soil washing technologies for remediation of pesticide-contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	Reagent used/ Operation conditions	Results/Pesticide removal	Reference
BHC, DDT	Organochlorine fungicide and insecticide	Laboratory	Abandoned OCPs manufacturing plant	Thermal desorption (225-500°) and solvent washing (n-alcohols and surfactants)	Ethanol at 1:20 soil:solvent ratio gave 87% OCPs removed	Gao et al. (2013)
DDTs, cis-chlordane, trans-chlordane, mirex	Organochlorine insecticides	Laboratory	Four abandoned pesticide factories	ethanol, 1-propanol, petroleum ether fractions	80-90% OCPs removed. Better parameters: petroleum ether, soil: solvent ratio 1:10, 50°C.	Ye et al. (2013)
Aldicarb	Carbamate insecticide	Laboratory	Artificially contaminated	Anionic (SDBS), cationic (HTAB) and non-ionic (OP) surfactants	Best desorption efficiency with anionic-nonionic surfactant mixture (77%).	Xu et al. (2006)
2,4-D	Alkylchlorophenoxy herbicide	Laboratory	Artificially contaminated	Sodium dodecyl sulfate (SDS) at 0.5%.	Up to 89% 2,4-D removed. Complete removal of pesticide and surfactant from wastewater using a photo-Fenton process.	Bandala et al. (2013)
Methyl parathion (MP)	Organophosphate insecticide	Laboratory	Artificially contaminated	9 synthetic surfactants and 3biosurfactants	63-98% of MP removed. The best results obtained using biosurfactants: locust bean, guar, mesquite gums.	Torres et al. (2012)
DDT (and DDE)	Organochlorine insecticide	Laboratory	Abandoned pesticide factory	Triton X-100	66% DDT and 80% DDE removed for three sequential washings. 99 and 95% degradation of DDT and DDE in wastewater using a photo-Fenton process.	Villa et al. (2010)
DDT	Organochlorine insecticide	Laboratory	Artificially contaminated	Tween 80, Brij 35, SDBS; in batch and soil columns	Better results: Batch, 18.5% with 2% Brij 35 + 0.5% SDBS + 0.5% EtOH. / Columns, 99.7% with 2% Brij 35 + 1% SDBS at very low leaching rate	Ríos et al. (2013)
DDT (and DDE, DDD)	Organochlorine insecticide	Laboratory	Long term contaminated agricultural soil	Tween 80 + biostimulation with nutrients	94% DDT reduction only with biostimulation , and 79% with Tween 80+biostimulation due to an increasing toxicity.	Betancur-Corredor (2015)
Atrazine	Triazine herbicide	Laboratory	Artificially contaminated	Sodium dodecyl sulfate (SDS) (0.01- 0.5%)	99% removal of atrazine can be attained with 0.5 g surfactant/kg soil. Total depletion of atrazine in wastewater using electrolysis with diamond electrodes.	Dos Santos et al. (2015)
PCP	Organochlorine pesticide	Laboratory	Artificially contaminated	Triton X-100 (1%) and rhamnolipid (1%), both in the form of foam	85% removed by Triton-X100 (60% by volatilization), 60% removed by rhamnolipid 40% by volatilization)	Mulligan and Eftekhari (2003)
Lindane (and their HCH isomers)	Organochlorine insecticide	Laboratory	Artificially contaminated	Rhamnolipid, sophorolipid and trehalose-containing lipid	30–50% enhanced degradation of lindane and HCH isomers. Sophorolipid offered highest degradation	Manickam et al. (2012)
Lindane	Organochlorine insecticide	Laboratory	Artificially contaminated	Rhamnolipids + citric acid	85.4% lindane desorption from soil using 1% rhamnolipids + 0.1 mol l ⁻¹ citric acid	Wan et al. (2015)
Norflurazon	Pyridazinone	Laboratory	Artificially contaminated	β-Cyclodextrin (β-CD) six soils with different	Desorption depends on the soil. With low amount of NFL adsorbed, desorption range 25-100% with β-CD	Villaverde et al. (2005)

Table 3. Selected reports on the use of soil flushing technologies for remediation of pesticide-contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	Reagent used/ Operation conditions	Results/Pesticide removal	Reference
Phosalone	Organophosphate insecticide	Laboratory	Artificially contaminated	Ethanol aqueous solution (5-10%), several pHs and temperatures. Solution flow rate 0.15 L hr ⁻¹	99% extraction efficiency with 7 PV extraction volume and 10% ethanol concentration. Hydrolysis treatment of the extracting solution	Di Palma (2003)
Atrazine	Triazine herbicide	Laboratory	Artificially contaminated	Ethanol aqueous solution 5%	95% extraction efficiency with 15PV extraction volume. Fenton's oxidation on the extracted solution achieved only 21% atrazine degradation.	Di Palma et al. (2003)
2,4-D	Alkylchlorophenoxy herbicide	Laboratory	Artificially contaminated	Electrokinetic soil flushing (EKSF) on sterilized silt soil. Addition of <i>Burkholderia spp.</i> RASC c2	2,4-D moved towards the bacteria. 87.1% removed from the soil, 5.8% recovered as CO ₂ .	Jackman et al. (2001)
DDT	Organochlorine insecticide	Laboratory	Artificially contaminated	EKSF in soil columns using surfactants.	No flushing with Tween 80 due to its adsorption on the soil. Much better results with SDBS.	Karagunduz et al. (2007)
HCB	Organochlorine fungicide	Bench-scale plants	Artificially contaminated	EKSF using Pd/Fe permeable reactive barrier (PRB) and triton X-100	60% HCB removed by EK-PRB versus 13% with EK alone	Wan et al. (2010)
Molinate Bentazone	Thiocarbamate and Benzothiazinone herbicides	Laboratory	Contaminated agricultural soils (rice crops)	EKSF in three soils. Changing current intensity, pH (3-6) and flow rate (1.4-5 ml min ⁻¹)	Mobilization of pesticides from soils and removal from soil solution towards both electrodes (bentazone) or only to cathode (molinate)	Ribeiro et al. (2011)
PCP	Organochlorine pesticide	Laboratory	Artificially contaminated	EKSF in soil columns using Pd/Fe permeable reactive barrier (PRB)	49% PCP removed, 22.9 recovered as phenol	Li et al. (2011)
Pyrimethanil	Anilinopyrimidine fungicide	Laboratory	Artificially contaminated	EKSF-Fenton treatment using complexing agents (ascorbic acid, citric acid, oxalic acid and EDTA) and H ₂ O ₂ as flushing agent.	58 and 100% degraded after 27d without and with citric acid pH 5 as complexing agent, respectively.	Bocos et al. (2015)
2,4-D, oxyfluorfen, chlosulfuron, atrazine	Alkylchlorophenoxy, Diphenyl ether, Sulfonylurea and Triazine herbicides	Bench-scale plants	Artificially contaminated	EKSF. Water used as flushing fluid. SDS used as solubilizing agent for oxyfluorfen and atrazine	95, 60, 80, 80 % 2,4-D, oxyfluorfen, chlosulfuron, atrazine removed from soil, respectively, but 60, 40, 65 and 60 % due to evaporation.	Vieira dos Santos et al. (2016)
2,4-D	Alkylchlorophenoxy herbicide	Pilot plant (175 dm ³)	Artificially contaminated	EKSF. Two different electrode configurations.	With one configuration 70% 2,4-D removed from soil in 35 days. With the other, 8% in 58 days.	Risco et al. (2016)
Commercial 2,4-D and oxyfluorfen	Alkylchlorophenoxy, Diphenyl ether herbicides	Pilot plant (32 m ³)	Artificially contaminated	EKSF. Compare results with those from smaller plants: pilot-scale (175 L) and lab-scale soil column (1 L).	Electric heating of soil increased pesticides volatility. 85% oxyfluorfen and 87% 2,4-D were volatilized. Removal of herbicides from soil is affected by the size of the plant.	López-Vizcaíno et al. (2017)

Table 4. Selected reports on the use of chemical technologies for remediation of pesticide-contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	Reagent used/ Operation conditions	Results/Pesticide removal	Reference
Metolachlor, alachlor, atrazine, pendimethalin, chlorpyrifos	Chloroacetamide (2), triazine, dinitroaniline herbicides and organophosphate insecticide	Field-scale <i>in situ</i> (3.5 x 1.20 x 26–60 m ³)	Contaminated soil due to accidental spill	Zerovalent iron (ZVI) 5% (w/w) to promote reductive dechlorination and nitro group reduction	>60% degradation of all pesticides in 90 d >90% when 2% (w/w) Al ₂ (SO ₄) ₃ was added to the Fe ⁰	Shea et al. (2004)
HCHs DDTs	Organochlorine pesticides and metabolites	Laboratory	Soil from a pesticide-manufacturing plant	ZVI as reducing agent (10% w/w)	Reductive dechlorination rate HCHs > DDTs . Limited by dissolution rate in aqueous phase.	Cong et al. (2010)
HCHs DDTs	Organochlorine pesticides and metabolites	Laboratory	Soil from a pesticide-manufacturing plant	ZVI as reducing agent (0.5–5% w/w). Ultrasonic extraction	Increased DDT degradation with Fe ⁰ concentration, but not for all metabolites. Σ DDTs not decreased markedly.	Yang et al. (2010)
DDT	Organochlorine insecticide	Laboratory and in situ treatments	DDT spiked soil and DDT-contaminated field.	ZVI, different conditions: iron sources and dosage, and soil moisture, temperature, and types.	The degradation half-life of p,p'-DDT decreased significantly from 58.3 to 27.6 h with nZVI dosage from 0.5 to 2.0% and from 46.5 to 32.0 h with temperature from 15 to 35 °C.	Han et al. (2016)
DDT	Organochlorine insecticide	Laboratory	DDT historically contaminated soil	Two types of nZVI in soil columns	25.4% DDTdegradation in 24h. Both types of nZVI had negative impact on some tested organisms.	El-Temseh et al. (2016)
Atrazine Metolachlor	Triazine and Chloroacetamide herbicides	Field-scale <i>in situ</i>	Contaminated soil due to accidental spill	ZVI (5% w/w), aluminum sulfate (2% w/w), sucrose (5% w/w)	ZVI (5% w/w) and aluminum sulfate (2% w/w) degraded 100% metolachlor in 95 days. For atrazine reduction addition of sucrose (5% w/w) was necessary	Boparai et al. (2008)
Atrazine Cyanazine	Triazine herbicides	Field-Scale (275 m ³ soil)	Soil from a pesticide-manufacturing plant	Chemical-biological treatment (Fe ⁰ + FeSO ₄ + emulsified soybean oil to stimulate biodegradation	Atrazine and cyanazine concentrations decreased by 79 to 91% in 342d.	Waria et al. (2009)
Diuron	Phenylurea herbicide	Laboratory	Artificially contaminated	Photocatalysis with solar light in presence of TiO ₂ (0–2%).	100% diuron degradation in the top 4 cm of contaminated soil in 50h with 0.1% TiO ₂	Higarashi and Jardim (2002)
Glyphosate	Phosphonoglycine herbicide	Laboratory	Artificially contaminated	Photocatalysis with solar light in presence of Fe ₃ O ₄ /SiO ₂ /TiO ₂ (0.5%).	90% degradation in 2h. the best results with 30–50% moisture content and 6–10 mW/cm ² sunlight intensity.	Xu et al. (2011)
Imidacloprid	Neonicotinoid insecticide	Laboratory	Artificially contaminated	Photocatalysis with UV light in presence of TiO ₂ (0.1–0.5 g kg ⁻¹)	Best result: 83% degradation with pH 3, UV light 30 W m ² , soil depth 0.2 cm, initial concentration of imidacloprid 10 mg kg ⁻¹ .	Sharma et al. (2015)
DDT	Organochlorine insecticide	Laboratory	Soil from a pesticide-manufacturing plant	Fenton process	75% DDT disappear from the slurry system in 70h, but in great part due to volatilization. 80% soil OM degraded. Drastic increase in metals in filtrates.	Villa et al. (2008)

Table 5. Selected reports on the use of bioremediation by microorganisms in pesticide contaminated soils.

Pesticide/ biological function	Scale/ Contamination	Bioremediation Technique	Microorganisms involved	Results/Pesticide removal	References
Molinate (herbicide)	Laboratory (paddy field soils)	Natural attenuation	Endogenous flora	39% mineralised	Lopes et al., 2012
		Bioaugmentation	Microbial consortium: <i>G. molinivorax</i> ON4T, <i>Pseudomonas</i> (two strains), <i>Stenotrophomonas</i> and <i>Achromobacter</i>	63% mineralised after 42 days	
Myclobutanil, tetraconazole, and flusilazole (fungicides)	Pilot (vineyard plots)	Bioaugmentation	<i>Bacillus</i> strains, namely, DR-39, CS-126, TL- 171, and TS-204	>85% biodegraded after 20 days	Salunkhe et al., 2015
Fenprothrin (insecticide)	Laboratory (solution)	Bioaugmentation	<i>Bacillus</i> sp. DG-02	93.3% biodegraded after 72 hours	Chen et al., 2014
2,4-dichlorophenoxyacetic (herbicide)	Laboratory (paddy- planted field)	Bioaugmentation	<i>Novosphingobium</i> , strain DY4	50-95% biodegraded after 3 and 7 days, respectively	Dai et al., 2015
Chlorpyrifos (herbicide)	Laboratory (Agricultural soil)	Bioaugmentation	<i>Bacillus cereus</i> , strain Ct3	88% biodegraded after 7 days	Farhan et al., (2014)
	Laboratory (paddy field soils)	Bioaugmentation	<i>Aspergillus terreus</i> JAS1	100% biodegraded after 48 hours	Silambarasan and Abraham, 2013
bensulphuron-methyl (herbicide)	Laboratory (Agricultural soil)	Bioaugmentation	<i>Penicillium pinophilum</i> strain, BP-H-02	87 % biodegraded after 60 hours	Peng et al. (2012)
organochlorine pesticides	Pilot (Agricultural soil)	Bioestimulation (Soil Macronutrients C:N:P 100:10:1)	Endogenous flora	Biodegradation	Islas-García et al., (2015)
DDTs (insecticide)	Laboratory (Soil from rural areas)	Natural attenuation	Endogenous flora	23% biodegraded after 7 weeks	Ortiz et al., (2013)
		Bioestimulation (phenol, hexane and toluene)		>56% biodegraded after 7 weeks	
Pentachlorophenol (herbicide)	Laboratory (paddy field soils)	Bioestimulation (lactate and anthraquinone-2,6-disulfonate)	Endogenous flora	Up to 97% biodegraded after 6 days	Chen et al., (2012)
Atrazine (herbicide)	Laboratory (Agricultural soil)	Natural attenuation	Endogenous flora	54.4% mineralised after 67 days	Silva et al. (2004)
		Bioaugmentation	<i>Pseudomonas</i> sp. strain ADP	30.6% mineralised after 7 days	
		Bioaugmentation, Bioestimulation (Citrate and succinate)	<i>Pseudomonas</i> sp. strain ADP	79.9% mineralised after 13 days	
Chlorpyrifos (herbicide)	Laboratory (Agricultural soil)	Bioaugmentation	CS2 strain	55% biodegraded after 6 days	Singh et al., (2016)
		Bioaugmentation, Bioavailability enhancer	CS2 strain, bio-surfactant rhamnolipid	82.3% biodegraded after 6 days	
Atrazine (herbicide)	Laboratory (Agricultural soil)	Bioaugmentation	Strain A6 (<i>Acinetobacter</i>)	30% biodegraded after 6 days	Singh and Cameotra (2014)
		Bioaugmentation, Bioavailability enhancer	Strain A6, rhamnolipids and triton X-100	80% biodegraded after 6 days	
Diuron (herbicide)	Laboratory (Agricultural soil)	Bioaugmentation	Bacterial consortium: <i>Arthrobacter</i> sp. N2, <i>Variovorax</i> sp. SRS16	45% mineralised after 120 days	Villaverde et al., (2012)

Table 6. Selected reports on the use of phytoremediation in pesticide contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	Plant used / Operation conditions	Results/Pesticide removal	Reference
DDE	Organochlorine insecticide (metabolite)	Field experiment	Agricultural soil (up to 500 mg/kg)	Zucchini, pumpkin, spinach	After 3 months 40, 70 and 20% DDE removed from soil grown with zucchini, pumpkin, and spinach, respectively.	White (2001)
Aldicarb	Carbamate pesticide	Growth chamber	Artificially contaminated (20 mg/kg)	Corn, mung bean and cowpea.	Aldicarb $t_{1/2}$ in soil was 2.7d, but it was 1.6, 1.4 and 1.7d in the soil grown with corn, mung bean and cowpea, respectively.	Sun et al. (2004)
PCP	Organochlorine pesticide	Greenhouse experiment	Artificially contaminated (100 mg/kg)	Rhizoremediation (P) (wheat) +Bioaugmentation (I) (<i>S. chlorophenolicum</i>)	After 20d 40% removal from soil only with P. After 6d 80% removal with I+P.	Dams et al. (2007)
DDT	Organochlorine insecticide	Greenhouse experiment	Artificially contaminated (2.5-10 mg/kg)	Alfalfa + arbuscular mycorrhizal fungus + Triton X-100	66.8-95.4% removed in the rhizosphere soils, 13.1-64.8% in the bulk soils after 4 weeks, depending on initial concentration.	Wu et al. (2008)
DDT	Organochlorine insecticide	Greenhouse experiment	Soil in a former military site	<i>Cucurbita pepo</i> ssp. Six amendments to increase soil OM (2.4-27.3%)	Root DDT concentrations lower in soils with high OM. No significant adverse effects on phytoextraction.	Lunney et al. (2010)
DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Contaminated soil (1500mg/kg)	Pumpkin/ Surfactants (Biosolve, Aqueduct) or mycorrhizal fungi	Soil amendments did not increase DDTs extracted from soil, but a different distribution on plants.	Whitfield Aslund et al. (2010)
Endosulfan	Organochlorine insecticide	Greenhouse experiment	Artificially contaminated (100 mg/kg)	<i>Ocimum basilicum</i> L. and <i>Ocimum minimum</i> L.	Both species can endure endosulfan pollution up to 1 g/kg in soils. 37% removed from soil with <i>O. basilicum</i> , but not with <i>O. minimum</i> .	Ramírez-Sandoval et al. (2011)
DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Agricultural soil	Willow trees + organic amendments: root exudates, Tween 80, sodium citrate and oxalate	Increased p,p'-DDE/p,p'-DDT ratio when compared with initial soil. Leaves translocation in willow plants especially with carboxylic acids.	Mitton et al. (2012)
Cypermethrin	Pyrethroid insecticide	Greenhouse experiment	Artificially contaminated (10-100 mg/kg)	<i>Pennisetum pedicellatum</i> . Rhizoremediation	100-65% removed from soil for 10-100 mg/kg in 60d. Degrading strain <i>Stenotrophomonas maltophilia</i> MHF ENV 22 isolated from rhizosphere	Dubey and Fulekar (2013)
Lindane	Organochlorine insecticide	Greenhouse experiment	Artificially contaminated (5-20 mg/kg)	<i>Jatropha curcas</i> L. Rhizoremediation	89-72% removed from soil for 5-20 mg/kg in 300d	Abhilash et al. (2013)
DDTs and HCHs	Organochlorine pesticides and metabolites	Greenhouse and field experiments	Old pesticide storehouses (up to 6.3 mg/kg)	17 naturally growing plants	<i>Artemisia annua</i> accumulated 8 mg/kg of pesticides in plant tissue. <i>X. Strumarium</i> and <i>S. dulcamara</i> extracted 70-80% pesticides from soil in 6 months.	Nurzhanova et al. (2013)
DDTs	Organochlorine insecticide and metabolites	Greenhouse experiment	Agricultural soil	Tomato, sunflower, soybean, alfalfa	Tomato the best phytoremediator, increased bioavailability in rhizosphere.. Translocation to roots > leaves.	Mitton et al. (2014)

Table 7. Selected reports on the use of vermiremediation in pesticide-contaminated soils.

Pesticide	Pesticide class	Scale	Contamination in soil	organism used/ Operation conditions	Results/Pesticide removal	Reference
Atrazine	Triazine herbicide	Laboratory experiment	Artificially contaminated (3.64 mg/kg)	<i>Lumbricus terrestris</i> L.	Half-life in soil was 23.6, 16.5 and 19.1 in soil without worms, soil with worms, and soil conditioned with worms prior to herbicide application, respectively.	Farenhorst et al. (2000)
Isoproturon (I) dicamba (D) atrazine (A)	Urea, benzoic acid and triazine herbicides	Laboratory experiment	Artificially contaminated (2.6, 0.2 and 2 mg/kg, respectively)	<i>Aporrectodea longa</i>	After 28d 30, 20, and 90% of A, I and D, respectively, remained as bound residue in soils without earthworms; 5, 10, and 50%, respectively, in soils with earthworms.	Gevao et al. (2001)
Atrazine	Triazine herbicide	Laboratory experiment	Artificially contaminated (1 kg/ha)	<i>Lumbricus terrestris</i> and <i>Aporrectodea caliginosa</i> . Inoculation with <i>Pseudomonas</i> sp. ADP	70% atrazine mineralized in soil without worms, 60% in soil with worms. Only 30% mineralized in burrow linings and 15% in casts.	Kersanté et al. (2006)
Atrazine	Triazine herbicide	Laboratory experiment	Artificially contaminated	<i>Aporrectodea giardia</i> + <i>Pseudomonas</i> sp. ADP	Adsorption in earthworm casts higher than in bulk soil. Degradation higher in bulk soil than in bulk soil + earthworm casts	Alekseeva et al. (2006)
Atrazine	Triazine herbicide	Laboratory experiment	Artificially contaminated (1 kg/ha)	<i>Lumbricus terrestris</i> and <i>Aporrectodea caliginosa</i> . Soil columns	Reduced mineralization from 15.2 to 11.7% in the presence of earthworms at 86 d. Greater leaching losses in soil amended with earthworms.	Binet et al. (2006)
λ-Cyhalothrin (C) Chlorpyrifos-ethyl (CE) Metalaxyl (Me) Myclobutanil (My)	Pyrethroid and organophosphate insecticides Phenylamide and triazole fungicides	Laboratory experiment	Concentrations of pesticides used in vineyard soils.	<i>Aporrectodea caliginosa nocturna</i>	After 34 d, 99, 21, 99.5, 28.1% of C, CE, Me, My, respectively, removed from soils without earthworms; 15, 4, 19, 17.2%, respectively, from soils with earthworms.	Schreck et al. (2008)
DDE	Organochlorine insecticide (metabolite)	Laboratory experiment	Old agricultural soil (0.2 mg/kg)	<i>Eisenia fetida</i> , <i>Lumbricus terrestris</i> , <i>Aporrectodea caliginosa</i> Plants: <i>Cucurbita pepo</i> ssp and ssp. <i>ovifera</i>	DDE phytoextraction by ssp. <i>pepo</i> increased 25% in the presence of any of the earthworm species. No effect in ssp. <i>ovifera</i>	Kelsey et al. (2011)
DDT	Organochlorine insecticide	Laboratory experiment	Artificially contaminated (2 and 4 mg/kg)	<i>Eisenia fetida</i> and <i>Amyntas robustus</i>	After 360 d, 25% DDT removed from soils without earthworms, and 65% in soils with earthworms.	Lin et al. (2012)
PCP	Organochlorine pesticide	Greenhouse experiment	Artificially contaminated (40 mg/kg)	<i>Eisenia fetida</i> and <i>Amyntas robustus</i>	Both earthworm species enhanced soil PCP disappearance. Earthworms introduce PCP-degrading bacteria into soils.	Li et al. (2015)
PCP	Organochlorine pesticide	Greenhouse experiment	Artificially contaminated (40 mg/kg)	<i>Eisenia fetida</i> and <i>Amyntas robustus</i>	After 42d <i>A. Robustus</i> removed 82.5% PCP, and 50% <i>E. Fetida</i> . Both stimulated indigenous PCP bacterial degraders.	Lin et al. (2016)