

# REMEDICATION OF SOILS CONTAMINATED WITH PESTICIDES: A REVIEW

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## Abstract:

Nowadays, there is a generalized concern with the problem of water contamination, forgetting that the soil is not only the support of life, but also the support for clean water. The aim of this work is to present the problem of soil contamination by pesticides, as well as the need for new and cleaner technologies for soil remediation, which should not significantly modify the soil structure. It is in this perspective that the technology of extraction with supercritical fluids emerges as a cleaner technology with high potential for application in soil remediation.

## 1. Soil

It is commonly believed that soil contamination is a relatively recent issue when, in reality, it has started long time ago, even though only recently mankind has been aware of its dimension and persistence. In fact, even though soil is the support of our ecosystem [1], man, by ignorance, and mainly for economical reasons, keeps throwing all types of organic and inorganic matter into the soil, maintaining the idea that it possesses an infinite assimilation capability. Only in 1972 (European Soil Charter-Council of Europe, 1972) it was recognized that appropriated protection measures should be implemented quickly whenever soil integrity is in danger. Soil must be considered as a non renewable natural resource, as the estimated time for originating 1 cm<sup>3</sup> of savage soil is situated between 200 and 400 years [2]. Hence we have the obligation to ourselves and to the coming generations to take care of such a precious good.

It is very clear that the soil is a complex and living structure and that is very difficult to study [3]. The scientist have to be able to over come all the different areas that are implied in the study of soil; chemistry, physics, mathematics, biology and health and safety. If the study is not made in situ, probably will appear some conditions that were not taken in consideration in the laboratory. A case were this usually happens is bioremediation [4].

## 2. Pesticides

The needs of the modern industrial societies to increase agricultural production and to maintain organoleptic characteristics of fresh food by longer periods of time, leads to an increase in the use of pesticides, and more recently of transgenic products. Pesticide is any

substance or mixture of substances that are used to destroy, eradicate, control or change the cycle of a certain plague. Pesticides may be natural, synthesized or even living organisms (NSW - National Registration Authority for Agricultural and Veterinary Chemicals) [5].

In fact pesticides are a two-edged sword, being the big solution to the fight against starvation and human diseases, having helped to save millions of human lives, but its continuous use, produces the contamination of food and natural resources with substances dangerous to the health of mankind, some of which are many times carcinogenic [6]. As pointed above, pesticides are natural or synthetic chemical composites which are used to control insects, mites, harmful grass, fungus and other forms of life animal or vegetal, that harm the farming, cattle and other products. The bad use of these composites (disrespect of the appropriated concentrations to be used, the testing periods, and the security techniques) can unchain besides the contamination of soil, the contamination of the water in the soil, the contamination of rivers and of the man.

### **3. Remediation Techniques**

A polluted soil can be defined as a soil with a concentration of a contaminant that exceeds the level defined by the regulations. The water and air have been subject to environmental regulation, but in some countries the soil has not yet a regulation.

In the last decade the solution used for contaminated soils, was more commonly to excavate and put it in a landfill or isolated with some different types of barriers that were available and capable to prevent the flow off of the contaminant from the site or able to avoid the contact with humans or animals [7]. It was a good practice in terms of risk management, because it controlled the dangers for the surrounding environment, but it actually was not capable to treat the source of contamination. Recently, the remediation of contaminated soil [8], in part because of changes in regulatory (e.g. landfill directive 199/31/EC), has improved (mainly in what the treatment process is concerned and also is not restricted only to the polluted soil). In some countries, the in situ containment today is viewed as waste disposal and so it has to be under some regulation [9]. Because of this, we are experiencing a much higher effort to treat contaminated soil and therefore today different technologies are available. These techniques may be applied in the spot (in-situ) or out of the place (ex-situ) of contamination, which is usually preferable to the solution of confinement/isolation of the contaminated area, as this last process does not provide a true resolution of the problem in hands, constituting only a provisional solution. Decontamination techniques can be classified based in the nature of the treatment, as physical-chemical, biological, thermal or other techniques [10]. In some cases it may be necessary to combine two or more of these techniques in order to have a more economical and effective treatment [11]. It is necessary to understand that the success of the decontamination relays on proper selection, design, and adjustment of the operations of the remediation technology based on the properties of the contaminants and soils and on the performance of the system.

#### **3.1 Classical Techniques**

##### **3.1.1 Passive/Reactive treatment walls**

The confinement technique consists in the use of barriers that can be passive or reactive. The functions of the barriers are to prevent the migration of the contaminants to underground water levels, and to inhibit clean water to flow into the contaminated place. The normal configuration is the total enclosure of the contaminated area.

### ***3.2 Biological Techniques***

Biological techniques are based on the bioremediation principle [12] where microorganisms are used for the removal of the contaminants of the soil and for the treatment of sludge and underground water. It is necessary to point out that other biological techniques exist, that will not be detailed in this paper, as we have restricted only to the presentation of the techniques that currently present a greater potential of application [13].

#### ***3.2.1 Biopiles and Landfarming***

Two examples of biological techniques are the agrarian techniques (“Land Farming”) [14] and biopiles, which consist in the excavation of the contaminated soil and stimulation of the activity of micro-organisms by the addition of air and nutrients, and a control of the humidity. In bio piles airing is done by pipes placed in the inferior part of the bio pile with the help of a compressor, but in the agrarian techniques airing is made by a tractor that digs the soil [5, 15].

#### ***3.2.2 Natural Attenuation***

Another biological process is the natural attenuation, which is a controversial process, being considered for many as the “do-nothing” solution. This technique requires a restrictive and constant monitorarization, possessing a very slow kinetics, being able not to reach the intended values in the estimated time of degradation [4, 5, 15].

#### ***3.2.3 Composting***

Composting is a controlled biological process through which organic biodegradable contaminants are converted into innocuous and stabilized by-products, due to the activity of microorganisms (in aerobic or anaerobic conditions). Generally thermophilic conditions are kept (54°C 65°C) so that the composting of soils contaminated with dangerous organic contaminants may be carried through adequately. The contaminated excavated soil is mixed with organic dispersants and corrective agents, such as vegetal and animal wastes sawdust and residues, in order to increase the porosity of the material to treat.

#### ***3.2.4 Bio-Airsparging***

When it is intended to reduce the volatile composite concentration adsorbed in the soil, in the saturated zone, or dissolved in the underground water, we may apply the technique of Bio-Airsparging, also a biological technology [4, 6, 15] where from time to time we inject oxygen and nutrients in the saturated zone in order to increase the activity of the microorganisms. This in situ technology generally uses micro organisms that are indigenous in the area [5, 16].

#### ***3.2.5 Bioventing***

In this technology the air is injected into the contaminated media at a rate designed to maximize in situ biodegradation and minimize or eliminate the off-gassing of volatilized contaminants to the atmosphere. Contrary to bio-airsparging, which involves pumping air and

nutrients into the saturated zone, bioventing pumps the air only into the unsaturated or vadose zone [17, 18].

### 3.2.6 Bio-rehabilitation

Another biological technique that is frequently used is bio-rehabilitation, which is based on the water removal of the subsoil prior to its entrance in the contaminated place by pumping it to the surface where oxygen and nutrients are added, being then later re-injected in the downstream of the contaminated place [4].

### 3.2.7 Phytoremediation

A promising biological technology is the phytoremediation, which is an in-situ and clean technique based on the use of some species of plants with ability to degrade organic pollutants [19-22], being its cost 20-50% inferior to the ones presented by the chemical, physical, and thermal in-situ processes.

## 3.3 Physical-Chemical Techniques

Physical-chemical techniques are based on physical and chemical phenomena. In this section the most important techniques of the application of physical-chemical methods in soil decontamination will be seen in detail.

### 3.3.1 Soil Vapour Extraction

Within the physical-chemical techniques, one of the mostly used is the Soil Vapour Extraction ("SVE"), which is an inorganic technology for the treatment of volatile organic compounds (VOCs), half-volatile organic compounds (SVOCs), polychlorinated compounds (PCBs) and existing dioxins in the non-saturated zone of the soil (i.e., infiltration zone). Here a source of vacuum is applied to the soil matrix, creating a pressure gradient that originates the movement of the air present in the wells of extraction [15, 23].

### 3.3.2 Airsparging

This technology, which is also known as "*in situ* air stripping" and "*in situ* volatilization," involves the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapour phase. The air is then vented through the unsaturated zone.

This technique allows the efficient removal of COVs existing in underground water of aquifers through its volatilization and biodegradation [24, 25].

### 3.3.3 Dechlorination

Dechlorination, also called dehalogenation, is a chemical technique that is based on the loss of atoms of halogen (i.e. atoms of chlorine, fluorine, bromine and iodine) from the halogenated organic molecules converting toxic compounds into less toxic substances, that are many times soluble in water facilitating its separation from the soil [26, 27]. This technique applies the nucleophile substitution reaction of atoms of chlorine (or other halogens) for the other less dangerous ones, using as agents of the dehalogenation, sodium and the potassium hydroxides and polyethylene glycol (APEG) among others [3, 4, 15].

### 3.3.4 Soil Flushing

Soil decontamination is also possible through the in-situ washing of the soil (“Soil Flushing”) [28], that consists in the extraction of contaminants from the soil by dissolution, suspension in watery solutions or through the chemical reaction with the liquid that passes through the contaminated soil layers ([26, 27]). The washing of the soil may be carried through also ex-situ, comprehending in this case the following stages: excavation, fragmentation, separation in different grain size, washing of the different fractions and destination to give to the final residues. This technique is many times considered as a pre-treatment ([23]) for the reduction of the amount of contaminated material, which is then processed by another technology of decontamination.

### 3.3.5 Solidification /stabilization

Soil remediation is also possible through the solidification/stabilization technique which consists of a mixture of reactive materials (cement, concrete) with solids, semisolids and sludge for immobilization of the contaminants. The solidification produces blocks with a great physical stability through the addition of stabilizing agents (e.g., leached ashes and wastes from the furnaces) in order to limit the mobility and solubility of the constituent of the residues.

## 3.4 Thermal techniques

### 3.4.1 Thermal incineration

One of the mostly used technologies is the thermal incineration, that consists of a combustion of the organic contaminants at high temperature and in the presence of enough oxygen to convert the contaminants into dioxide of carbon (CO<sub>2</sub>) and water (H<sub>2</sub>O), thus promoting its destruction ([29]). This technique allows an effective soil treatment, of mainly halogenated and non-halogenated sediments and composites, pesticides, PCBs and dioxins /furans, and there are several units operating at industrial scale. The incinerators can be divided in two types: recuperative (pipe and shell exchanging system) and regenerative (ceramic exchanging system), depending on the type of energy recovery adopted. The incineration process produces, however three types of residues: solids coming from the incinerator, gases of fuel (combustion gases) and when applied to the treatment of soil containing acid gases, the water of the washing system.

The catalytic incinerators are safer than the thermal incinerators, having inferior energy costs and less pollutant gaseous emissions ([4]), however, the capital costs are superior, it is necessary a periodic regeneration/ substitution of the catalyst, and requires a bigger area of implementation in the soil ([26, 30, 31]).

### 3.4.2 Thermal desorption

Thermal desorption constitutes a physical and thermal separation process, not having as objective the destruction of the organic contaminants. The soil is heated to volatilize the organic water and contaminants. A gaseous flow or a vacuum system transports to a gas treatment unit the previously volatilized composites. The reached temperatures and the time of residence are determined in a way to promote the volatilization of the selected contaminants but without occurring their oxidation.

### *3.4.3 Vitrification*

Another thermal technique of soil decontamination is the vitrification, where the soil contaminated is converted into a glass product and therefore stabilized. This technique can be applied ex-situ or in-situ. The vitrification in-situ consists of the insertion of graphite electrodes in the soil creating a high electric current, being that the freed heat provokes the fusing of the soil matrix ([26]). As the vitrified zone is growing, it incorporates inorganic contaminants. The paralyzed organic components migrate until the vitrification zone where they are burned in the presence of oxygen, being necessary a treatment area for the gases before they are freed into the atmosphere. The ex-situ vitrification is based on a similar treatment, with the difference of that the soil is excavated and introduced in a vitrification system that functions in identical way to the described process ([27]).

## *3.5 Special Techniques*

Some techniques can be considered as special, are in a development stage and have shown that deserve a more careful study with sight to improve its efficiency. Some of these techniques (the ones that probably will have more impact next to the public) will be related in the following paragraphs. They can be applied to specific locations without the need for excavation. However, they are less effective in organic and carbonate-rich media and a control of the pH of the soil is a key management factor in these techniques as it determines solubility of pollutants and thus, treatment rates.

### *3.5.1 Electro-kinetic*

In this technique, the movement of the contaminants in the soil is induced by an electric current of low voltage, in the order of  $\mu\text{e}/\text{cm}^2$ , which is created by two electrodes placed in the soil. When electric current is applied the first phenomenon that occurs is the electrolyzation of the water, becoming the solution near to the anode, acid due to hydrogen production and release of oxygen. This “acid front” of the anode dislocates by migration to the cathode leading to desorption of the contaminants of the soil. This migration involves phenomena as the electro-osmosis (movement of the soil mixture to the cathode), electro migration (ionic transport of ions and complexes for opposing electrodes), and electrophoreses (loaded and colloid particle transport under the influence of the electric field) ([32]). The contaminants that arrive at the electrode can be removed by precipitation/co-precipitation or complexation with ions of the ionic exchange.

### *3.5.2 Plasma*

One technique that is becoming more and more researched and applied in some sectors, namely in the soil decontamination, is the plasma technique. In the plasma system a gas is heated at extreme temperatures to create the plasma. When the contaminated soil is placed next to the plasma it heats up until extreme temperatures are reached, existing in these conditions an absence of oxygen molecules. Hence organic composites are degraded being able, however, not to be totally broken and the inorganic composites (metals, reactive radicals) suffer a process of vitrification.

### *3.5.3 Supercritical Extraction*

Another technique that has been recently suggested for soil decontamination is the supercritical extraction, which is a technology that is based on the supercritical fluid

application as agents of separation ([26, 33]). A supercritical fluid is any substance with a temperature and pressure above its critical point. This technique has as great advantage the possible composites such as CO<sub>2</sub> and H<sub>2</sub>O, which are solvent “friends of the environment”. One other advantage in the supercritical fluid use is the possibility to control its characteristics, (e.g. its power of dissolution), through small modifications in the pressure and operating temperature, what turns these solvents adequate for the extraction of a widened spectrum of contaminants. One of the main reasons behind the choosing of the supercritical extraction for soil pesticide removal, is the possibility of carrying through the extraction of contaminants without modifying the structure of the soil and without leaving residues of solvent [34-37].

## 5. Choosing the best technique for soil remediation. Case of contamination by pesticides.

After all the pointed above it is clearly that many techniques may be applied in a specific situations and that one can be more effective or cheaper than the others in that particular situation. In table 1 are shown the main advantages and disadvantages of some of technologies discussed previously. An important step to determine the best technology to apply in a particular case, is the verification of the suitability of the chosen technique and the type of contaminant.

In table 2 is presented a hint on the suitability and efficiency of each remediation technique to treat soils contaminated with pesticides; some techniques are potentially capable of treating pesticides, but of course they rely on many variables: concentration of the pollutant, type of soil, present status of the technique and others; only few have proved to be capable to treat soils contaminated with pesticides.

## 6. Conclusions

Soil contamination is a quite actual and complex problem due to the number of variables involved, such as soil structure, climatic conditions and the huge number of existing contaminants. Pesticides constitute a modern soil contamination problem. There are currently many techniques to remediate soils contaminated with pesticides. All of them present advantages and disadvantages. In this paper we review the main decontamination techniques. Readers are also advised to consult review references like [38], where larger review details are given.

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Table 1 - Main advantages and disadvantages of the core remediation techniques



Remediation Technique	Advantages	Disadvantages
Passive walls	Provisional solution for the problem. In some cases is enough.	Some physic properties may be altered at large periods of time. Depth limitations. Non-perfect mixture of the constituents.
Reactive Permeable Walls	Conversion of the contaminants in non-toxic species or barely soluble.  Easy to implement and project. Short treatment, between 6 months and 2 years, under optimum conditions.	The permeability of the reactive zone must be equal or above the permeability of the aquifer.  It requires a high area. Reduction of concentrations above 95% and concentrations below 0,1 p.p.m. are hard to achieve.
Agricultural Techniques		It is not possible to apply it when the concentration of heavy metals > 2500 p.p.m. or the total concentration of hydrocarbons of oily origin > 50 000 p.p.m.
Bio-rehabilitation	Degradation of the adsorbed material and dissolved in the infiltrated and saturated zones. Easy to use and always prompt equipment. Does not create any residues.	The pit may be clogged by biomass or precipitates. The total concentration of hydrocarbons of oily origin must be < 50 000 p.p.m. It is difficult to implement if $k < 10^{-4}$ cm/s. Rehabilitation may occur only at the most permeable zone.
Fito-remediation	The costs are much less than in the other conventional options. The set-up costs are similar to the ones of farming equipments.	It is a seasonal technique. May originate bioaccumulation in animals. Is applicable only at low depths.
Soil Venting (SVE)	Proven performance, easily available equipment and simple set-up. Minimal disturbance at the operation site. Small time of use (from 6 to 12 years under optimal conditions). May be applied into sites with free products, and may be combined with other technologies.	May not be able to achieve the intended levels. Reduction of concentrations above 90% are hard to achieve. Low efficiency when applied at sites of low permeability. May require treatment of the extracted vapor. Only the non-saturated area is treated and may force the use of other methods to treat the saturated areas and the underground water.
Solidification/Stabilization	This technique either <i>in-situ</i> or <i>ex-situ</i> is available at large scale for non-volatile heavy metals. It is a relatively simple technology. It is a motivating technique at small period of time. It is a technique applicable with success to inorganic compounds and metals.	The increase of the treated material volume implies an increase in the reagents quantity. Environmental conditions may affect at large periods of time the immobilization. Some preliminary studies may be needed to determine the adequate stabilizing agents. Leachate and compressibility tests are needed to calculate product integrity. The toxicity of the contaminant is not reduced.

**Tab. 1: Advantages and disadvantages of the main remediation techniques (continuation)**

<b>Remediation Technique</b>	<b>Advantages</b>	<b>Disadvantages</b>
Solvent Extraction	<p>The volume of the contaminated stream is reduced.</p> <p>The recovery and treatment of the contaminant may be achieved.</p>	<p>Does not reduce the toxicity of the contaminant, only promotes its concentration.</p> <p>Generally, this technique is less efficient in molecules of high molecular weight.</p> <p>Is not efficient in non-organic compounds.</p> <p>Depending over the type of contaminant we may have a higher or lesser recovery, having also sometimes to use co-solvents to attain higher recoveries.</p> <p>It is a technique still under development in the soil treatment area.</p> <p>This technique presents higher equipment costs as compared with traditional techniques, presenting however small operation costs.</p>
Supercritical Extraction (SCE)	<p>The supercritical extraction of organic pollutants of soil samples, using CO<sub>2</sub>, is a quicker, less demanding in terms of man-power, and many times more complete than the extraction using organic solvents. Due to its efficiency and quickness laboratories have been adopted this technique for environmental analysis, being hence an accepted method for the analysis of contaminated soils. Many manufacturers have been producing analytical equipment based on this technique.</p> <p>SCE may also be used, besides soil remediation, in other environmental applications such as the regeneration of activated carbon and the cleaning of watery effluents.</p> <p>SCE may also be allied with other technologies, which will reduce or eliminate the extracted contaminant, as it is the case of biodegradation.</p> <p>It is an in-situ technique.</p> <p>The energy needs are low when compared with other decontamination processes.</p> <p>Recovers ionic contaminants that are hard to remove by other techniques, as they usually stay adsorbed in soil particles.</p>	<p>It is a process limited by the solubility of the contaminants and by soil adsorption.</p> <p>Heavy metals at its solid state have not been sufficiently dissolved and separated in soil samples.</p> <p>Electrolyte reactions in the electrodes neighbourhood may cause variations of pH in the media, and cause changes in the solubility of the contaminant.</p> <p>Heterogeneity or anomalies at the site, such as iron and iron oxide quantities, may cause a decrease in the removal efficiency.</p> <p>Sometimes migration may be slow, making decontamination insufficient.</p>
Electro-kinetics	<p>Techniques such SVE are not very efficient at soils of low permeability, allowing this process the overlapping of this problem.</p>	<p>High energy costs.</p> <p>Heavy metals such as arsenic, mercury, cadmium and chromium are not destroyed by the combustion, thus being some of them present in the ashes or released in the gases.</p> <p>Soils containing rocks may need to be fragmented.</p>
Incineration	<p>Simple operation, maintenance and relatively low capital costs.</p> <p>Light equipment and easy to adapt to the existing facilities.</p>	<p>High energy costs.</p> <p>Heavy metals such as arsenic, mercury, cadmium and chromium are not destroyed by the combustion, thus being some of them present in the ashes or released in the gases.</p> <p>Soils containing rocks may need to be fragmented.</p>

Table 2 - Suitability of each remediation technique to treat soils contaminated with pesticides.

Name	Suitability	Name	Suitability	Name	Suitability
Agricultural Thniques		Vitrification		SVE	----
Ex-situ Soil Washing		Thermal Desorption at low Temperatures		Dechloration	
In-situ Soil Washing		Thermal Desorption at high Temperatures		Bio-Rehabilitation	*
Solvent Extraction		Incineration			

 - Demonstrated efficiency;  - Potential efficiency.

\* depends on many conditions among which the contaminants concentration

