



COMPARATIVE STUDY OF DIFFERENT DEPOLLUTION TECHNIQUES AND THE IMPACT OF PHYTOREMEDIATION ON THE REHABILITATION OF SOILS POLLUTED BY HEAVY METALS: (ARTICLE REVIEWED)

Redouane Tarik^{*1}, Nouredine EL Moulaj², Touriya Zair³, Mohamed Tarik⁴, Jalila El Amri⁵

^{1,2,3}Laboratory of Materials Chemistry and Biotechnology of Natural Products, Faculty of Sciences, Moulay Ismail University, BP 11201 Zitoune, Meknes, Morocco.

⁴Bioenergy and Catalysis Laboratory (LBK), Energy and Environment Research Division (ENE), Paul Scherrer Institute (PSI), 5232 Villigen PSI, Switzerland.

⁵Laboratory of Environment and Health, Faculty of Sciences, Moulay Ismail University, BP 11201 Zitoune, Meknes, Morocco.

***Corresponding Author: Redouane Tarik**

Laboratory of Materials Chemistry and Biotechnology of Natural Products, Faculty of Sciences, Moulay Ismail University, BP 11201 Zitoune, Meknes, Morocco.

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ABSTRACT

Because of pollutants spread by industry, mining activity or intensive agriculture such as Zn, Pb, hydrocarbons, Cd, Hg, etc. soils become uncultivable or uninhabitable for future generation. Heavy metals are not biodegradable and therefore persist in the environment for long periods. Moreover, they are continually added to the soil by various activities. The accumulation of heavy metals in the environment can therefore affect the health of humans and animals. At the microscopic scale, heavy metals also have adverse effects on bacterial populations, which is not without consequences on the functioning of the ecosystem. The development of effective techniques to decontaminate polluted sites has become essential. Different soil remediation techniques exist. One of these techniques is phytoremediation which exploits the properties of some plants to accumulate large quantities of heavy metals. Phytoremediation has attracted attention as a potential alternative to traditional methods of depollution (thermal, physicochemical) due to lower cost and minimal soil disturbance, so a study is needed to evaluate different soil remediation techniques. To choose the best technology (s) for polluted soils and the implementation of innovative solutions to overcome the problem of soil contamination by heavy metals and therefore the rehabilitation of these soils,

KEYWORDS: Phytoremediation, heavy metals, rehabilitation, environment, depollution technique.

INTRODUCTION

In order to overcome the main limitations of the methods currently available in soil remediation strategies, research has been focusing for several years on the use of plants. It has long been known that the presence of a vegetative cover induces or stimulates the biodegradation of a large variety of organic contaminants (Reilley et al., 1996). In addition, some so-called metallophyte plants are able to develop normally on sites heavily contaminated by various metals and some of these plants, which are known as hyperaccumulators (Brooks, 1998), are able to massively store metals in their aerial parts. For example, studies on the ecophysiology and metabolism of higher plants in contaminated environments have gradually introduced the concept of phytoremediation alongside that of bio-remediation of polluted sites. Numerous studies highlight the purification possibilities offered by poplar cultivation, particularly in the decontamination of

sites polluted by zinc (Di Baccio et al., 2003, Sebastiani et al., 2004), cadmium (Robinson et al., 2000), chromium (Pulford et al., 2001), copper (Castiglione et al., 2009), mercury (Rugh et al., 1998). These new methods are inexpensive, low-waste and environmentally friendly (Raskin et al., 1994, Salt et al., 1995, Cost, 2002).

Today, the term phytoremediation is widely accepted and includes all methods based on the use of higher plants for the purpose of depollution. Despite their recent development, these methods are varied and encouraging results have already been obtained for various problems. More precisely, the studies carried out to date make it possible to envisage five types of phytoremediation strategies, grouped under various terminologies (phytoextraction, phytostimulation, phytovolatilization, rhizofiltration, phytostabilisation).

They are particularly promising. This shows that the use of higher plants in remediation strategies is considered with increasing interest. However, at present, the main obstacle to the development of phytoremediation lies in the small number of potentially usable species on an industrial scale. Indeed, most known metallophytes are characterized by shallow rooting, slow growth and low biomass production. All these criteria considerably limit the predictable extraction rates. Moreover, an optimal yield requires that the cultivation conditions (climatic and edaphic) on polluted sites correspond to the natural requirements of the plants used; this parameter is in essence very difficult to control and represents an additional limitation of the method. Therefore, further research is needed to select new tolerant and / or accumulating plants and to better understand their behavior (Senou, 2014).

1. Origin of soil contamination by heavy metals

Metallic pollution of soils due to human activities (agricultural, domestic and industrial) on the one hand and metals on the other hand naturally occur in soils because they are present in the source rock which undergoes particular erosion phenomena and alteration.

Heavy metals such as lead, cadmium, copper and mercury can not be biodegraded and therefore persist for long periods in the soil; which is a serious problem.

1.1. Natural origins

The natural pedo-geochemical background (FPGN) of a soil is the natural concentration of a substance in a soil horizon, resulting from geological and pedological evolution, excluding any anthropogenic input. This FPGN can vary widely, depending on the nature of the parent material (inheritance) and the type of soil that has developed there (Baize, 2000).

1.2. Anthropogenic origins

Soils are subject to more or less heavy metal inputs resulting from human activity. Over the past few decades, the world's heavy metals input has expanded. Today, it is estimated at 22,000 tonnes of cadmium, 939,000 tonnes of copper, 783,000 tonnes of lead and 135,000 tonnes of zinc (Singh *et al.*, 2003). The main types of anthropogenic pollution are responsible for the increase of metal flows and are related to atmospheric pollution and pollution (Senou, 2014)

2. Methods for decontaminating polluted soils

Several physical, chemical and biological decontamination methods have been developed in recent decades, depending on the type of site contamination. These conventional processes, whether performed *ex situ* or *in situ*, require a great deal of resources, particularly manpower, and result in a profound change in the physical, chemical and biological characteristics of the treated soils (Khan, 2005).). In addition, these methods represent imposing costs; in the United States they are estimated at between \$ 7 and \$ 8 billion a year, of which about 35% would

involve metals (Memon & Schroder, 2009). According to several authors, remediation costs average between \$ 0.27 and \$ 1.6 million per hectare of soil (Kidd *et al.*, 2009). In addition, their scope is more focused on small spaces and are often inadequate for large areas, such as old mine sites and brownfields (Khan, 2005). In addition, many of the existing technologies are not appropriate for diffuse pollution sites where contaminants are superficial and at low concentrations. As a result, costs associated with decontamination often exceed the value of the land involved, which is not an incentive for restoration (Batty & Dolan, 2011, Dickinson & Pulford, 2005).

The most commonly used decontamination method is digging and burying. This process, though efficient and expeditious, is considerably expensive, up to \$ 3 million (US) per hectare of soil. Moreover, this solution does not solve the problem, it only delocalizes it, and it is inconceivable for agricultural sites (McGrath *et al.*, 2001). *In situ* technologies include soil leaching, where coarse particles (sand and gravel) are separated from fine particles (silt and clay). The latter, on which the contaminants are generally bound and absorbed, are then chemically treated. The method of extracting soil vapors is also used, which requires the installation of wells in the contaminated area. A pump is used to evacuate these wells in order to evaporate the volatile constituents of the contaminants, which are then removed by extraction wells and treated. Another method used by the industry is to flush the soil by flooding it with a solution that moves the contaminants to a place where they can then be removed. The extraction is done by injecting another fluid into the soil, and then the recovered materials are treated. Among the main physical methods used is stabilization, where the contaminants are converted into a less soluble, mobile and toxic form, in order to reduce their ecotoxicological risk (Marques *et al.*, 2009).

2.1. Physico-chemical stabilization

Physico-chemical stabilization is also called inerting, stabilization / solidification or immobilization technique. It can be applied *in situ* or *ex situ*. This remediation method includes all the techniques that consist of reducing the risk of spread of contaminants in the surrounding environment, in a stable and perennial manner, by immobilizing them in a less soluble and / or less toxic form through the implementation. physicochemical mechanisms. This can be done either by direct action in the soil (*in situ*), or by means of a mobile installation sent to the site (*on-site*), or in a dedicated facility (*off-site*) (ADEME, 2010).

In the case of physicochemical stabilization *in situ*, the chemical agents in solution are brought into contact with the soil via particular drilling, injection and mixing methods and they immobilize the pollutants. *Ex situ* physicochemical stabilization techniques apply in the same way but on excavated soil. They require more equipment since it is necessary to gather all the instruments necessary for the construction site and that after

mixing the stabilized product must be deposited in basins, caissons, containers... In all cases, it is then necessary to monitor the behavior. soil stabilized with respect to long-term toxicity and bioavailability of pollutants (ADEME, 2010).

In order to transform the contaminants into a less soluble and / or less toxic form, chemical mechanisms are implemented such as the mechanisms of insolubilization by precipitation, adsorption on particular matrices, neutralization or complexation, oxidation-reduction, of substitution reactions where the polluting ions are exchanged with other alkaline or alkaline earth ions and are fixed in the crystalline structure of certain minerals. All these mechanisms are subject to the conditions of the medium (in situ) or the operating conditions (ex situ) such as pH, redox potential, solubility, etc. (ADEME, 2010).

In some cases, the physicochemical stabilization is accompanied by a solidification which is obtained by the use of mineral, hydraulic or vitrification binders and which makes it possible to reduce the transfer of external agents to the contaminated soil and mobilizable pollutants. outward or oxidation phenomena (ADEME, 2010; CPEO, 2010) Physico-chemical stabilization techniques face several difficulties. First, there are limits related to the nature of the soil and the homogeneity between the soil and the binders brought.

Secondly, there are limits related to the nature of the mineral pollution and the depth of the contamination. During the physico-chemical stabilization, there is transformation of heavy metals. Care must be taken that undesired or uncontrolled changes do not interfere with the immobilization of contaminants. In the case of mixed pollutants, care must be taken with possible chemical interactions between organic and metallic contaminants and stabilizing agents (ADEME, 2010, CPEO, 2010).

Thirdly, there is the cost, that is to say, the expenses related to the consumption of reagents, energy, those related to the transport or the setting up of the mobile units of treatment and the maintenance. According to ADEME, the average cost of physico-chemical stabilization varies between 30 and 110 € / tonne when the technique is applied in situ and on site; and between 70 and 200 € when the technique is applied off site.

Finally, if stabilization reduces the mobility of pollutants, the site should not be considered as being cleared. Especially since, according to Mulligan *et al.* (Mulligan 2001), the long-term stability of the solidification and stabilization matrices is unknown.

2.2. The washing of the grounds

This technique is also known by other names such as flushing, leaching and chemical extraction with solvents, acid-base or by surfactants. The aim of soil washing is to mobilize contaminants either by solubilization with water, with solvents or with acid bases, or by chemical

transformation with oxidants or reducing agents. When the technique is applied in situ, this is done by direct action in the soil: it brings the soil into contact with extraction agents, solubilization of pollutants, recovery and treatment of liquid effluents. When this technique is applied ex situ, it is preceded by an extraction of the soil and followed by a particle size classification allowing to isolate the fine parts in which the pollution is concentrated (ADEME, 2010).

The washing techniques are carried out by percolation and stirring. In situ washing is only carried out via percolation: The reagent solutions are injected by pumping or watering at the level of contaminations. After pollutants are dissolved, the percolates are recovered by drainage structures (boreholes, draining trenches, etc.), then treated and most often reinjected into the subsoil. (Vanobberghen, 2010).

The implementation of ex-situ percolation washing techniques essentially consists in the leaching of contaminated soil in heaps on waterproof tarpaulins. Chemical extractants are pumped through drains and sent to a storage tank, treated and recycled or discarded (Dechamp and Meerts, 2003). The agitation soil washing techniques apply only to ex situ methods: after screening, the soils are brought into contact with the solution in stirred reactors in order to increase the exchange kinetics. Then, the solid phase and the liquid phase are separated by methods such as decantation, filtration, centrifugation, etc. The liquid phase is treated while the solid phase is rinsed to remove residual contaminated solution (Vanobberghen, 2010).

The boundaries of land washing are multiple. First, by increasing the mobility of contaminants, there is increased risk. It is; therefore, necessary that the equipment set up ensures recovery of all the percolates. Moreover, as for the physico-chemical stabilization technique, it is necessary to avoid undesired or uncontrolled physico-chemical changes resulting from the transformation of the pollutant.

Third, if the content of fine particles in the soil is too high, there is a risk of clogging of the soil during treatment percolation pile. Enfin, the cost of this technique is quite important: between 35 and 80 € / ton when applying on site, between 350 and 500 € / tonne during off-site application (ADEME, 2010, Cliquot de Mentque, 1998).

2.3. Containment

Containment is more of a solution than a clean-up method. This method allows the treatment of large areas and multiple pollutants. Pollution is not removed or removed. Containment with the aim of reducing its effects on human health and the environment (Legrand *et al.*, 2006). It can be applied according to three methodologies (Perchet, 2008): Surface containment with geomembrane placement Vertical containment, behind con-

crete waterproof walls, retaining materials or plastic mortars Deep horizontal confinement (Robinson et al. 2009, Mercier, 2016).

2.4. The electrokinetic

After excavation, it is possible to treat the land through electrical extraction. This method is based on the application of an electric field in the soil inducing the transport of pollutants to the electrodes where they are recovered. Four mechanisms can be applied (Impens et al., 1991, Mulligan et al., 2001):

Electromigration: Movement of atoms, via a flow of electrons, into the ground;

Electrophoresis: Generation of a movement of particles in the aqueous phase of the soil;

Electroosmosis: Production of a movement of the aqueous solution of the soil from the anode to the cathode, this method can be applied in situ also

Electrolysis: displacement of ions and complexes in the aqueous phase of the soil.

The presence of metal objects, rocks, foundations, rubble can interfere with the smooth running of electrokinetic processes. This process is effective with clay soils of low permeability (Mulligan et al., 2001).

The cost of these mechanisms depends on the electrical power to be developed and the time during which it must be maintained. The necessary electrical energy is also a function of the concentration of the ions present, the objectives of concentration to reach, the pH around the electrodes in the ground, etc. (Impens et al., 1991).

2.5. Thermal desorption

In the context of these physical techniques, there are also heat treatments that can be performed on the site itself "on-site" and on appropriate sites "off-site" as an incineration plant. This technique is adapted to soils contaminated by easily oxidizable organic compound and convertible into CO₂ and H₂O. Soil excavation, grinding and sieving are required prior to heat treatment. There are two methods of heating:

Direct heating where the floor is heated to 1000°C directly by introducing oxygen and indirect heating where the soil is in a sealed furnace and is not in contact with the heat source. The temperature is around 800°C and is sufficient to extract pollutants from intermediate vapors released (Samaksaman, 2016). Both methods are very efficient but very expensive energy. There are currently several types of ovens (Perchet, 2008, Lim et al., 2016).

2.6. Biological methods

The use of biological methods makes it possible, among other things, to promote the total or partial degradation of pollutants. These techniques can use bacteria, fungi,

yeasts and plants to decontaminate a polluted site. Organisms used in biological treatments have the capacity to transform pollutants into substances that are less toxic to the environment. In addition, some plants have the ability to accumulate large amounts of metals in their tissues. Table 1 demonstrates different biological treatments for contaminated soils.

Table 1: Methods for the biological rehabilitation of contaminated soils (Chevrier, 2013).

Biological rehabilitation method	Ex situ	In situ
Bioventilation		X
Bioremédiation		X
Phytoremédiation		X
Atténuation naturelle contrôlée		X
Biopiles	X	
bioreactor	X	
bioreactor	X	

3. Phytoremediation

Phytoremediation is defined as a group of technologies that use plants to reduce, remove, degrade, or immobilize contaminants in soils, sludge, sediments, surface water, groundwater, and wastewater. These techniques are applicable to a variety of contaminants, including petroleum hydrocarbons, chlorinated solvents, metals, radionuclides, nutrients, pentachlorophenol and Polycyclic Aromatic Hydrocarbons (Vishnoi and Srivastava, 2008). Plants have been studied extensively to understand the mechanisms that govern their ability to decontaminate polluted environments and the role they play in them.

3.1. The role of plants in phytoremediation

Plants are so-called autotrophic organisms since they produce organic matter from inorganic matter. This process of conversion, called photosynthesis, consists of transforming solar energy into chemical energy in order to fix carbon in the form of organic compounds. Here is a repealed representation of photosynthesis:

$$3\text{CO}_2 + 6\text{H}_2\text{O} + \text{Lumière} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

(Raven et al., 2007). The carbon dioxide that plants take from the stomata comes from the atmosphere while the water and minerals necessary for their development are captured at the root level in the soil. In contaminated soil, there is a multitude of contaminants that can be absorbed by plants in different forms. Thus, the pollutants present in excess in the soil can be degraded by several biological mechanisms, either by the plant itself or in the rhizosphere by microorganisms.

There are specific and non-specific interactions between plants and microorganisms present in the soil (Sicillano and Germida, 1998). These associations allow among other things bacteria and fungi to have access to a significant source of carbon. This high energy availability means that large populations of microorganisms in the rhizosphere grow close to the roots. However, several advantages are observed thanks to these associations. In

particular, they provide a form of protection at the roots against pathogens present in the soil, this barrier has the function of destroying them (ITRC, 2009). In addition, microorganisms can make available certain nutrients necessary for plant growth and at the same time facilitate their uptake by the roots without forgetting that some bacteria have the capacity to reduce the toxicity of contaminants so that plants can grow without negative effects (Sicillano and Germida, 1998).

The use of living organisms to decontaminate soils is one way to reduce the costs associated with traditional decontamination techniques, and plants are part of it. They are used to decontaminate soils because their root system can explore a large volume of soil and absorb pollutants that are present. Their absorption is carried out *inter alia* according to the bioavailability of the contaminants and the mechanisms that operate the entry to the plant. Some plants have also developed mechanisms of resistance against certain pollutants, either by the ability to store contaminants in non-vital areas of the plant or by the ability to make them less harmful to the environment (San Miguel, 2011). This is also the case for so-called hyperaccumulative plants which can store in their tissues quantities of contaminants normally toxic for the majority of plants. Indian mustard (*Brassica juncea*) belongs to this category of plants because it can accumulate significant quantities of lead and copper (Labrecque and Lefebvre, 2006).

In addition, other types of plants known as fast-growing plants such as willows and poplars can also be used to rehabilitate contaminated sites. Many qualities are associated with these woody plants, the main ones being: their great power of evapotranspiration, their speed of growth, the extent of their root system as well as their ease of vegetative propagation (Kuzovkina and Volk, 2009). These qualities provide fast growing plants with a unique advantage in decontamination efficiency. Moreover, the species belonging to the family Salicaceae are known to have a very extensive root system, which allows them to capture much more water and nutrients (Fortier, 2008). Studies by the Plant Biology Research Institute (VVRI) have shown that some willow and poplar species have the capacity to absorb large quantities of metals (Labrecque and Lefebvre, 2006). That is why their use in phytoremediation is more and more frequent without forgetting that these plants can at the same time solve several other environmental problems.

3.2. Phytoremediation techniques

The different types of phytoremediation are not exclusive, that is, they can operate simultaneously. Table 2 shows the different mechanisms that can occur during decontamination by phytoremediation. In the following sections, the various technologies will be described in more detail in order to highlight certain elements such as their effectiveness, the advantages and disadvantages, the limits and the costs that the choice of this phytotechnology in question generates.

Table 2: Overview of the different phytoremediation technologies (from: EPA, 2000, p.15).

Mechanism	Purpose of the process	Middle	Contaminants	Plants
Rhizofiltration	Extraction and capture of the contaminant	Groundwater and surface water	Metals and radionuclides	Sunflower, Indian mustard, water hyacinth
Phytostabilisation	Containing the contaminant	Soil, sediments and sludge	Arsenic, cadmium, chromium, copper, lead and zinc	Indian mustard, hybrid poplars, grasses
Phytoextraction	Extraction and capture of the contaminant	Soil, sediments and sludge	Metals: silver, cadmium, cobalt, chromium, copper, manganese, mercury, molybdenum, nickel, lead and zinc Radionuclides: Strontium 90, Cesium 137, Plutonium 129, Uranium 234 and 238	Indian mustard, Thlaspi, Alyssum, sunflower, hybrid poplars
Phytodegradation	Destroy the contaminant	Soil, sediments, sludge, groundwater and surface water	Organic compounds, chlorinated solvents, phenols, herbicides and ammunition	Poplars and herbs
Rhizodegradation	Destroy the contaminant	Soil, sediments, sludge and groundwater	Organic compounds (PAHs, pesticides, chlorinated solvents and PCBs)	Hybrid Poplar, Deltoid Poplar, Willow
Phytovolatilisation	Extraction of the contaminant and relaxation in the atmosphere	Surface water, soil, sediment and sludge	chlorinated solvents and some inorganic compounds (arsenic, mercury and selenium)	Poplars

3.2.1. Rhizofiltration

Rhizofiltration is the adsorption or precipitation of plant roots (or root uptake) from contaminants in groundwater, surface water, and wastewater (UNEP, 2002; EPA, 2000). This technique is generally used to treat sites contaminated with metals and radionuclides such as lead, copper, zinc, nickel, uranium, cesium and strontium (EPA, 2000).

Plants used to decontaminate water may be terrestrial or aquatic (Ghosh and Singh, 2005). In order for the plants selected for this type of technique to perform effective decontamination of the medium, they must preferably have a large contact area at their roots. These plants, which are used for rhizofiltration, are first grown in greenhouses and their roots are in water before being transplanted into the contaminated environment (EPA, 1999).

When plant roots are saturated by contamination, plants are harvested and new plants are planted to continue decontamination work (Government of Canada, 2008). To recycle contaminants that have accumulated in plant roots, plants are incinerated or composted (EPA, 1999). Several types of both aquatic and terrestrial plants can be used to decontaminate wetlands. Their use is justified by their high efficiency in filtering contaminants by their roots. In general, aquatic plants are smaller and have a slow-growing root system compared to terrestrial plants that have greater biomass and faster root system growth (EPA, 1999). Terrestrial plants are then favored for this type of phytoremediation since they are able to absorb a large amount of contaminants in their roots (Eapen *et al.*, 2007). In fact, studies have shown that sunflower (*Helianthus annuus* L.), because of its roots, can reduce the concentration of several contaminants. In fact, a pond near the nuclear disaster that occurred on April 26, 1986 in Chernobyl, Ukraine, was the site of rhizofiltration decontamination. In two weeks, a 90% reduction in Strontium-90 was observed, and merit was awarded to *Helianthus annuus* (University of Hawaii, 2001). Unfortunately, several technical disadvantages are associated with this phytotechnology, including the need to constantly adjust the pH in order to obtain optimal absorption of the metals present in the environment and that of having to first grow the plants in the greenhouse (Henry, 2000). Finally, rhizofiltration can generate costs estimated at between two and six dollars per 5.55 m³ of treated water (EPA, 2000).

3.2.2. Phytostabilisation

Phytostabilization is a decontamination technique that involves the use of plants to contain or immobilize pollutants (ADEME, 2013b). As a result, the mobility of pollutants is reduced, which prevents migration of the contamination plume to groundwater or the atmosphere (EPA, 1999). This technique is mainly used to treat soils, sediments and sludge (EPA, 2000). Not to mention that it is very effective in cases where it is desired to act

quickly to immobilize contaminants in order to preserve the water table (ITRC, 1997).

The biological mechanisms involved during phytostabilization are the absorption and accumulation of contaminants by the roots, adsorption on the roots or precipitation in the rhizosphere. The amount of water that seeps into the soil can lead to the formation of contaminated leachate. Thus, the presence of plants reduces the amount of water that infiltrates the soil and at the same time prevents the erosion and transfer of toxic metals to other compartments such as the water table and the atmosphere (Ghosh and Singh, 2005). Moreover, for metals, which obviously can not be degraded, phytostabilization is an interesting option since it prevents their distribution in surface or underground water (Government of Canada, 2008). Indeed, if we found harmful concentrations of contaminants it could have a significant impact on living things and the environment. The choice of plants is a step that should not be neglected when opting for a phytostabilization technique. Thus, plants best suited for phytostabilization are plants that must have low levels of metal accumulation in their aerial parts (Evans, 1997). Phytostabilization may require the use of fertilizer amendments or stabilizers. That is, before introducing plants selected for phytostabilization, alkaline agents, phosphates, organic matter, biosolids and inorganic oxides are added to the soil. This has the effect of inactivating contaminants, preventing leaching and minimizing the accumulation of contaminants in plants (Huang and Chen, 2003). Finally, several disadvantages are associated with this type of phytoremediation, including the one that stands out most of the others by the fact that the contaminants remain in place. In addition, ongoing and long-term monitoring must be conducted to prevent the release of contaminants into the environment (EPA, 1999).

3.2.3. Phytoextraction

Phytoextraction is the most widely used phytoremediation method because pollutants are isolated without altering soil structure and biological activity (Ghosh and Singh 2005). Also known as phytoaccumulation, phytoextraction refers to the absorption of contaminants present in the soil by the roots of the plant. Subsequently, these contaminants are transferred (or translocated) and accumulated in the aerial parts of the plant, such as stems and leaves, which are then harvested (Chevrier, 2013). Some plants are called "hyperaccumulators" because they have the ability to absorb a large amount of metals compared to other plants (UNEP, 2002). These hyperaccumulating plants must be capable of accumulating at least 1000 mg of a specific metal per kilogram (kg) of dry matter without any apparent damage to their physiology (ITRC, 2009). According to a study conducted by Barbaroux *et al.* (2011), plants of the genus *Alyssum* can concentrate in their tissues up to 16.9 grams (g) of nickel per kilogram of dry matter. This phytotechnology is applicable to both soil and polluted water, it is sufficient to use aquatic plants with the capacity to accumulate large quantities of pollutants (Dabouineau *et al.*, 2005).

However, it is only effective on sites with a low to moderate level of contamination so that the plants are able to grow properly (Padmavathamma and Li, 2007).

There are two types of phytoextraction: induced and continuous (Salt *et al.*, 1998). The induced phytoextraction requires the addition of chelators in the soil to increase the mobility and uptake of contaminants in the plant (Ghosh and Singh, 2005). For example, the addition of ethylene diamine tetraacetic acid (EDTA) to soils can make the lead bio-available so that it can be absorbed by the plant (Prasad, 2011). Chelating / metal ion complexes will thus be formed in order to be absorbed by the roots (Dabouineau *et al.*, 2005). While continuous phytoextraction is more dependent on the genetic and physiological capabilities of plants, that is, plants must be able to accumulate particularly high levels of contaminants in their lifetime (Peer *et al.*, 2006).

3.2.4. Phytodegradation

Phytodegradation is commonly used to degrade organic pollutants such as chlorinated solvents, herbicides, insecticides and hydrocarbons (Vishnoi and Srivastava 2008).

This phytoremediation technique, also called phytotransformation, consists of the degradation of organic pollutants into less toxic and simpler molecules. These mechanisms of degradation that operate are either directly by the release of enzymes produced by the plant in the rhizosphere or are the result of metabolic activity in plant tissues (Greipsson, 2011). The enzymes involved in external degradation to the plant are usually dehalogenases, oxygenases and reductases (Black, 1995). Once degraded, the contaminants will be absorbed by the plant, incorporated into the tissues and used as nutrients to contribute to the growth of the plant.

Phytodegradation can be used for both soil and water decontamination. However, it is not suitable for heavy metals since they do not degrade. It is important not to confuse phytodegradation with rhizodegradation, as these are two similar but still distinct techniques (see below). In other words, anything that involves microbial activity in the rhizosphere or degradation of contaminants by other microorganisms such as fungi is considered to be rhizodegradation (Chevrier, 2013).

Poplars (*Populus* spp.) Are the most commonly used plants for phytoremediation and especially for phytodegradation. These trees are effective in decontamination since they have a high rate of transpiration, tolerate high concentrations of organic contaminants and are rapidly established at a site (Chang *et al.*, 2005). Although the use of plants with the ability to degrade organic components is considered a more environmental option compared to conventional techniques, some disadvantages are still associated. Among other things, contaminant degradation can produce toxic intermediates that in some cases will pose environmental risks (EPA, 2000).

3.2.5. Rhizodégradation

Rhizodegradation, also called phytostimulation, consists of the degradation of contaminants in the rhizosphere through microbial activity that is favored by the presence of plants (UNEP, 2002). Plants can alter the physico-chemical and biological properties of the rhizosphere through the secretion of exudates by the roots and the penetration of roots into the soil. These compounds (sugars, amino acids, fatty acids, nucleotides, enzymes, etc.) that vary among species will have a positive influence on microorganism populations (Shimp *et al.*, 1993). Thus, when a site is vegetated, there may be greater variety, higher quantity, and increased activity of microorganisms, resulting in increased biodegradation of contaminants in the soil (EPA 2000). In particular, some microorganisms (yeasts, fungi or bacteria) have the ability to degrade organic contaminants such as solvents and hydrocarbons for use as a source of nutrition and energy (UNEP, 2002). In the rhizosphere, plant / microorganism associations can be found. These associations will be self-sufficient, that is, the plants will provide the necessary nutrients for the microorganisms while these will ensure that the plants are able to grow in an appropriate soil (ITRC, 2009).

Other things we are talking about designing bacterial genes that reduce mercury so that they can be introduced into plants (Prasad, 2011). In fact, the common tulip tree (*Liriodendron tulipifera*) has been inserted with modified *Escherichia coli* genes to improve its ability to volatilize methylmercury in contaminated soils (Greipsson 2011). Poplar is the most widely used plant species for the phytovolatilization of volatile organic compounds (VOCs) (Pilo Smits, 2005). Because of the high rate of transpiration they have, poplars are able to decontaminate groundwater, soil, sediment and sludge (EPA, 2000). One study has shown that hybrid poplars have been able to remove nearly 97% of the 50 parts per million (ppm) of tetrachlorethylene in polluted water within two years (Newman *et al.*, 1997). Although this phytoremediation technique is considered a green measure compared to conventional techniques, it is still necessary to consider the risks associated with the transfer of contaminants to the atmosphere. We are talking about risks to human health and the environment (Vishnoi and Srivastava, 2008).

3.3. Benefits of phytoremediation

Phytoremediation is increasingly used today as it contributes to the maintenance of soil structure as it does not require excavation (EPA, 2012). In addition to being recognized as an economic choice compared to conventional decontamination techniques, phytoremediation is widely accepted by the general public as there are few impacts associated with it. Several other benefits are attributed to this decontamination technique, including the amount of residues generated by phytoremediation. However, when using conventional technologies, the volume of material to be buried or incinerated is higher than if phytoremediation is used (over 95% reduction)

(Forget, 2004, Ghosh and Singh, 2005). In addition, the use of these phytotechnologies is applicable to a wide variety of contaminated sites. Whether for organic or inorganic contamination, soil contamination or groundwater, phytoremediation is now an option to consider. Not to mention that the presence of vegetation on a site helps to reduce or prevent erosion and provides a visual benefit to the landscape (Vishnoi and Srivastava, 2008). The energy used to decontaminate sites where phytoremediation techniques take place is the sun, which is beneficial for the environment since traditional techniques, will instead opt for dirty energy. For example for excavation, it is the essence that rolls the machinery and which unfortunately pollutes enormously and create noise disturbances. In addition to using no fossil energy during decontamination, phytoremediation generally has a positive impact on the environment. Indeed, plants are known to improve air quality and their ability to sequester greenhouse gases (GHGs) (ITRC, 2009).

3.4. Limitations of the phytoremediation method

As Forget (Forget, 2004) has so aptly said in one of his articles: "Like any technique of soil decontamination, phytoremediation has certain limits with which it is necessary to compose". One of the first limitations is the contact between the rhizosphere and the contaminants present in the medium to be decontaminated (EPA, 2000). The ability of plants to reach a certain depth from their roots depends on plant species and geomorphological and climatic conditions (EPA, 2000). For example, some tree species such as poplar have roots that can potentially reach a depth of 4.6 m in soils while those of shrubs will be more superficial (EPA, 2000). Finally, phytoremediation should be restricted to sites with shallow contamination and relatively low concentrations so that plants are able to grow appropriately to capture all contaminants (Ghosh and Singh 2005). These plant-absorbed contaminants may also pose a potential risk to the environment as they may end up in the food chain if animals ingest contaminated plants (Government of Canada, 2008). In fact, several studies have shown that some animals and insects do not consume contaminated plants because they have a bad taste (Chaney *et al.*, 2000). The growth rate of plants will also influence phytoremediation as it may take several years to reach an acceptable level of decontamination.

Finally, although some plants are known to accumulate high levels of contaminants, the choice of plants for phytoremediation needs to be considered. That said, it is best not to opt for plants that are not native to the site where in situ decontamination takes place and to avoid invasive ones. These precautions will help maintain biodiversity already in place (Ghosh and Singh, 2005).

3.5. Costs of phytoremediation methods

There are many benefits associated with phytoremediation, including the low cost of decontamination that can be up to 10 times lower than conventional techniques (Peer *et al.*, 2006). As a comparison, the costs associated

with conventional decontamination techniques, such as excavation, are estimated to be between 0.4 and 1.7 million for a site of one lead-contaminated acre at a depth of 50 centimeters (cm); only US \$ 60,000 to US \$ 100,000 would be needed to decontaminate the same site using a phytoremediation technique (Khan *et al.*, 2004). Not to mention that these costs, which are relatively low compared to excavation, can be amortized over several years (Forget, 2004).

4. Innovative techniques

The most innovative biological techniques developed in the laboratory and promising from the point of view of their application in the field have been identified. They mainly concern the combination of existing and well-known processes: we will mention the four most well-known methods.

4.1. Coupling bioremediation (rhizosphere) / phytoremediation

According to Lawton and Jones (1995), plant roots can be considered as "soil biological engineers". In fact, they create and maintain their own environment, and this is not only by their physical presence but also by their activity. By processes such as the exudation of organic acids and enzymes in the rhizosphere, the roots will be able, for example, to allow the maintenance of microbial communities (Curl and Truelove, 1986) or the increase of the erosion of minerals (Hinsinger *et al.*, 1992). Thus, despite the small volume of the rhizosphere in soils, it plays a central role in maintaining the soil-plant system (Gobran *et al.*, 1998). Among the microorganisms found in the soil, some live in symbiosis or mutualism with the plants, that is to say, in association with mutual benefits. The supply of water and nutrients to the plant in exchange for carbonaceous substances and physical protection for microorganisms can define these exchanges. In these associations, microorganisms can be classified into two categories:

The ectosymbionts which constitute the micro-organisms colonizing the outside of the root, that is to say, the rhizosphere or the rhizoplane (surface of the roots). These organisms include bacteria such as *Pseudomonas*, *Azotobacter*, *Bacillus*, *Enterobacter* (Gray and Smith, 2005) and fungi (*Trichoderma*). Bacteria of this type are then defined as rhizobacteria or rhizoplane bacteria;

The endosymbionts which gather the microorganisms living inside the cells of the host plant. The plasmalemma can also be pierced, this being the work of so-called endophytic bacteria. These bacteria, mainly belonging to the genera *Rhizobium* and *Frankia*, can then form root nodules, and this on the roots of legumes and ligneous trees (Lugtenberg and Kamilova, 2009). Due to their rhizosphere and endophytic characteristics, bacteria have been receiving attention in recent years to promote plant establishment under adverse conditions, favoring phytoremediation processes. These bacteria can be iso-

lated from plants living on soils contaminated with metals or organic compounds (Nouri, 2016).

4.2. Coupling bioaugmentation / phytoremediation

It is the inoculation of specific micro-organisms (bio-increase) in porous matrices (soils, sediments), capable of:

To degrade organic molecules (especially pesticides) and increase the stock of metals available for plants used for phytoextraction (with siderophore-producing microorganisms for example). As a result, the growth of inoculated microorganisms is enhanced by the supply of nutrients exuded by plant roots used for phytoextraction.

4.3. Coupling phytoextraction / energy recovery of biomass

In 2003, the Federal Ministry of Research (BMBF) of Germany launched a program aimed at setting up an interdisciplinary network on the theme "Renewable energy from biomass from phytoextraction of contaminated soil". This program is managed by the CUTEC Institute (Clausthaler Umwelttechnik-Institut, Germany) for a period of two years. Under this program, nine projects have been carried out to achieve the following objectives: (i) the establishment of a network of experts to assess the state of science and technology in field of use of biomass from soils decontaminated by phytoextraction; ii) evaluation of the possibilities and limitations of this process; iii) design of priority projects. Currently, this network is made up of 35 experts from various scientific and industrial sectors working on topics such as: the recovery of heavy metals in plants; the different techniques currently available; the best methods for the energy use of plants (Ex: combustion); the limits of the current processes and the new solutions that can be envisaged.

4.4. Multiprocess phytoremediation system

Combination of various bioremediation techniques around a phytoremediation system to decontaminate soils polluted by persistent petroleum hydrocarbons (TPH). The techniques involved in the system are: landfarming (aeration), bioremediation (bacteria) and phytoremediation.

5. Other techniques, already old, evolve little

Organic soil remediation techniques marketed by companies are already old and are no longer the subject of major research and development. These are bioremediation techniques that either stimulate the endogenous bacterial population or operate in a controlled space. They use the following eight methods:

1. Bioventing (ventilation, air and nutrient injection into the soil): Bioventing is a promising technology that stimulates the in situ biodegradation of pollutants in soils by providing the necessary microflora with the required oxygen. Oxygen is supplied by the injection of air into the contaminated area. In order for this method to be effective, it is necessary for the

porous medium to have a good content of mineral elements, and a soil colonized by microorganisms adapted to pollution for the bioventing technique to be possible (Perchet, 2008);

2. Soil treatment by hydrogen peroxide injection (H₂O₂): Chemical oxidation consists of injecting an oxidant into contaminated soils. It can be done *ex situ*;
3. Landfarming: This technique is effective, but slow (it takes usually several months of treatment). It has the advantage of being relatively inexpensive. However, used without any particular precaution, it presents harmful effects: the strongly recalcitrant compounds accumulate in the treated zone, if the device is not closed, the neighboring zones are contaminated by runoff of the waters having crossed the mass in treatment and regular mixing may result in the volatilization of compounds in the atmosphere;
4. Biosparging (washing): stimulates the in situ biodegradation of pollutants in soils by providing the microflora in place with the oxygen needed for bacterial metabolism. Oxygen, which is often the limiting element of aerobic microbial action, is provided by the injection of pressurized air into the contaminated zone in a saturated zone. The principle of soil treatment by biosparging is the same as that of bioventing, with the difference that it concerns pollution located in the saturated zone (ADEM, 2008);
5. Combination bioventing / biosparging (ventilation / washing);
6. Pump and treat (soil treatment associated with groundwater treatment); biofuel (biopile: excavation of land before addition of micro-organisms adapted to the pollutant, corresponding to bioaugmentation);
7. Composting: This is a process that uses aerobic and thermophilic micro-organisms and is traditionally used to degrade vegetable waste from agriculture and turn it into a smaller, nutrient-enriched product that can be reused as fertilizer. This process can be applied to contaminated soil. The excavated soil is placed on an impermeable film and crossed by drains to allow forced ventilation in the mass. The microflora-friendly nutrients are supplied as a solution by sprinklers. The aqueous phase, which percolates through the entire soil pile, is evacuated in its lowest part by a drain. The soil to be treated can also be enriched with different organic substrates to promote aeration of the soil and promote microbial activity (Chen *et al.*, 2015).
8. Coupling of compost, lime and phosphate (Chen *et al.*, 2015, Nouri, 2016).

CONCLUSION

Some plants can absorb or reduce the toxicity of different organic pollutants or metals and radioelements present in soils. They accumulate, transform, degrade, concentrate, stabilize or volatilize. Four methods are being studied as biodegradation processes: phytostabilization, phytoextraction, phytodegradation and phytovolatilization.

Mining activity as well as human activity is the basis of the production of waste rich in toxic metal elements can be generated a soil contamination, can even spread to the surrounding soil and contaminate the groundwater.

Decontamination of contaminated soils is therefore a necessity and a priority in order to protect the environment and human health. In light of this comparative study of the different methods and technologies of contamination, it is noted that phytoremediation has no adverse effects on the environment, but has several positive aspects. Moreover, the many benefits of phytoremediation must be highlighted to promote this approach for the good of the planet and future generations as we borrow the land of our children. It remains to be hoped that government agencies will do their best to promote in situ technologies, including phytoremediation, as part of contaminated soil remediation projects, and that research and developments on the subject come to the conclusion that phytoremediation is just as important technically and legally competitive than conventional techniques and for underdeveloped countries and developing countries phytoremediation, thus becomes an ecological solution with great potential for the purpose of the rehabilitation of polluted areas.

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