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Chapter 6

Soil Contamination with Heavy Metals and Petroleum Derivates: Impact on Edaphic Fauna and Remediation Strategies

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Additional information is available at the end of the chapter

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1. Introduction

Soil is characterized as a complex and dynamic system. It is constituted by several layers that differ in relation to the physical, chemical, mineralogical and biological nature, which are influenced by the climate and activities of the living organisms. Besides contributing to the maintenance of all forms of life that occur in the terrestrial surface, soil plays an important role in protecting the groundwater acting as a collector filter of organic and inorganic residues, helping in sequestering possible toxic compounds [1].

During the last decades of the twentieth century there was an awareness of the importance of the soil as an environmental component and recognition of the need to maintain or improve its capacity to allow it to perform its various functions. At the same time there was a confirmation that the soil is not an inexhaustible resource and, if used improperly or poorly managed, its characteristics can be lost in a short period of time, with limited opportunities for regeneration [2].

However, the final disposal of potentially toxic residues in the soil has become a practical and inexpensive alternative and can cause alterations in the arthropod community [3, 4]. These species can present individual biological alterations (physiological, morphological and behavioural), which can be extrapolated to field studies in order to analyze ecological

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aspects, such as population dynamics and richness of diversity in the contaminated areas. Therefore, the gathering of biological studies, both laboratorial and field, combined with chemical analysis of the contaminants, provides a real scenario of the effects that the toxic substances can cause in the ecosystem.

Among the substances released in the soil it can be highlighted the petroleum derivatives and heavy metals [5]. In soils contaminated with petroleum and derivatives, some contaminants stand out compared to others, such as benzene, toluene, ethylbenzene and xylenes, known as BTEX, polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) [6, 7]. Pollution by heavy metals is derived from the anthropogenic activity, mainly associated to the industrial process and natural sources, such as volcanic eruptions [8].

Although researches involving soil quality are facing an important technologic challenge with several actions being taken in order to assess, correct and reduce the risks of contaminants in the soil, standardized monitoring combined with remediation strategies are still needed [5].

Thus, several researches aiming to remediate the effects of the soil contaminants have been carried out worldwide. Remediation of a contaminated area involves the application of one or more techniques aiming to remove or contain harmful substances in order to allow the reuse of the area with acceptable risk limits for human and environmental health. For this purpose, an ideal remediation process must remove all the contaminants of the soil or, at least, reduce the percentage of contamination of the environment to acceptable limits; should also avoid the migration of contaminants to other areas.

For the remediation of soils contaminated with petroleum and heavy metals, several physical, chemical and biological techniques have been developed for the removal or degradation *in situ* or *ex situ* of the pollutant [6, 9]. In this context, the chapter aims to provide a thorough revision of techniques for the removal or degradation of the pollutants as well as a discussion on the implementation of such techniques for the development of remediation strategies and policies.

2. Dynamic of pollutants in the soil

Geosphere, or terrestrial layer, is that part of the earth on which the human beings live and extract the maximum of its resources. Erstwhile it was believed that the earth had unlimited capacity to absorb the impacts of humankind. Currently, the geosphere is considered very fragile and vulnerable to injuries originating from anthropogenic activities. According to Manahan [10] the definition of pollutant can be described as the increase in the concentration of a certain substance to higher levels than that they occur naturally, arising from an external source, generally related to the human activity.

There is great difficulty in predicting the behaviour of a xenobiotic in the soil, since its composition is totally complex and heterogeneous. Therefore, the knowledge of the physico-

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chemical characteristics of the contaminant compounds and the environment is fundamental to predict its dynamic [11].

It should be noted that several soils have the capacity to assimilate and neutralize such pollutants, since chemical and biochemical phenomena are capable of attenuating the harmful nature of the pollutants. These phenomena include processes of oxi-reduction, hydrolysis, acid-base reactions, precipitation, adsorption and biochemical degradation. Some hazardous organic chemical products can be degraded to innocuous products on the soil and the heavy metals can be sorbed, immobilized or mineralized. In general, a lot of care should be taken in the elimination of the residues, rejects and other potentially hazardous materials to the soil, particularly where there is the possibility of contaminating the existing water.

When the contaminant reaches the soil, either on purpose or accidentally, it suffers the action of geochemical and biological phenomena and is distributed by the subsurface in the vaporized, residual or adsorbed phases, free phase and dissolved phase. The distribution of such phases will depend on their physico-chemical characteristics and also on the type of the soil [12]. Thus, the mobility of the contaminants and, consequently, their toxicity are directly related to the capacity of the soil in maintaining them retained in their solid phase, making them unavailable to be absorbed by plants, eroded and/or leachate [13]. Among the factors that determine the binding of contaminants to the soil there is the available surface area of the particles (m^2/g). Moreover, the electrical charges of the particles of the soil matrix also influence in the adsorption of the contaminants to the environment. It is noteworthy that in relation to their physico-chemical properties the contaminants are classified as Dense Non-Aqueous Phase Liquid (DNAPL), when the substance is more dense than the water and Light Non-Aqueous Phase Liquid (LNAPL), when it is less dense [14].

The main processes of interaction between the organic compounds or metals and the environment are the retention by adsorption, absorption or precipitation; biotic and abiotic transformations and transport by volatilization, leaching or runoff [15]. There are compounds highly resistant to degradation that can interact strongly in a reversible or irreversible way with the colloidal components of the soil. This process is called sorption, both for adsorption and absorption. Adsorption is characterized as an interfacial process while absorption differs for involving the penetration of the compound in the particles of the soil and can be accumulated inside the absorber system [11].

In general, the dynamic of the contaminants in the soil can be modelled by three mechanisms of mass transference, namely: advection, dispersion and attenuation.

a. *Advection* – it consists in the mechanism where the contaminants coincidentally follow the flow vectors and keep a direct relationship with the speed of percolation in the soil. It is the mechanism responsible for the formation and mobilization of the free phase of hydrocarbons.

b. *Dispersion* – Consists in the mechanism responsible for the decrease in the concentration of the contaminants in the fluid percolation and that can occur by two processes: hydro-

dynamic dispersion and molecular diffusion. Hydrodynamic dispersion occurs by the flow restriction in the pores of the soil that generates the reduction in the percolation velocity of the more viscous components while the molecular diffusion is, intrinsically, a phenomenon of dilution of the more soluble compounds, and is the main formation process of the dissolved phase, responsible for the greater mobility of the contaminants. In the case of emulsions, such as hydrocarbons, the dispersion can occur in a more complex mechanism, due to the phenomena of hysteresis (delay) of the entrainment of the contaminants, especially in the saturation fronts and capillary fringe. This process is associated to the formation of the adsorbed phase and also by the production of a fraction of emulsions that can compose the dissolved phase.

c. *Attenuation* – Consists in the reduction of contaminants transported by advection or dilution by chemical or physico-chemical reactions. Chemical attenuation is the more intense in soils with higher cation exchange capacity and acts reducing compounds in the free and adsorbed phase. Also in the list of reactions there are the bioconversion reactions, in which a part of the hydrocarbons is transformed or totally oxidized in organic acids. Chemical attenuation is more intense in the region with higher availability of oxygen.

Physico-chemical attenuation is responsible for the formation of the adsorbed phase and consists in the imprisonment of the contaminants that adhere to the grains of the soil, especially to the grumes of clay with higher activity. However, associated with the mechanisms of chemical attenuation, it is responsible for the formation of the dissolved phase (facilitated by the reduction of pH) [16].

3. Contamination of soil and its effects on the edaphic fauna

Soil ecosystem harbours an enormous biodiversity and is increasingly being recognized that this diversity is essential for the maintenance of the function of other ecosystems [17], since the activities of the invertebrates have significative effects in its organization and structure, dynamics of the organic matter and in the growth of plants [18]. Despite this importance, soil has become a practical and cheap alternative for the final disposal of several toxic residues, resulting in negative consequences [4].

Contaminants can be resistant to the decomposition processes and, therefore, can be accumulated in the soil [19]. Invertebrates easily become exposed to such contaminants, which can affect their ecological function [20] and influence indirectly the ecosystem and alter the ratio predator/prey and affect the complex food chain [21]. In order to evaluate the ecological effects of this contamination it is developed tests that aim to quantify the abundance, mortality and reproduction of the organisms exposed [20].

In this sense, the following topic will address the effects caused in the edaphic fauna due to the contamination of the soil by heavy metals and petroleum derivatives.

http://dx.doi.org/10.5772/52868

3.1. Petroleum and its derivatives

According to Leblond [22], it is expected the production of 95 million barrels of petroleum per day in order to meet the growing worldwide demand of this resource. Crude petroleum is a complex mixture constituted, mainly, by hydrocarbons, organic sulphur compounds, nitrogen and oxygen [23]. Although about 80% of the total production of crude petroleum is generated from terrestrial fields, few studies about its impact on the soil are available [24].

Studies on the toxicity of petroleum have shown that some species present higher sensitivity to these contaminants. Survival of earthworms (*Eisenia andrei* and *E. fetida*) and enchytraeids (*Enchytraeus crypticus*) can be reduced in soil containing crude petroleum [25, 26], while the abundance of Isopoda and Hymenoptera in areas contaminated with complex mixtures derived from refineries can be higher in relation to uncontaminated areas [27].

Among the petroleum derivatives, the Polycyclic Aromatic Hydrocarbons (PAH) have a prominent role. Chemically, they are aromatic compounds formed by two or more benzene rings, constituted exclusively by atoms of carbon and hydrogen, arranged in a linear, angular or grouped form [28], and are residues of combustion, petroleum refinery and other industrial processes of high temperature [29]. There are thousands of these substances in the environment, each one differing in the number and position of the aromatic ring [30], but only 16 substances cause environmental concern: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a, h)anthracene, phenanthrene, fuoranteno, fuoreno, indeno(1,2,3-cd)pyrene, naphthalene and pyrene [31].

Although van Brummelen et al. [19] asserted that the exposure of invertebrates to PAH accumulated in the soil can affect the ecological function of these organisms, little is known about their effects [32, 33]. However, it is known that terrestrial invertebrates do not have the ability to metabolize aromatic compounds, with exception of some species that have microorganisms associated to the intestine [34], which implies in a broader problem, since it generates the bioaccumulation in the organism, enhancing the possibility of contaminating their predators via the food chain [35].

A small review performed by Souza et al. [7] discusses the main ecotoxicological assays that can be applied in soils contaminated by petroleum hydrocarbons. In this review, the authors affirm that bioassays with invertebrates have been efficient, thanks to the important role that these animals play in the ecological processes of the soil, such as cycling and decomposition.

Studies using earthworms as bioindicator organisms of contamination of the soil by PAH showed that the impact in these organisms is limited. Both the survival and reproduction rates were not altered and the concentrations of these substances in the individuals were low, suggesting low absorption by them [36]. Schaub and Achazi [apud 36] observed that PAH did not influence the survival and growth of the earthworm *E. fetida* in the concentration of 100.8 mg/kg, but the reproduction was affected in the concentration of 1.008 mg/kg. Chrysene did not alter the survival of *E. fetida* in a study carried out by Bowmer [37].

The non-toxicity of PAH for earthworms can be explained by the fact that there is a mutual interference between them [38, 39]. Earthworms are responsible for assisting the elimination

of the PAH in the soil by improving the natural conditions of biodegradation, contributing to the increase of its oxygenation due to the intimate contact of the microorganisms present in their intestine with the soil [36].

In relation to Collembola, Sverdrup et al. [33] affirm that they are more sensitive to PAH when compared to other organisms, such as earthworms, being, therefore, good models of toxicity for this class of contaminants. To reach this conclusion, the authors tested 16 different PAH, from which eight affected the reproduction and survival rates of Collembola. Eom et al. [40] corroborate the fact that Collembola are more sensitive to PAH. Isopoda did not show to be more sensitive to contamination by PAH. The species *Oniscus asellus* presented a small alteration in the abundance after exposure to benzo(a)anthracene and no effect after exposure to benzo(a)pyrene. The species *Porcellio scaber* did not present alteration for any of the two substances [19].

PAH can also act indirectly on organisms and cause alterations in the populations, since the increase in the density of the soil due to their presence and their hydrophobic properties decrease the inhabitable space within the pores of the soil. Moreover, PAH can also act as fungicides, eliminating the source of food of some organisms [41].

Due to the reduced number of studies there is not a base to predict alterations in the community of invertebrates caused by contaminations of PAH. Studies with this focus does not seem to be a promising tool to assess the risks of this substance and the use of more sensitive biochemical markers (concentration of metabolites, damages in the DNA) are better strategies for this purpose [3].

In this sense, besides the traditional tests with Annelida and Collembola, studies with other terrestrial invertebrates have been developed to assess the quality of soils [42]. Diplopoda also make part of the edaphic fauna and are continuously exposed to the contaminants present in the soil. In these animals, histopathological markers have been applied [43-47].

Tissular alterations in the midgut and perivisceral fat body of the diplopod *Rhinocricus padbergi* were studied by Souza and Fontanetti [46] and Souza et al. [42], after exposure of these animals to a landfarming soil. According to the authors, the chemical analysis showed the presence of high concentrations of compounds such as PAH and metals, the authors also inferred that the histological and physiological alterations observed can be an attempt of defence of the animals exposed to this residue, in an attempt to eliminate and/or neutralize the assimilation of toxic residues [42].

3.2. Heavy metals

As a consequence of the technological development and global population growth, the agricultural and industrial activities have intensified, leading to a considerable increase of metals in the different compartments of the environment. Unlike organic pollutants, the toxicity of metals is intrinsic to their atomic structure and they cannot be transmuted/mineralized to a total innocuous form [48].

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Pollution by heavy metals in terrestrial ecosystems has been recognized as a serious environmental concern, due to their non-biodegradability and tendency to accumulate in plants and animal tissues [49]. The extreme sensitivity of the macrofauna to the conditions of the soil make them potential indicators of the disturbance occurred in this environment [50]. For studies of this nature, the most used organisms are nematodes, earthworms, Collembola [apud 51], as well as molluscs [49] and ants, despite the last two ones be quite resistant to this type of contamination [52].

Among the most common responses of these organisms to the contamination by heavy metals it can be highlighted the decrease in the diversity of species due to changes in the composition of the community that eliminate the most sensitive species [53, 54] and promote the tolerance of opportunistic species [55] (Syrek et al., 2006) or invasive species [56].

Despite the increase in the abundance, richness and/or uniformity is not commonly found, some studies reported these types of alterations with the increase of pollution by heavy metals. It can be cited the studies developed by Russell and Alberti [57] that observed that Protura present tolerance to heavy metals, since this group was the only one found in sites highly contaminated; by Nahmani and Lavelle [51] that also found that the abundance of some groups of arthropods, such as larvae of beetles of the subfamily Hoplinae and family Staphylinidae, was positively correlated with pollution by heavy metals; by Migliorini et al. [58] that verified increase in the abundance of Protura, Diplura and Collembola with increase in the pollution by metals; by Grzés [52] that presented clear evidence of the increase of the diversity of species of ants with the increase in the pollution by metals.

Although no direct explanation for these patterns has been proposed, some of the authors point out the importance of the interactions between fauna and soil, mainly related to decrease of predation and competition between the edaphic organisms [52]. For this reason, considering all the macrofauna communities as indicator seems logical, since they have a wider range of adaptive mechanisms than a single taxonomic group [51, 59].

Pollution by metals can still influence directly the communities by the alteration of the abiotic conditions such as temperature and humidity. If the pollution decreases the density of the vegetation, the temperature of the environment will increase and this will facilitate the increase in the diversity of thermophilic organisms [52]. According to the same author, pollution by metals can favour species with affinity to humidity by reducing the microbial activity, allowing an accumulation of organic matter [52].

4. Types of treatment of contaminated soils

Geochemical and biological processes that determine the mobilization and transformation of the compounds in the soil involve countless variables, making the remediation process a complex task. Thus, for the remediation be satisfactory and complies the environmental legislation, it is necessary to know the treatment technologies available, their advantages and disadvantages (table 1), cost-benefit relationships, applicability regarding the hydrogeology of the place and the nature of the contaminant [60].

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Solidification/stabilization	• Simple design • Cost-effective • Large soil volume can be treated • Very recommended for metals	• Does not promote the treatment of the contaminant, promotes only immobilization • Short-lived • Dependent on the soil characteristics and homogeneity of the mixture • Process hindered by the depth of the contaminant
Advanced Oxidative Processes (AOP)	• Cost-effective • Mineralization capacity • Recommended for soils with high permeability • Different reagents may be employed	• Mass transfer of the adsorbed phase to the aqueous phase • Risk of aquifer contamination by not recovered solvent • Limitations for large-scale application (*ex-situ* treatment) • The use of strong acids causes destruction of the basic structure of the soil
Advanced Oxidative Processes (AOP)	• *In situ* treatment • Cost-effective • Rapid process • Little or no waste is generated	• Lower efficiency for insoluble compounds • Susceptible to changes in pH • May be harmful to soil microorganisms
Thermal desorption or extraction with supercritical CO_2	• High efficiency for volatile compounds • Soil aeration can facilitate the bioremediation process • Rapid process • Low environmental impact	• Low efficiency for soils with low permeability • Not recommended in saturated areas • Treatment of the realeased vapors is required
Incineration	• High efficiency • Rapid process • Compounds mineralization • May be used where other processes are not effective	• High cost • Release of secondary compounds to the atmosphere • Periodic and rigorous monitoring are riquered • *In situ* treatment is not possible
Adsorption with clay	• Cost-effective • Simple design • Can be combined with other techniques	• Soil exchange is required • Limited by buffer capacity of the soil • Selectivity for specific ions
Electrokinetic	• High efficiency • *In situ* treatment	• Treatment time depends on the distance between the electrodes • pH change in areas near the electrode

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TECHNOLOGY	ADVANTAGES	DISADVANTAGES
	• May be combined with bioremedition techniques	• Cost depends on the contaminant concentration and soil • Lower efficiency in soils with low permeability

Table 1. Advantages and disadvantages in the use of different techniques in the remediation of soils contaminated by petroleum and heavy metals

According to Andrade et al. [6], the technique to be used depend on some factors, such as: physical, chemical and biological conditions of the contaminated site, concentration of the contaminants and time needed for the degradation/removal of the target compounds, according to the technique to be employed.

The main processes of interaction between the hydrocarbons or metals and the environment are retentions (adsorption, absorption or precipitation); biotic and abiotic transformations, transport by volatilization, leaching or runoff [15]. There are compounds highly resistant to degradation that can interact strongly in a reversible or irreversible way with the colloidal components of the soil. This process is called sorption, both for adsorption and absorption. Adsorption is characterized as an interfacial process while absorption differs for involving the penetration of the compound in the particles of the soil and can be accumulated inside the absorber system [11].

Since 1993, information of the Environmental Protection Agency (EPA) was considered to indicate the need for innovative technologies, such as remediation, to replace conventional processes. New technologies have as objective the treatment of organic compounds, however, few alternatives are available for the removal of metals in the soil, particularly *in situ*.

Among the existing remediation processes it can be highlighted the technologies of immobilization, destruction of the contaminants and separation. Immobilization technology consists in the creation of physical barriers to avoid the migration of the contaminants, such as processes of solidification/stabilization (encapsulation of the contaminants). The processes of destruction are based, mainly, on the use of high temperatures and chemical methods, such as incineration, chemical reduction, chemical oxidation, photolysis and bioremediation; and the separation consists in retaining, isolating or extracting the contaminants to a phase of easier management or to a more concentrated phase, reducing the volume of the material to be remediated or disposed, such as processes of thermal desorption, washing the soil, extraction by solvent and supercritical extraction [61, 62].

4.1. Solidification/stabilization

The process of solidification/stabilization, also known as immobilization, modifies the physico-chemical characteristics of the residue to contain the contaminants. Metals are commonly remediated by solidification *ex situ* by encapsulation and sometimes complexation.

The encapsulation technology has become an important alternative treatment for the disposal of hazardous residues in landfills and control of contaminated areas, since it provides an improvement of the physical and toxicological characteristics of the residue and/or soil, facilitating its management in a safe and effective form. Moreover, the cost of the encapsulation has been considered low in relation to other treatment techniques, fact that has stimulated the development of this technology in the last years. However, there is an increasing interest in more durable and safer solutions [63].

The frequently used agents for encapsulation are Portland cement and lime. In physical terms, the cement presents response in a smaller interval of time than lime, since its curing takes place in less time. Chemically, both act to alkalinize the environment, increasing the pH of the compound, decreasing the solubility of the contaminants, since it is known that the solubility is dependent on the pH [64]. Physically, it occurs the cementing of the particles, causing a decrease in the mobility of the contaminant within the soil. Therefore, the reduction in the mobility of the contaminant can be enhanced by the alkalinisation of the environment and also by the cementing effect of the particles.

After application of the encapsulation technique, some assays become necessary for analyzing the effectiveness of the method, which consist in chemical and physical analysis of the treated compound. Chemical analysis are performed based on leaching assays and chemical extraction. Physically, it is performed analysis of compressing, resistance to simple compression, permeability, durability, among others [63].

Another solidification technique involves the vitrification by the passage of an electric current between electrodes. This process results in the retention of solids and incorporation of metals in the vitrified method. This technology is being commercially evaluated and presents very promising results. Vitrification has been used for capturing mercury and other volatile metals such as lead and arsenic [65].

4.2. Washing and extraction by solvent and chemical oxidation

One technique of separation of organics in soils very used is the extraction by organic solvents. In these cases, the organic contaminant is extracted from the contaminated site and later destined to the destruction treatment. The process occurs by washing the soil using adequate solvents for each type of contaminant, such as detergents for oils or petroleum and chelators for metals. It has the disadvantage of being a process that requires specific machinery, demands specialized staff and, at the end of the process, generates great quantities of contaminated liquid residues, which must be adequately treated and disposed posteriorly [11].

Chemical oxidation or *In Situ Chemical Oxidation* (ISCO) has shown to be a promising technique for the remediation of soils contaminated by organic compounds [66]. This technique is based on the application of strong oxidant agents to degrade the organic. It has been applied both *in situ* and *ex situ*, and its application in the field is more appropriate.

ISCO also has its limitations, especially regarding the reactivity of the agent with the contaminant and mass transference between the adsorbed and aqueous phases, where generally

http://dx.doi.org/10.5772/52868

occurs the oxidation reaction [67]. The most used agents in ISCO processes are ozone (O_3), hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$). Each one has advantages and disadvantages and the application depends on the environment to be treated and the contaminant to be degraded [68].

4.3. Advanced Oxidative Processes (AOP)

The most effective processes in the destruction of organic pollutants are known as advanced oxidative processes (AOP). AOP are characterized by the generation of hydroxyl radicals (HO*), which presents high potential pattern of oxidation, superior to those of other oxidant species, such as O_3, H_2O_2 and chloride (Cl_2) [69], capable of reacting with practically all classes of organic and inorganic compounds. These processes are emerging as a promising alternative for the treatment of matrices contaminated with highly toxic and recalcitrant substances, leading them to total mineralization or formation of more biodegradable intermediates [70, 71].

Although there are more economical processes, not always the time needed to achieve the expected results allow their use, thus, AOP can be used when these limits of time and other logistics become hierarchically more important.

Fenton system is one of the most known advanced oxidative processes and consists in the combination of hydrogen peroxide and ferrous ions to form hydroxyl radicals. The oxidizing power of Fenton's reagent (H_2O_2/Fe^{2+}) is attributed to the hydroxyl radicals resulted from the catalytic decomposition of hydrogen peroxide in acid medium, whose general reaction is represented by:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^*OH$$

Hydroxyl radicals generated oxidize the organic compounds of the environment, generating intermediates that are attacked again by other hydroxyl radicals and can reach the complete mineralization (CO_2 and H_2O). This system has been widely studied in the oxidation of organic compounds of high toxicity.

The reagents that compose the Fenton system present advantages over the others because they are compounds relatively inexpensive and non-toxic, besides the reaction occurs at room temperature and pressure. It is known that the hydroxyl radical oxidize effectively organic compounds in aqueous phase, including the polychlorinated biphenyls (PCB) [72].

The efficiency of the chemical oxidation in soil is influenced, mainly, by factors such as concentration of iron, concentration of peroxide, presence of other organic compounds competitive by hydroxyl and pH [62]. Moreover, some researchers have observed a strong increase in the oxidant power of the Fenton reagent when combined with radiation UV or UV-visible, called Photo-Fenton. This technique has shown to be an extremely promising alternative, especially on tropical countries, like Brazil, where the incidence of sunlight is high practically during the entire year, configuring an important source of energy, hitherto unexplored [11].

4.4. Thermal desorption or extraction with supercritical CO_2

The most applied system of thermal desorption is the process of injecting steam water in the soil with a system of pumps and vacuum, i.e., it is installed in the area to be remediated a series of pipes from which will be injected in the soil steam water and other suction pipes. The steam at high temperature drags the contaminants, extracting them from the soil, which are then sucked by vacuum sites and sent to filters or condensers to receive appropriate treatment [66].

Extraction of compounds using supercritical fluid consists in making the extraction of the contaminants by passing a gas at high pressure (400 bar) and high temperature (150ºC) through the contaminated soil. In general, CO_2 is the fluid chosen due to its low toxicity and environmental acceptability and this extraction has shown to be very efficient for compounds with high solubility in CO_2, such as PAH, PCB, dioxins and organochlorine pesticides [11].

In the United States, an area with more than 170 tons of soil contaminated with benzene, arsenic, chromium and PAH was remediated using the process of thermal desorption [73].

4.5. Incineration

The use of heat to destroy toxic compounds is a very old practice. Incineration has been used for centuries to destroy or diminish the volume of domestic or agricultural residues that are unnecessary or undesirable. However, during the combustion process occurs the formation of undesirable by-products, such as dioxins and furans, highly toxic and carcinogenic. To avoid the formation of such compounds it is necessary to have strict control over the combustion conditions [74].

To remediate soils contaminated with PAH, this process is one of the most efficient and used, despite the high cost due to the need of soil excavation, transport and treatment with heat [75]. Although the treatments with high temperatures are effective in the treatment of organic residues, a serious problem occurs when the residue has metals, since a fraction of them will volatilize during the treatment and, after the gas cooling, they will condense on particles of metal [76].

4.6. Adsorption with clay

Clays have structures in layers of lamellae that consist on sheets of silicon oxide alternating with sheets of aluminium oxide. The sheets of silicon oxide are arranged in tetrahedra in which each atom of silicon is surrounded by four atoms of oxygen, some variations can present geometrical structure in form of octahedrons. Many clays contain large quantities of sodium, potassium, magnesium, calcium and iron and other metals. Clays can attract cations such as Ca_2^+, Mg_2^+, K^+, Na^+ and $NH4^+$, retaining them between their lamellar structure in order to avoid leaching by water, but maintain then available in the soil as nutrients for the plants [10].

http://dx.doi.org/10.5772/52868

Thus, heavy metals and other charged species are strongly attracted and adsorbed in the clay surfaces. Heavy metals have different sorption characteristics and the mechanisms depend on the adsorbents. The sorption mechanisms include complexation of the surface (adsorption) and ion exchange. Adsorbents show difference in the sequence of selectivity for different metals. One example is lead when compared to other metals, since it is highly attracted and adsorbed by several types of clay.

4.7. Electrokinetic

Electrokinetic remediation, also called electrokinetic processing of the soil, electromigration, electrokinetic decontamination or electrocorrection, can be used to extract metals and some types of organic residues, such as PAH, of saturated or unsaturated soils, sludges and sediments [66]. This technique consists on the application of a direct current of low intensity between the electrodes located in the soil. The materials used for the construction of the electrodes can be graphite, stainless steel and platinum. Electrolysis of the water (in the disperse electrolyte) produces ions H^+ in the anodes and ions OH^- in the cathodes, generating a localized change of pH, which leads to the desorption of the contaminated ions.

Some variations of this technique involve the direct extraction of metallic ions already in the metal form and the others involve the extraction of metallic ions using a posterior process of ion exchange resins. Electrokinetic remediation can be also used to delay or prevent the migration and/or diffusion of the contaminants, directing them to specific sites and diverting them from the freatic sheets.

Currently, the application of electrokinetic process has been considered promising, especially for the remediation of low permeability contaminated soils, where the electric field generated mobilizes electrically charged species, particles and ions in the soil by the processes of electromigration, electrophoresis and eletroosmosis [66]. For the migration process in the electrodes, the contaminants can be removed by reduction in the cathode, precipitation, pumping next to the electrode, or in a more complex form with ion exchange resins.

However, the electrokinetic process is limited by the solubility of the contaminant and by desorption of the contaminants in the surface of the soil. Heavy metals in their metallic state are not being sufficiently dissolved and separated from the samples of soil. The process is also not efficient when the concentration of the ions to be removed is low and the concentration of diverse ions is high. Moreover, factors such as heterogeneity and anomalies in the local surface (boulder, large quantities of iron or iron oxides, large rocks and gravel or materials such as shells) can reduce the efficiency of removal.

The cost of remediating soils contaminated by metals, using the electrokinetic technique is strongly influenced by the soil conductivity, since the consumption of energy is directly related to the conductivity of the soil between the electrodes. The electrokinetic treatment of the soils with high ion conductivity may not be feasible due to the high cost [63].

Another method that uses the electrokinetic technology is the electroacoustic decontamination of the soil. This technology combines the eletrokinetic with the sonic vibration. The properties of the liquid contaminant in the soil can be altered in order to increase the rate of

the contaminant removal by the application of a mechanical vibratory energy in the form of sonic or ultra-sonic energy. The elecroacoustic technology is technically feasible for the removal of inorganic species from the soil with clay (and partially effective for the removal of hydrocarbons) [63].

4.8. Bioremediation

According to Yeung et al. [77], biological processes are gaining increasing importance in the treatment of soils. To meet the challenges presented by environmental pollution, the objective of bioremediation (along with prevention and physical and chemical methods for remediation) is reduce the quantity and availability of hazardous chemical compounds and convert them into useful products and/or less innocuous [48]. However, biological processes, when compared to the conventional physical and chemical processes, are safer, less costly and less aggressive to the environment [78].

Bioremediation process can be defined as the use of microorganisms, such as bacteria, fungi, yeasts and algae or their enzymes to treat polluted areas or "return" them to their original condition [48, 79, 80]. In general, bioremediation is based on the biochemical degradation of contaminants [6, 81], resulting in the transformation in metabolites or their mineralization [78].

The types of treatment involved in the remediation process can be of two types: *ex situ*, in which there is an excavation and removal of the contaminated soil to another place and the *in situ*, where the treatment is performed in the local. The *in situ* bioremediation is the most worldwide used type of process regarding the place of treatment [6].

Briefly, the main techniques involved in the bioremediation process are:

a. *Bioattenuation* (natural process) - used to described the passive remediation of the soil, which involves several natural processes, such as biodegradation, volatilization, dispersion, dilution and adsorption of the contaminants, promoted in the sub-surface by native microorganisms [6, 80].

b. *Biostimulation* (or accelerated natural attenuation) - consists in the addition of nutrients and/or descompacting agents in the contaminated soil, increasing the population of endogenous or native microorganisms [42].

c. *Biomagnification* (or bioaugmentation) - characterized by the increase of the native microbiota by the inoculation of exogenous microorganisms (allochthonous) [6, 82, 83]. In this case, according to the literature, generally, the used microorganisms are bacteria, philamentous fungi and yeasts.

d. *Landfarming* - is an *ex situ* remediation technique, based on the placement of the contaminated soil in layers with at maximum 40 cm of thickness and their processing with agricultural machines [84].

e. *Biopiles* - is an *ex situ* technology of bioremediation, which involves the stacking of contaminated soils, which stimulates the aerobic microbial activity, accelerating the degradation of the pollutant by aeration, addition of nutrients and correction of humidity.

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f. *Composting* - technology that involves the addition of organic structuring agents in the contaminated soil/compounds, increasing the porosity and airflow in them. Such agents still serve as easy access source of carbon to the biomass growth. The energy released during the degradation of the organic matter result in temperature increase, which facilitates the action of different microbiological phases: mesophilic, thermophilic, cooling and maturation [85].

g. *Phytoremediation* - technique that uses plants as decontamination agent. Involves several mechanisms such as phytoextraction, phytostabilization, rhizofiltration, phytodegradation, phytostimulation, phytovolatilization, vegetative strains, artificial ponds and hydraulic barriers [86].

4.8.1. Bioremediation of sites contaminated by petroleum derivatives and heavy metals

Contaminations of soils with petroleum hydrocarbons have become a worldwide problem in the mid 80's [77]. The contamination sources by these compounds are related with exploration, production, storage, transport, distribution and final disposal of petroleum and their derivatives.

In the biological treatment of soils contaminated by petroleum, microorganisms, being bacteria the most studied, use hydrocarbons, major components of petroleum, as source of carbon and alternative energy in the production of biomass. This process involves the transformation of hydrocarbons into smaller unities and later incorporation as cellular material (biotransformation) or conversion to carbon dioxide (mineralization), resulting in the reduction of the concentration of the petroleum hydrocarbons [87].

There are, in the scientific literature, a considerable number of studies on bioremediation of soils contaminated by PAH, using different remediation methodologies such as treatment of the solid phase, landfarming/composting, phytoremediation, biostimulation among several others [85].

In the landfarming process, petroleum derivatives are removed by volatilization, biodegradation and absorption. The more volatile products, such as gasoline, are removed by volatilization during the aeration process and a small portion is degraded by the microorganism respiration. Derivatives such as diesel and kerosene have less volatile constituents than gasoline and, therefore, the biodegradation is more significative than volatilization. The heavier compounds, such as lubricating oil, are not volatile, suffering only biodegradation [88].

Composting has obtained success in the bioremediation of petroleum derivatives using different compounds, such as mushrooms [89], soot residues [90], green residues [91, 92], maple leaves and alfalfa [93] and horse manure [94]. Plants, by phytoremediation, have shown positive results in the degradation of PAH, since it stimulates the growth and microbial activity in the rhizosphere (interface soil/root) [95].

Besides the individuals use of these processes, it is possible to combine more than one technology in the bioremediaton of contaminated soils. According to Straube et al. [96], microorganisms naturally present in the soil that degrade PAH can have their degradation capacity

limited due to several environmental factors, such as low solubility and low bioavailability of PAH and limitation of nitrogen or other nutrient. Thus, it is possible to combine landfarming with biostimulation and bioaugmentation to increase the efficiency of the technique. In the bioremediation process by biopile it can be also employed procedures such as aeration, bioaugmentation, biostimulation and composting in order to increase the efficiency of the remediation of petroleum hydrocarbons [97].

Mohan et al. [85] and Megharaj et al. [80] presented a review on the main techniques used in the bioremediation of soils contaminated by organic pollutants. The different strategies of the bioremediation process have specific advantages and disadvantages (table 2), which, according to the same authors, need to be considered in several situations, since there are many factors that limit the efficiency of the microbial degradation of organic pollutants: bioavailability of the pollutant, low temperatures, anaerobic conditions, low levels of nutrients and co-substrates, presence of toxic substances and physiological potential of microorganisms.

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Landfarming	• Simple desing and implementation • Cost-effective • Large soil volumes can be treated • Favourable public opinion • Complete destruction of waste material	• Large treatment area is required • Risk of human pollutant exposure • Limited to removal of biodegradable pollutants
Phytoremediation	• Cost-effective • Easy to implement and operate • Environment-friendly • Favourable public opinion • Reduced pollutant exposure	• Slower than other methods • Soil properties, toxicity level and climate should allow plant growth • Limitations for large-scale application
Bioaugmentation	• Cost-effective • Increase the bioavailability of pollutants • Short treatment times	• Laboratory strains of microorganisms rarely grow in contaminated soil • The use of genetically modified organisms does not have public acceptance • Recent and under development • Possible environmental risk by introducing non-indigenous microorganisms
Biostimulation	• Improve the degradation potential of the inhabiting microbial population	• Dependent on the indigenous organisms

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TECHNOLOGY	ADVANTAGES	DISADVANTAGES
		• Inorganic nutrients that are injected may precipitate metals, swell clays, change redox potentials and conductivity
Bioattenuation	• Efficient and continuous process • Equipment are not required • Less impact on the environment	• Preliminary studies are required • Slow and unpredictable process • Periodic and rigorous monitoring are riquered • May be costly
Biopiles	• Rapid process	• *Ex situ* treatment • High cost • Other sites may be contaminated
Composting	• Cost-effective • Simple design • High efficiency	• Depending on the compound employed, there may be a small increase in contamination, pH, solubility and mobility of toxic elements • Poor public reception due to odour and insects

Table 2. Advantages and disadvantages in the use of different techniques in the bioremediation of soils contaminated by petroleum and heavy metals

To illustrate the difficulty and success/failure of the bioremediation of soils contaminated by petroleum and its derivatives, there are some studies performed in different parts of the world, which use different techniques of bioremediation. Bento et al. [98] assessed the efficiency of the natural attenuation, biostimulation and bioaugmentation in the degradation of TPH (Total Petroleum Hydrocarbons) in soils contaminated by diesel, in samples from California and Hong Kong. After 12 weeks of incubation, the authors observed that the three techniques employed show different effects in the degradation of light fractions (C_{12}-C_{23}) and heavy fractions (C_{23}-C_{40}) of TPH in the soil samples. However, the authors noted that the number of microorganisms that degrade diesel and the heterotrophic population were not influenced by the treatments, suggesting, therefore, that detailed studies on the characterization of the site are needed before deciding the adequate bioremediation method.

Haderlein et al. [93] studied the effects of composting or simple addition of manure in the soil, during the mineralization of pyrene and benzo[a]pyrene. It was reported that composting and addition of manure had no effect on the mineralization of benzo[a]pyrene. In contrast, the mineralization rate of pyrene increased dramatically with the amount of time that the soil was composted (more than 60% of mineralization after 20 days).

Bioremediation of metals face major obstacles in relation to the bioremediation of organic compounds, since metals introduced in the environment cannot be degraded. They per-

sist indefinitely and can cause pollution of water, air and soil, and the main strategies in the control of their contamination are the reduction of their bioavailability, mobility and toxicity [99].

The oxidation state, solubility and association of metals with other organic and inorganic molecules can vary, however, the microorganisms, as well higher organisms can play an important role in the bioremediation of the concentration of metals, so that they become less available and less hazardous [48].

Among the main methods involved in the remediation of environments contaminated by heavy metals it is included the phytoremediation [99] and the use of microorganisms [100].

In this context, phytoremediation of heavy metals present in the soil, also called phytoextraction, is the technique that uses the capacity of the plants to absorb the metals [101]. As a general rule, metals bioavailable for absorption by plants include Cd, Ni, Zn, As, Se and Cu. Metals moderately bioavailable are Co, Mn and Fe; while the least are Pb, Cr and U [apud 101]).

Phytoremediation process can be divided into three types: phytoextraction, phytostabilization and rhizofiltration. Phytoextraction uses species of hyperaccumulator plants to transport metals to soil and concentrate them into the roots or buds, which will be later collected; in the phytostabilization the plants are used to limit the mobility and bioavailability of metals in the soil by sorption, precipitation, complexation or reduction of the valences of metals; rhizofiltration uses roots of plants in order to absorb, concentrate and precipitate metals from residual waters, which can include soil leachates [102].

Microorganisms, frequently used in the bioremediation of organic pollutants, can be also used in the bioremediation of soils contaminated with metals by biosorption (process in which metals are absorbed and/or complexed in live or dead biomass), alterations in the redox state (transformations catalyzed by enzymes) [103, 104]), by biosurfactants [105], bioleaching (immobilization of metals by excretion of organic acids or methylation reactions), biomineralization (immobilization of metals by the formation of insoluble sulphides or polymeric complexes) and intracellular accumulation [apud 100].

Since metals cannot be biodegraded in CO_2 and water, microorganisms can only modify their speciation, converting them into non-toxic forms [105]. In order to ensure the efficiency of the bioremediation process, the microorganisms added in the contaminated site must have, besides enzymes of biodegradation, resistance to the metal target [101].

5. Current policies for soil remediation

Bredehoeft [106] suggested that the problem of the remediation of toxic substances would be present in the society for a long time and taking into consideration the policies and expenses of the period with the issue, it would exist until mid twenty first century. Fifteen years after this statement, management of contaminated soils and waters still continue to be a current

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environmental issue due to the great number of areas around the world that face this problem [107].

In the countries member of the EEA (European Environment Agency), according to estimates performed in 2007, about 250,000 areas need remediation. Potentially toxic activities occurred in about 3 million areas, which are under study to determine the need for remediation and, if this tendency continues, the number of areas requiring remediation will increase in 50% until 2025. In these countries, approximately 35% of the costs with remediation were public [108].

In the USA, the report of USEPA [109] state that, despite much has already been done in the last decades of the last century, a considerable amount of work is still needed. According to the report, about 300,000 areas will still need remediation in the next three decades. The estimate cost for the remediation of these areas is around 209 billion dollars, funded by the responsible for the contamination, private or public entity.

According to Fernandes et al. [110], the resources needed, both human and economic, to overcome the challenges in the implementation of remediation programs can be great. The resources destined to this purpose will not be the same in different countries. Some countries are more prepared to deal with the costs of the remediation programs in relation to others, since they have appropriate mechanisms (technical and economic) to implement projects on a large scale. In the countries where this is not possible, the existence of contaminated areas should be a livelong problem.

New remediation technologies are under development in the physical and/or chemical areas, however most of them are still in the initial phase of elaboration [111]. However, the trend of emerging technologies are focused in methods in which the contaminants can be destroyed or carefully removed with low risk of secondary contamination [112]. The methodologies traditionally used, physical and chemical, simply transfer the contaminants, creating other sources of contamination and not eliminating the problem [113].

According to Koenigsberg et al. [114] there is the intention to use tools of molecular biology of microorganisms in contaminated areas, which can and must influence the conception and management of bioremediation engineer and open new paradigms so that the closure of a contaminated site does not occur.

Due to this, in the last years, the bioremediation methodologies have a significative portion of the remediation market [112]. According to Singh et al. [115], bioremediation entered in a new era with the use of genetically modified bacteria, however its use is still limited due to the fact that environmental factors can interfere in the process, making the results unpredictable. A study performed by Liu et al. [116] using genetically modified bacteria showed that its use is a promising strategy in the bioremediation process of environments contaminated by arsenic. Other technologies of bioremediation in development include the use of protein engineering, metabolic engineering, transcriptome and proteomics [117, 118].

For the development of tests in field using genetically modified bacteria, the major obstacle is the environmental concern and political restrictions for the use of these organisms [113].

As most of the researches on this theme are still basic, there is a growing need for regulatory and cost protocols and, thus, transform this potential technology into reality [119].

6. Conclusion

Contamination of the soil by petroleum and heavy metals has shown to be one of the major environmental problems that the governments and researchers must solve in the next decades. Several studies available in the literature warn about the negative effects of these substances in the living organisms, mainly in terrestrial invertebrates, since they are in direct contact with the contamination. In order to avoid that this problem become more serious, several remediation technologies have been elaborated and improved. Physical and chemical techniques are very used, however bioremediation, as it is ecologically correct, has gained great prominence, both in the remediation of petroleum and heavy metals.

Soil remediation standards are based on the protection of human health and on the protection of the ecosystem. Critical values for concentration in the soil are calculated based on human toxicology and others based on ecotoxicology. The most critical value is retained as soil remediation standard. The methodology for site specific risk assessment is based on the approach followed to derive soil remediation standards. A generic approach is followed for the derivation of soil remediation standards, while for site-specific risk assessments certain parameters, such as soil properties, can be evaluated.

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