Phytoremediation of contaminated areas by organochlorines: a review.

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Abstract. All over the planet, there are many contaminated areas, which has become a highly significant environmental problem due to the toxic effects produced, affecting the entire ecosystem and the surrounding life, including human beings. One of the forms of contamination found is by organochlorines, which comprise among others the Persistent Organic Pollutants (POPs), compounds that represent a great threat due to their lipophilic character, causing the phenomena of bioaccumulation and biomagnification. Phytoremediation, which involves the use of plants to remove pollutants from the soil, emerges as a very promising technique because plants can absorb and metabolize these toxic compounds, transforming them into less harmful or even inert forms. To better understand how phytoremediation can be applied in the remediation of organochlorines, a literature review was conducted, evaluating the application methods, advantages, disadvantages, and associated costs, as well as the main species recommended for chemical groups such as hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs). Based on these data, it has been found that phytoremediation is ideal for the remediation of organochlorine compounds, being relatively inexpensive and non-invasive, which does not cause damage to soil and does not require large amounts of energy. Through it, it is possible to plan and implement more effective and tailored strategies for specific contaminated areas. It is hoped that this study will provide valuable information for researchers and professionals working in the field of environmental remediation, encouraging production of new studies on the subject, especially regarding the search for native species, and for the public in general, increasing awareness about the importance of protecting the environment.

Keywords. contamination, phytoremediation, pesticides, organochlorines, remediation.

1. Introduction

Organochlorines were the first pesticides synthesized and widely used in agriculture and disease vector control between the 1940s and 1960s. Although they are an important aspect of modern agriculture, their excessive use results in damage to farmland and causes severe pollution, being dispersed through soil, water and air [1]. It was soon discovered that substances classified as Persistent Organic Pollutants (POPs) had an extremely toxic character because of the high chemical stability, accumulating easily in plants and animals and being incorporated into the food chain [2]. From 1960 to 2019, more than 17 million deaths have been reported to occur as a result of pesticide poisoning [3].

Once the risks to health and to the ecosystem were confirmed, the 12th Stockholm Convention began to regulate them, in which organochlorine pesticides were proposed to be controlled as persistent organic pollutants. The treaty also determined that governments should promote better technologies and prevent the development of new POPs, defining as the ultimate goal their total elimination [4].

Some methods have already been developed to perform the removal of these contaminants from soil, such as incineration or soil excavation and transfer to landfills, but these technologies consume energy and water, generate residual byproducts and other types of pollution. In addition, many techniques are expensive and result in physical, chemical, and/or biological alteration of the site [5]. In contrast, one of the most promising technologies is phytoremediation, using a plant's innate abilities to tolerate and accumulate toxic contaminants [6]. Phytoremediation is increasingly considered as an alternative to conventional remediation methods and has the advantages of being cost-effective, environmentally friendly and less disruptive to the soil [7].

There are still few studies regarding the identification of plants that have the potential of phytoremediation, which are necessary to survey species with this potential, as well as to diagnose pollutants that can be removed or immobilized in the soil, improving more this technology [8].

Thus, this research aims to survey the main characteristics and threats of organochlorine pesticides and how the phytoremediation technique can be applied to their remediation, identifying the most commonly used species and their associated efficiency and cost.

2. Research Methods

Bibliographic searches were conducted in Google Scholar and Scopus databases, using the keywords of the article and their synonyms, combined with connectors such as OR, AND and "". As an example, for the theme phytoremediation, more than 227,000 results are found in Google Scholar and 19,900 in Scopus, which also indicated statistics such as the main authors and countries with more publications, being China, India, US, Italy, Spain, Pakistan and Brazil, respectively. Combining the words phytoremediation and organochlorine, 5,710 results were found in Google Scholar and 626 in Scopus, 322 of which were published in the last five years. In other words, the more combinations and filters are used, the more refined the result becomes.

Based on these parameters, the articles were filtered and those with greater relevance were used in this study.

3. Results and discussion

3.1 Organochlorines

Organochlorines are organic compounds in which at least one hydrogen atom is replaced by chlorine, covalently bonded. They were the first synthetic pesticides, widely used in agriculture and in disease vector control, due to their low cost and high efficiency. Among the most known chemical classes are hexachlorobenzene (HCH), pentachlorophenol (PCP), dichlorodiphenyltrichloroethane (DDT) and biphenyl polychloride (PCB), compounds that are also classified as Persistent Organic Pollutants (POPs), which are liposoluble organic compounds resistant to environmental degradation [9].

Only in 1970 was their polluting capacity evidenced, revealing the highly toxic potential of POPs. In tropical agroecosystems, characterized by high temperatures and heavy rainfall, semivolatile organic compounds are rapidly dissipated, so they can travel in the atmosphere and be deposited thousands of kilometers away [9][10]. Residues have been widely identified and reported worldwide, even in Antarctica and the Arctic Zone [4].

One of its most relevant properties is the lipophilic character, which allows the substance to settle in the tissues of living beings through fat, which makes it neither biodegradable nor metabolized by organisms, generating the phenomena of bioaccumulation and biomagnification [11]. Bioaccumulation occurs at the individual trophic level and represents the increase in concentration of the substance over time, while biomagnification occurs between different levels of the food chain, both schematized in Fig. 1.

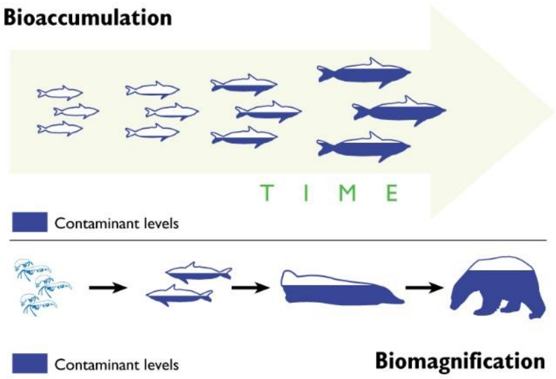

Fig. 1 - Bioaccumulation and Biomagnification.

Humans are mainly exposed to POPs through food, water and air, and they also accumulate them in their adipose tissue. Under some circumstances, human exposure to POPs, even at low levels, can result in increased cancer risk, reproductive disorders, alterations of the immune system, neurotoxicity, endocrine disruption, genotoxicity, and birth defects [9].

Considering the eminent danger of the substance, its use has been banned in several countries. In 1995, the Governing Council of the United Nations Environment Programme recognized only 12 Persistent Organic Pollutants (POPs) due to their adverse effects on the environment and human health. A global ban on these toxic compounds was placed, requiring that steps be taken to eliminate or reduce the release of these POPs into the environment. Eight of these POPs were insecticides (endrin, heptachlor, mirex, toxaphene, aldrin, chlordane, dieldrin, and DDT), one was a fungicide (hexachlorobencene, HCB), and the rest were dioxins (some of them byproducts in pesticide production), PCBs, and PCDFs [1]. However, after a ban, measures and procedures to properly dispose of these products are still lacking.

3.2 Remediation

Remediation is the technique responsible for reducing the contaminants in the soil at safe levels, preventing the spread of harmful substances to the environment. The management of contaminated areas is extremely important, since it is necessary to identify, diagnose, and intervene in the area, so that remediation is feasible and the chosen technique can be successfully implemented. The selection of appropriate technologies depends on several factors, such as site characteristics and contamination (punctual or diffuse), concentration and type of pesticides to be removed, and the end use of the contaminated media [1].

To reduce, eliminate, isolate or stabilize a pesticide, several physical, chemical and biological methods have been developed [12]. Classical remediation technologies for contaminated areas with POPs include physicochemical methods such as incineration, burning, land filling, composting and chemical amendments, but as these methods are mainly ex situ, there is a high cost associated with excavation and transportation, and since a significant part of the soil is removed, these methods are invasive and destructive to the overall ecosystem. Consequently, over the last decades there has been increasing interest for in situ remediation technologies, since they are noninvasive, low-cost, low-maintenance and often solar-driven [13].

3.3 Phytoremediation

Phytoremediation is a biological treatment that uses vegetation and enzymes capable of modifying the dynamics of contaminants, reducing their concentrations and making them less available in the ecosystem. This process is accomplished through water, where pollutants are drained away through the same transpiration mechanism used to move nutrients from the soil to the site of photosynthesis [14].

It is defined as the use of plants to extract, degrade or immobilize contaminants, and there are five main mechanisms that occur in phytoremediation, being these the phytostabilization, phytoextraction, phytovolatilization, phytodegradation and rhizodegradation [15](Fig. 2).

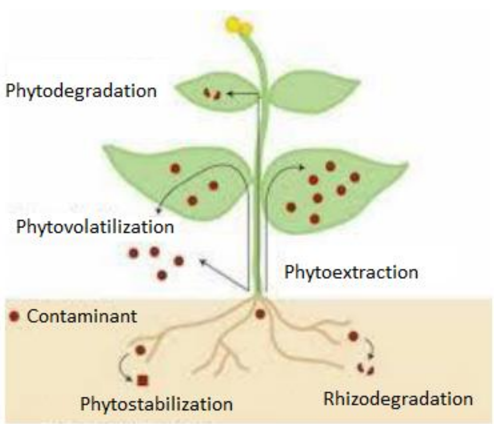

Fig. 2 – Phytoremediation mechanisms.

Chemical phytostabilization is responsible for stabilizing the contaminant, preventing the contaminant from migrating to soil and groundwater by converting it to inert, more stable and/or less bioavailable forms through substances that are released by the roots. These substances are also effective in degrading contaminants and stimulating microorganisms (phytostimulation), creating a mutualistic relationship [16]. Some are translocated from roots to aboveground biomass (phytoextraction)[17].

Plants are also capable of metabolizing organic contaminants, by the phytodegradation. Metabolic processes can be divided into transformation, conjugation, and compartmentalization, and the degradation of organic compounds can take place inside the plant or within the rhizosphere [17] [18].

Rhizodegradation is a naturally occurring process, but it can be enhanced by adding pesticide-degrading bacteria through inoculation. Plant root systems can excrete enzymes that degrade pesticides in the rhizosphere [19].

Phytovolatalization is a technique that uses the metabolic capacity of plants and rhizospheric-related microorganisms to convert pollutants into volatile molecules that are released into the atmosphe [14].

Several studies point to the phytoremediation of contaminated soils as promising. Several species are described as capable of tolerating high concentrations of contaminants and developing mechanisms of retention, immobilization and degradation, either by exclusive action of their enzymes or by joint action with microorganisms [20]. In 2013, a research was conducted that allowed the evaluation of tolerance by the germination capacity and the ecophysiological performance of seven plant species, and the species Brachiaria decumbens, Schinus molle and Schinus terebentifolius were able to absorb HCH [20]. The degradation of 98% of HCH isomers by Kochia sp, through microbial activity present in its root, was also evidenced, and the results showed that in vegetated soils the concentration of HCH reduced four to five times more in soils adjacent to the rhizosphere when compared to soils without plants [21].

In Tab. 1, the main species found and the contaminants on which they have proven effective for remediation are listed.

Tab. 1 - Recommended species for phytoremediation of organochlorines.

Species	Contaminant	Reference
Brachiaria decumbens	HCH	[20]
Corymbia citriodora	TCB, PCP, DDE, DDD, DDT	[22]
Eichhornia	PCP, PCE, TCE	[16]

crassipes		
Eucalyptus grandis	TCB, PCP, DDE, DDT, HCH	[22]
Hodeum vulgare	HCB, PCBs, PCB, TCB	[16]
Kochia sp	HCH	[21]
Leucaena	TCE	[23]
Medicago sativa L	PCBs	[24] [25]
Miscanthus sinensis	DDT, DDE	[26]
Paulownia tomentosa	HCH, HCB	[27]
Ricinus communis L.	PCBs	[28]
Schinus molle	HCH	[20]
Schinus terebentifolius	HCH	[20]
Typha latifolia	HCB	[29]
Urtica dioica	PCBs	[30]

Among the advantages listed in the respective studies, the low cost and efficiency stand out, when compared to other techniques, as shown in Table 2 [31]. In addition, the plants help in the control of the erosive, wind and hydric process, protecting the soil and avoiding the dispersion of the contaminant, especially with respect to groundwater [16].

Tab. 2 - Comparison of different soil remediation technologies.

Technology	Removal efficiency	Cost (US)/m^3
Soil Washing	66%	In-situ: $50-80
		Ex-situ: $150-200
Thermal Desorption	99.3%	In-situ: $834
Biodegradation	55-99%	In-situ: $50-100
		Ex-situ: $150-500
Phytoremediation	70-80%	In-situ: $12-60
Vermiremediation	35%	In-situ: $140

Its main disadvantages are with respect to time, which can be longer than usual and varies according to the concentration and depth of the contaminant. In addition, high concentrations of contaminants tend to inhibit plant growth due to oxidative stress and lack of nutrients, which will limit the rate of phytoremediation [19]. If the parent compound is only partially degraded, products might appear that are more toxic and persistent than the original contaminant [14].

In addition to contaminant concentration, factors such as root structure, soil structure, organic composition of the soil, soil pH, moisture content and microbial activity often exhibit spatial variability at a given site, and can change over time, and this can affect plant and microbial growth,and therefore, remediation potential [19].

Their effectiveness varies according to the degree of contamination and the substances present in the soil, and may take weeks, months or even years. Because of this, other strategies combined with phytoremediation can be used, such as the genetic improvement of plants with phytoremediation potential and the combination with microorganisms and fungi that degrade the substance, acting as biocontrol agents and facilitate the growth and development of plants [16] [32].

An important category of microorganisms that can form symbiotic relations with plants and in the same time to estimulate the growth of plants under the action of pollutants are represented by fungi that form mycorrhizae (arbuscular mycorrhizae (AM) and ectomycorrhizae (ECM)), and bacteria that promote plant growth (PGPB). PGPB have the ability to produce substance capable to fix the nitrogen, solubilize the phosphate and mineralize the organic compounds that improve the plant growth. Furthermore, PGPB can reduce the oxidative stress caused by the presence of pollutants, by improving the oxidative enzyme systems and increasing the bioavailability of pollutants, which finally intensify the accumulation of pollutants in plants [32].

4. Conclusions

Based on the literature survey conducted, the phytoremediation technique is a promising alternative for the treatment of contaminated areas, which can be recovered in a less aggressive and efficient way, with low cost and simplicity in execution. Further studies on the subject are still needed, especially regarding the cataloging of new potential species, focusing on native species of each biome, which are more ecologically safe and can be used for ecological restoration, which is more beneficial to the environment.

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