Bioremediation

Subjects: Environmental Sciences
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Bioremediation can reduce pesticide contamination of agricultural soils by biodegradation processes via the metabolic activities of microorganisms. It is an efficient, cost-effective, and environment-friendly treatment.

pesticides bioremediation agricultural soil environmental pollution sustainable agriculture toxicity health effects

1. Introduction

Soil pollution is a worldwide problem that draws its origins from anthropologic and natural sources. Urbanization, industrialization, and food-demand increases have required the use of compounds, substances, and chemical agents, which, over the years, have brought on the dispersion and accumulation of pollutants in the environment. The common pollutants present in the soil are heavy metals, polycyclic aromatic hydrocarbons (PAHs), or pesticides [1].

Pesticides are chemical compounds used to eliminate pests. They are chemical or biological agents, that weaken, incapacitate, and kill pests. Based on the types of targeted pests, the pesticides can be divided into several groups, namely insecticides, herbicides, rodenticides, bactericides, fungicides, and larvicides.

During the 19th and 20th centuries, the extracts from plants, namely pyrethrins, were used as insecticides, fungicides, and herbicides. The increase in pesticide use happened with synthetic chemistry during the 1930s. In this period, inorganic chemicals such as arsenic and sulfur compounds were applied for crop protection. The arsenic poison was fatal to insects, while the sulfur was used as a fungicide. At the beginning of the Second World War, numerous pesticides were synthesized, mainly organic chemicals, such as dichlorodiphenyltrichloroethane (DDT), aldrin, and dieldrin used as insecticides, while 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) were used as herbicides [2].

After 1945, there was a rapid development of the agrochemical field, characterized by the introduction of many insecticides, fungicides, herbicides, and other chemicals, to control pests and ensure the yields of agricultural production. Moreover, pesticides are applied in aquaculture, horticulture, and for various general household applications. They are also used to control vector-borne diseases (e.g., malaria and dengue) [3].

From 1990 to 2018, there have been registered amounts of used pesticides by all countries in the world, especially in Asia and America. The world average quantity has increased from 1.55 $kg \cdot ha^{-1}$ in 1990 to 2.63 $kg \cdot ha^{-1}$ in 2018, as shown in **Figure 1**. Looking at the types, fungicides and bactericides are used more than the others (**Figure 2**).

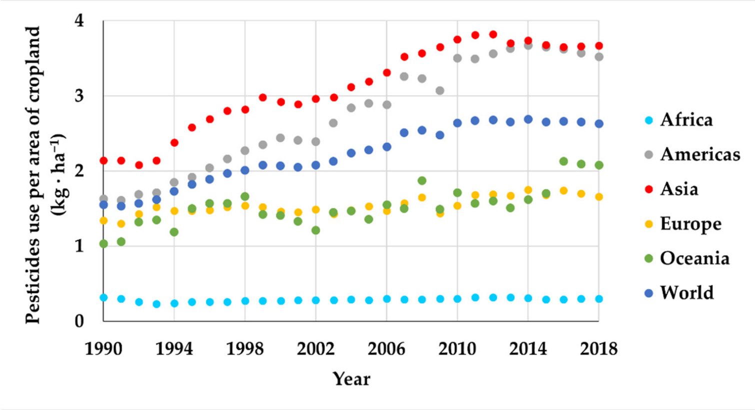

Figure 1. Pesticides use per area of cropland (data from [4]).

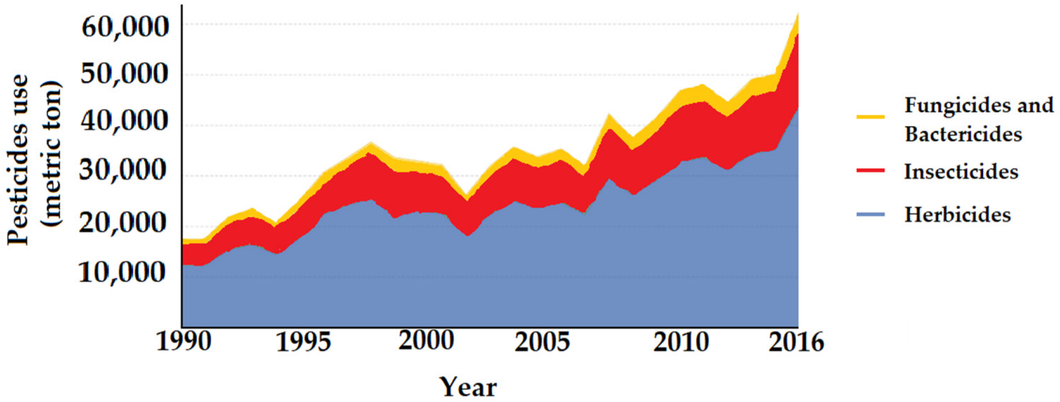

Figure 2. Pesticides use from 1990 to 2016 (data from [4]).

There has been no decrease even over the years, and directives have been implemented in many countries around the world to reduce the use of pesticides, for example, the Regulation (EC) 1107/2009 [5] of the European Union or the Stockholm Convention [6], which focuses on eliminating or reducing of persistent organic pollutants (POPs). To this purpose, the governments have to take measures to eliminate or reduce the release of POPs into the environment.

When pesticides are used, a part of them remains in the soil, and the accumulation affects the microorganisms living there. Human exposure can occur through the ingestion of pesticide-contaminated water and food, the inhalation of pesticide-contaminated air, and directly from occupational, agricultural, and household use. The pesticides can enter the human body by dermal, oral, eye, and respiratory pathways [7]. The toxicity of pesticides depends on the electronic properties and the structure of the molecule, dosage, and exposure times [8][9].

For these reasons, the residual pesticide concentration present in the soil must be reduced, and effective remediation techniques must be used to do this. An ecofriendly, cost-effective, rather efficient method is bioremediation, which is an alternative to more expensive and toxic approaches, such as chemical and physical methods. In biodegradation, the removal can be achieved by exploiting the microbial activity of microorganisms.

The microorganisms, primarily bacteria [10], or fungi [11] transform pesticides into less complex compounds, CO_2, water, oxides, or mineral salts, which can be used as carbon, mineral, and energy source. In these reactions, the enzymes have an important role since they act as catalysts [12].

Several techniques are available for the biodegradation of pesticides, which could develop in aerobic or anaerobic conditions based on types of microorganisms. Moreover, the bioremediation techniques can be divided into three categories depending on where the remediation treatment is done, namely in situ, ex situ, or on-site.

In the in situ approach, the treatment is involved in the contaminated zone, and usually, the process is aerobic. The main in situ techniques are natural attenuation, bioaugmentation, biostimulation, bioventing, and biosparging. In the ex situ methods, the contaminated soil is removed from polluted sites and transported to other places for treatment. Bioreactors, composting, landfarming, and biopiles are ex situ treatments. The on-site approach consists of the treatment of polluted soil on the surrounding site, to say the soil is removed from its original position but cleaned up in the neighborhood without any impact due to its transport.

In the literature, several reviews on pesticides have been published in the past years. Each of them is mainly focused on one topic. However, by this approach, the knowledge of the pesticide sector and its problems is lacking. **Table 1** reports a shortlist of these publications.

Table 1. Reviews on pesticides.

Topic	References
Pesticide diffusion in the environment	[13][14]
Toxic effects on living organisms	[13][15][16]
Legislation	[14]
Physical techniques for pesticide degradation	[17][18]
Chemical techniques for pesticide degradation	[16][17][18]
Biological techniques for pesticide degradation	[17][18][19][20][21][22]
Microorganisms capable of degrading pesticides	[13][19][21][22][23]
Enzymatic degradation	[24]
Economic analysis	[17]
Degradation of organochlorine pesticides	[14][16]
Degradation of herbicides.	[13]
Monitoring of pesticide clean-up	[20]

2. Biological Techniques for Pesticide Removal

Bioremediation can reduce pesticide contamination of agricultural soils by biodegradation processes via the metabolic activities of microorganisms.

During the bioremediation processes, the microorganisms use the pesticides as cosubstrates in their metabolic reactions together with other nutrients, thus eliminating them from the environment. The efficiency of these processes depends on the characteristics of pesticides, such as their distribution, their bioavailability, and their persistence in soil. It is necessary to promote the availability of pesticides to microorganisms: this is negatively affected by the adhesion of pesticides to soil particles and their low water solubility [25]. Moreover, the soil characteristics and the environmental conditions (pH, water content, microbial diversity, and temperature) influence the bioremediation efficacy.

2.1. Mechanisms of Microbial Degradation

During biodegradation processes, pesticides are transformed into degradation products or completely mineralized by microorganisms. A key role in the biotransformation mechanisms is carried out by enzymes, such as hydrolases, peroxidases, and oxygenases, that influence and catalyze the biochemical reactions.

The degradation process of pesticides can be divided into three phases, which can be summarized in:

- Phase 1: Pesticides are transformed into more water-soluble and less toxic products through oxidation, reduction, or hydrolysis reactions.
- Phase 2: The Phase-1 products are converted into sugars and amino acids, which have higher water solubility and lower toxicity.
- Phase 3: Conversion of the Phase-2 metabolites into less toxic secondary conjugates.

The microorganisms involved in the degradation process are bacteria or fungi, which may generate intra- or extra-cellular enzymes.

The degradation time is a relevant parameter to be assessed when a bioremediation activity is planned. It is typically interpreted by the first-order model [26], which depends on the pollutant concentration at the beginning and end of the process. This approach has limits because several parameters condition the process (microbial activity, temperature, water content, availability, and leaching of pesticide in the soil [27]).

2.2. Application of Microbial Remediation

The bioremediation techniques may be carried out in situ, ex situ, or on-site.

In the in situ approach, the treatment is carried out in the contaminated zone, and typically the process is aerobic. For this, it is necessary to provide oxygen to the soil. The main in situ techniques are:

- Natural attenuation, which exploits the microflora present in the polluted soil.
- Biostimulation, where the amounts and kind of nutrients to stimulate and promote the growth of indigenous microorganisms are optimized.
- Bioaugmentation, which is the addition of microbial strains or enzymes into the polluted soils.
- Bioventing, where oxygen is fed through unsaturated soil zones to stimulate the growth of indigenous microorganisms capable of degrading the contaminants.
- Biosparging, based on the injection of air under pressure into the saturated soil zone to increase the oxygen concentration and stimulate the microorganisms to degrade the pollutant.

These methods are very effective and cheap. Their main advantage is that the polluted soil is not moved.

Vice versa, in ex situ techniques, the contaminated soil is removed from polluted sites and transported to the site where the clean-up will occur. The main techniques are:

- Bioreactors, which treat the contaminated soil with wastewater to obtain a slurry and promote the microbial reactions capable of removing the pollutants.
- Composting, where the contaminated soil is mixed with amendments to promote the aerobic degradation of the pesticides. Landfarming and biopiles are included in this technique.

In on-site methods, the soil is removed and processed in the area close to the polluted site. For example, the landfarming treatment can also be carried our on-site, reducing the operation cost comparing to the ex situ approach.

In all bioremediation processes, nutrients, oxygen, pH, water content, and temperature must be controlled to maximize removal efficiency.

2.3. In-Field Applications

At present, few studies report information on real case studies.

Table 2 summarizes some examples. Unfortunately, the findings and results of large-scale remediation are usually neither published nor widely publicized, limiting the knowledge of experiences on real cases. A similar situation occurs for the costs of the clean-up.

Table 2. Some examples of case studies.

Bioremediation Technique	Pesticides	Description	References
Landfarming	Hexachlorocyclohexane (HCH) isomers (insecticides)	Contaminated soil with HCH isomers (>5000 $mg \cdot kg^{-1}$) derived from lindane production was studied in the field for 11 months, setting up two plots (each 2 m × 10 m). The α- and γ-HCH isomers were decreased by 89 and 82% of the initial concentration, respectively. The concentration of the most persistent β-isomer remained essentially unaffected.	[28]
Bioaugmentation	Myclobutanil, tetraconazole, and flusilazole.	Experimental tests were conducted on vineyard plots. In the crops, an agricultural formulation of pesticides by foliar spray was applied. After one h of pesticide application, vines were sprayed with a suspension of four *Bacillus* strains. DR-39, CS-126, TL-171, and TS-204 were tested. Residue analysis of field samples showed 87.4 and >99% degradation of myclobutanil and tetraconazole, respectively, by the strain DR-39, and 90.8% degradation of flusilazole by the strain CS-126 after 15−20 days of treatment.	[29]
Bioaugmentation	DDT	The bioremediation process was studied in 12 experimental plots, including greenhouse and open field soils. Each plot (area of 6 m^2) was inoculated with *Stenotrophomonas* sp. DDT-1 supplemented with 2% yeast powder. The results have shown that this microorganism is efficient for DDT degradation and does not adversely affect soil microbial activity.	[30]
Biostimulation	Organochlorine pesticides: toxaphene; DDT; DDE; DDD; endosulfan II; γ-chlordane; α-chlordane; dieldrin.	The Borello Property is a 14 acre area treated with soil amendment to help the indigenous bacteria to metabolize the pesticides. For the analysis, the area was divided into zones and in each of them, the soil samples were collected from four soil depths (0.5, 1, 1.5, and 2 ft). At the end of the test, OCPs were not detected; toxaphene, DDT, and DDE were detected in a single sample; dieldrin was detected in five samples at concentrations ranging from 1.2 to 1.8 $\mu g \cdot kg^{-1}$.	[31]

Bioremediation Technique	Pesticides	Description	References
Biostimulation	Organochlorine pesticides: toxaphene; DDT; DDE; DDD; endosulfan II; γ-chlordane; α-chlordane; dieldrin.	The Mantegani Property is a 0.8 acre area treated with soil amendment to help the indigenous bacteria to metabolize the pesticides. High concentrations of DDT and dieldrin were present. After treatment, DDT was degraded by 97% and dieldrin by 73%, while the concentrations of other OCPs were below their preliminary remediation goals.	[31]

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Soil bioremediation for their removal can be carried out exploiting either specific or indigenous microorganisms (bacteria and fungi), or enzymatic degradation.

While at a laboratory scale, many findings on soil bioremediation are available in the literature, few data on real-scale activities can be found. Unfortunately, this is mainly due to the poor cooperation among research laboratories, local authorities imposing a given soil clean-up, and companies involved in the sector of bioremediation in soils polluted with pesticides.

It would be beneficial that more and more this cooperation becomes united, to disseminate the experiences and results. Moreover, the cost data are lacking, too.

As for other pollutants, when required, the pesticide removal must take into account the chemical and toxicological characteristics of the compounds, without disregarding the national legislation. To this purpose, it must be outlined that several countries are still lacking in legislative acts, and this is the main drawback when polluted areas must be remediated.

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