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SOIL PESTICIDES AND THEIR MICROBIAL BIODEGRADATION FOR SUSTAINABLE AGRICULTURE : A REVIEW

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ABSTRACT:

Soil pollution is a global issue stemming from anthropogenic and natural sources. Pesticides are significant pollutants in intensive agriculture systems. Due to their frequent application and durability, certain pesticides may build in soil or leach into nearby water bodies. Pesticides are chemical substances utilized to eradicate pests, a characteristic leveraged to safeguard crops from undesirable vegetation. Pesticides are employed to safeguard and enhance the yield and quality of agricultural produce. The overuse of these compounds and their environmental persistence have created significant issues, specifically soil and water pollution, and to a lesser degree, air pollution, resulting in detrimental consequences on the ecosystem and the food chain. Soil pollution frequently exhibits pesticide residue concentrations that exceed regulatory limits. In such instances, the objective is to diminish the concentration of toxic pollutants and achieve agricultural soils conducive to cultivating environmentally sustainable crops. The metabolic processes of indigenous microorganisms can be utilized for degradation, as bioremediation is an environmentally acceptable, cost-effective, and relatively efficient procedure in comparison to physical and chemical alternatives. Various biodegradation methods exist, utilizing bacterial, fungal, or enzymatic processes. The efficacy of these mechanisms in pollutant removal is contingent upon the nature of the pollutant and the chemical and physical characteristics of the soil. The control of pesticide usage is closely linked to their environmental effects. Currently, every nation can implement legislation to limit pesticide usage, ban the most detrimental substances, and establish permissible soil concentrations. This variety indicates that each country possesses a distinct view of the toxicity of these substances, resulting in varying market prices for the cultivated crops. This research seeks to elucidate the bioremediation of soils contaminated with commercial pesticides, focusing on the characteristics of the predominant and most utilized pesticides, including their classification and toxicity, as well as relevant global legislative components.

KEYWORDS:

PESTICIDES, BIOREMEDIATION, AGRICULTURAL SOIL, ENVIRONMENTAL POLLUTION.

1. INTRODUCTION

Chemicals called pesticides are applied to pests to get rid of them. Pests are diminished, rendered unable, and killed by these chemicals. Insecticides, herbicides, bactericides, and fungicides are the different categories into which pesticides can be categorized according to the kinds of pests they are intended to control (Mirsal, 2008).

In the 19th and 20th centuries, plant extracts, specifically pyrethrins, served as insecticides, fungicides, and herbicides. The proliferation of pesticide usage coincided with advancements in synthetic chemistry during the 1930s, when inorganic chemicals such as arsenic and sulfur compounds were utilized for crop protection. Arsenic proved lethal to insects, while sulfur functioned as a fungicide. At the onset of the Second World War, numerous pesticides were synthesized, predominantly organic chemicals, including dichlorodiphenyl-trichloroethane (DDT), aldrin, and dieldrin as insecticides, alongside 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) as herbicides (Matthews, 2018).

The field of agrochemicals developed quickly after 1945, with the introduction of numerous insecticides, fungicides, herbicides, and other chemicals to control pests and guarantee agricultural production yields. Additionally, horticulture, aquaculture, and other ordinary household applications all employ pesticides. Additionally, they are employed to manage vector-borne illnesses like dengue and malaria (Van den Berg, 2012).

Between 1990 and 2018, global pesticide usage has been documented, particularly in Asia and America. The global average increased from 1.65 kg•ha−1 in 1990 to 2.66 kg•ha−1 in 2018. Residual pesticides persist in the soil, impacting the resident microorganisms. Human exposure may occur through the consumption of pesticide-contaminated water and food, inhalation of contaminated air, and direct contact during occupational, agricultural, and domestic activities. Pesticides can enter the human body via dermal, oral, ocular, and respiratory routes. The toxicity of pesticides is influenced by the electronic properties and molecular structure, dosage, and duration of exposure (Hamadache et al., 2016).

Consequently, the residual pesticide concentration in the soil must be diminished, necessitating the implementation of appropriate remediation measures. Bioremediation is an environmentally sustainable, economical, and efficient alternative to more costly and hazardous processes, such as chemical and physical remediation techniques. Biodegradation involves the elimination of substances through the utilization of microbial activity by microorganisms. The microorganisms, chiefly bacteria or fungus, convert pesticides into simpler chemicals, such as CO2, water, oxides, or mineral salts, which serve as sources of carbon, minerals, and energy. In these processes, enzymes serve a crucial function as catalysts (Senko, 2017).

A variety of approaches exist for the biodegradation of pesticides, which can occur under aerobic or anaerobic circumstances depending on the types of bacteria involved. Furthermore, bioremediation procedures can be classified into three categories based on the location of the remediation treatment: in situ, ex situ, or on-site. The in situ strategy entails treatment within the contaminated area, typically employing aerobic processes. The primary in situ strategies include natural attenuation, bioaugmentation, biostimulation, bioventing, and biosparging. Ex situ approaches involve the removal of contaminated soil from polluted sites and its subsequent transportation to alternative locations for treatment. Bioreactors, composting, landfarming, and biopiles constitute ex situ remediation methods. The on-site strategy involves the remediation of contaminated soil at the location itself, meaning the soil is extracted from its original site but treated in the vicinity, hence minimizing the impact of transportation (Erguven, 2018).

The purpose of this review is to give an overview of the different types of pesticides, how they break down or are cleaned up by microbes in polluted soils, and the things that make them unique, like how they are classified and any toxicological issues they may have. It will also look at some of the regulations that are in place around the world.

2. CLASSIFICATION OF PESTICIDES:

(2.1) BY CHEMICAL COMPOSITION- Four primary categories can be distinguished: organochlorines, organophosphates, carbamates, and pyrethrins and pyrethroids. The data regarding the chemical and physical properties of pesticides is essential for ascertaining the application method, necessary precautions during application, and the appropriate application rates. (Yadav, 2016)

(2.1.1)ORGANOCHLORINES-

Organochlorine pesticides (OCs) are chemical substances characterized by hydrocarbon chains that contain at least one covalently bound chlorine atom. These chemicals are extensively utilized in agriculture to manage a diverse array of insects. The predominant organochlorines include dichlorodiphenyl-trichloroethane (DDT), dichlorodiphenyl-dichloroethane (DDD), dicofol, dieldrin, lindane, aldrin, chlordane, endosulfan, isodrin, isobenzan, toxaphene, and chloropropylate (Jayaraj, 2016).

These chemicals exhibit lipophilicity and resistance to decomposition, resulting in a propensity for bioaccumulation in tissues and persistence in the environment. Due to their significant environmental persistence, OCs are classified as persistent organic pollutants (POPs). They may inflict harm on organisms, resulting in mutagenesis effects, histopathological alterations, enzyme induction or inhibition, carcinogenicity, and teratogenicity (Kolankaya, 2006).

(2.1.2) ORGANOPHOSPHATES;

Organophosphates (OPs) are synthetic pesticides comprising phosphoric or thiophosphoric acid esters. Hexaethyl tetraphosphate (HETP) was the first compound synthesized and employed as an agricultural insecticide. OPs exhibit acute toxicity towards insects, primarily due to the inhibition of acetylcholinesterase (AChE) in both the central and peripheral nervous systems. This enzymatic inhibition results in muscarinic and nicotinic effects (Roberts, 2013).

(2.1.3) CARBAMATES;

Carbamates are compounds derived from carbamic acid. Their chemical structure is characterized by an amino group bonded with an ester group. Carbamates are also biocides for industry and household products for the control of household pests. The common carbamate pesticides are aldicarb, carbofuran, fenoxycarb, carbaryl, ethienocarb, and fenobucarb. As the organophosphates, carbamates are inhibitors of acetylcholinesterase activity, and therefore, their toxicity acts on the neurological system (Wang,2015).

(2.1.4) PYRETHRINS AND PYRETHROIDS;

Pyrethroids are synthetic chemicals derived from the modification of the chrysanthemic acid component of pyrethrin I through esterification of the alcohols. Pyrethroids are engineered to enhance insecticidal efficacy and reduce sensitivity to air and light, in contrast to pyrethrins. In the atmosphere, pyrethrins and numerous pyrethroids are swiftly destroyed by sunlight, however they persist in the soil for extended periods due to their great binding affinity. Pyrethrins and pyrethroids might be present on leaves, fruits, and vegetables due to their direct application on crops and plants (Morgan, 2018).

Pyrethrins and pyrethroids interfere with sodium channels in axons, hence impairing the neurological system. They are detrimental to insects but comparatively less dangerous to humans. Nonetheless, it was observed that exposure to these pesticides may induce respiratory effects, including cough or upper respiratory irritation following the inhalation of dust or aerosol droplets; neurological effects, such as headache or dizziness; gastrointestinal effects, including nausea and vomiting; and irritation and/or dermal effects (Saillenfait, 2015).

2.2. CLASSIFICATION BY TARGETS;

Pesticides can be categorized based on their functions and the specific pests they target. The primary categories are insecticides, herbicides, rodenticides, bactericides, and fungicides.

(2.2.1) INSECTICIDES;

Insecticides are chemical and biological agents that target and eliminate insects. Larvicides are specialized insecticides that specifically target the larval stage of insects. These chemicals are utilized in agriculture, horticulture, forestry, and gardening, as well as for the control of vectors like mosquitoes and ticks, which transmit diseases to humans and animals, including dengue and malaria. The most prevalent insecticides are classified as organophosphates, pyrethroids, and carbamates (Kleinschmidt et al., 2018).

(2.2.3) RODENTICIDES:

Rodenticides are agents that exterminate rodents. All these rodents can inflict harm on crops, transmit diseases, and create ecological degradation. Rodent infestations occur in several environments, including agricultural soils, within and around structures, in waste disposal sites, and in open spaces. Most rodenticides function as anticoagulants, disrupting blood coagulation and resulting in mortality from severe hemorrhaging. Rodenticide products are available as baits in block or paste form (Koivisto et al., 2018).

(2.2.4) FUNGICIDES:

Fungicides are agents that eliminate parasitic fungus or their spores. They allow for the management of fungal infestations, particularly along the entire food supply chain. Fungicides are extensively utilized in the agriculture sector. Fungicides disrupt multiple metabolic pathways in the fungus cytoplasm and mitochondria. They inhibit many enzymes and proteins involved in lipid metabolism, fungal respiration, and adenosine triphosphate (ATP) synthesis (Thind, 2018).

3. DIFFUSION OF PESTICIDES INTO THE ENVIRONMENT AND THEIR TOXICOLOGY

Pesticides are designed to prevent, eliminate, and manage detrimental pests; yet, they can pose risks to environmental integrity and human health. Their overutilization can result in elevated amounts of pollutants in the environment. Over the years, the World Health Organization has assessed pesticides, documenting their toxicity and impact on human health. Over time, numerous pesticides have been prohibited in certain countries due to their elevated toxicity (WHO 2019).

3.1. ADSORPTION BY SOIL PARTICLES;

Pesticide molecules may be adsorbed onto soil particles by physical means (Van der Waals forces) or chemical means (electrostatic interactions). The process can be characterized by adsorption isotherms. The adsorption constant is assessed as it conveys information on solute mobility. Pesticides with low adsorption affinity tend to disperse more readily into the environment. Multiple soil characteristics affect the adsorption process, specifically soil organic matter concentration, clay content, clay mineralogy, and pH (Konda, 2002).

3.2. DEGRADATION PROCESSES;

Pesticides can undergo degradation and transformation into one or more metabolites via photochemical, chemical, and microbiological mechanisms. Photodegradation is an abiotic process triggered by the absorption of light energy, resulting in the disintegration of pollutant molecules. This process occurs with greater difficulty in soil, which is a heterogeneous system influenced by its qualities. For instance, photodegradation is more effective with particles of substantial size and elevated specific surface area, since they facilitate light diffusion (Siampiringue, 2019).

Chemical and biological degradation emerges through reactions including hydrolysis, oxidation, reduction, dehydrogenation, dehalogenation, decarboxylation, and condensation. Pesticides undergo breakdown by microbiological organisms via metabolic or enzymatic processes during biodegradation. The assessment of the kinetics of these reactions provides insights into the longevity of pesticides (Soulas, 2001).

4. BIOLOGICAL TECHNIQUES FOR PESTICIDE REMOVAL:

Bioremediation mitigates pesticide pollution in agricultural soils by biodegradation processes facilitated by the metabolic activity of microorganisms. It is an efficient, economical, and environmentally sustainable treatment. In bioremediation procedures, microorganisms utilize pesticides as co-substrates in their metabolic reactions with other nutrients, thereby removing them from the environment. The efficacy of these processes is contingent upon the attributes of pesticides, including their dispersion, bioavailability, and soil persistence. It is essential to enhance the accessibility of pesticides to microorganisms, as this is adversely influenced by the adherence of pesticides to soil particles and their limited water solubility.

Furthermore, soil properties and environmental factors, including pH, moisture levels, microbial diversity, and temperature, affect the effectiveness of bioremediation (Ortiz-Hernandez et al., 2014).

4.1. MECHANISMS OF MICROBIAL DEGRADATION;

During biodegradation processes, pesticides are transformed into degradation products or completely mineralized by microorganisms, which use the pollutant compounds as nutrients for their metabolic reactions. 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 , which depends on the pollutant concentration at the beginning and end of the process. This approach has limits because several parameters condition the process, such as microbial activity, temperature, water content, availability, and leaching of pesticide in the soil (Khajezadeh, 2020).

4.2 BACTERIAL DEGRADATION;

Multiple bacterial strains were discovered as proficient at decomposing the chemicals found in the soil. Each bacteria possesses a specialization that renders it especially adept for a degradative process. The operational parameters, including temperature, pH, moisture content, and pollutant kinds, influence the adaptation, development, and function of a bacterial strain. Furthermore, throughout the degradation process, metabolites may emerge and create additional environmental issues, as they might be more challenging to eliminate than the original chemical, which should be regarded as a disadvantage. Chlorpyrifos, an organophosphate pesticide, undergoes hydrolysis by microorganisms, resulting in 3,5,6-trichloro-2-pyridinol (TCP) as the principal breakdown product. TCP exhibits superior water solubility compared to chlorpyrifos and results in extensive pollution of soils and aquatic ecosystems. Limited bacteria can breakdown the pesticide and its metabolite, with the bacterium Ochabactrum sp. JAS2 demonstrating the ability to hydrolyze both chemicals (Abraham, 2016).

In numerous instances, degradation is more efficient when employing a bacterial consortium rather than an isolated pure culture. Bacteria in nature cohabit and rely on one another for their survival. In pesticide degrading metabolic pathways, one bacterium can produce metabolites that may serve as substrates for others (Doolotkeldieva, 2021).

4.3 FUNGAL DEGRADATION;

Agricultural soils host numerous fungi that can be utilized for pesticide biodegradation. This category of microorganisms encompasses yeasts, molds, and filamentous fungi. Fungal degradation is facilitated by its ability to generate numerous enzymes that participate in degradative processes. These microorganisms can also affect soil properties by altering soil permeability and ion exchange capacity. Fungi can outperform bacteria in degradation due to their specific bioactivity, growth morphology, and elevated resistance to high concentrations of pollutants(Oliveira,2015).

A prevalent method involves utilizing both fungi and bacteria to improve degradation. Fungi can convert pesticides into a more manageable and accessible form for bacteria (Purnomo, 2020).

4.4. ENZYMATIC DEGRADATION

Enzymatic biodegradation results from enzymes generated during the metabolic activities of microorganisms or plants. Enzymes are biological macromolecules that catalyze biochemical reactions related to pesticide degradation. These molecules influence the reaction rate by reducing the activation energy required for the reaction. The primary metabolic reactions involved are oxidation, hydrolysis, reduction, and conjugation (Scott et al., 2008).

Oxidation, the initial phase of pesticide degradation, involves the transfer of an electron from reductants to oxidants. Oxygenase and laccase enzymes may participate in this process. Oxygenases facilitate oxidation reactions by incorporating one or two oxygen molecules; laccases cleave the aromatic ring in compounds, reducing oxygen to water and generating free radicals. Heat or energy is produced during the reaction and is employed by microorganisms for their metabolic processes.

Hydrolysis facilitates the breaking of substrate bonds through the incorporation of hydrogen or hydroxyl groups from water molecules. The pesticide molecules are consequently fragmented into smaller chain compounds than their initial forms. Common enzymes participating in hydrolysis processes include lipases, esterases, and cellulases. The enzyme participates in the crucial hydrolysis step, specifically the cleavage of the ester bond in the fenpropathrin compound. Reduction facilitates transformation via reductive enzymes, specifically nitroreductase. The conjugation reaction is performed with existing enzymes and is characteristic of fungal biodegradation. The process entails the incorporation of exogenous or endogenous natural compounds to enhance the mineralization of pesticides (Luo et al., 2018).

4.5. MINERALIZATION

The mineralization process facilitates the breakdown of pesticides into inorganic substances, specifically carbon dioxide, salts, minerals, and water. The bacteria utilize the pesticide chemicals as a nutrition source. In this instance, degradation is affected by various factors, including microbial species, soil properties, and pollutant types. The pace of mineralization is contingent upon the concentration of the microbial community; specifically, a reduction in microbial population does not facilitate deterioration. Chlorothalonil (CTN), an organochlorine fungicide, degrades into CO2; but, a diminished soil microbial ecosystem can lead to the formation of numerous metabolites that are more toxic, persistent, and mobile than CTN itself. This results from the lack of actively degrading groups or the reduction in soil biodiversity, which leads to less microbial activity. Soil characteristics affect the mineralization process of glyphosate(DeSouza,2017).

Diverse soil factors in agricultural soils, including soil texture, organic matter concentration, pH, and exchangeable ions, have been examined. Through univariate and multiple regression analyses, they identified the parameters influencing glyphosate mineralization: cation exchange capacity, defined as the sum of exchangeable base cations and exchangeable acidity (expressed as Al3+ and H+); exchangeable base cations (expressed as Ca2+); and the available form of potassium, determined via ammonium lactate extraction. The limited mineralization of glyphosate in soils characterized by elevated exchangeable acidity may result from the establishment of robust chemical bonds with the carboxylic or phosphonic acid groups of glyphosate, thereby diminishing its bioavailability, or from the detrimental effects of exchangeable aluminum on soil microorganisms (Nguyen et al., 2018).

5. 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 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. Land farming 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 land farming treatment can also be effectuated 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.

6. LEGISLATION

The necessity of having sustainable food production and a reduction, or even a ban, of the use of pesticides, has made it so that each country in the world is committed to implement measures and laws in this regard. Dealing with the topic at the world level, the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) have released a pair of updated guidelines on pesticide legislation and labeling. A code for pesticide legislation has been published in 2020, aiming to guide governments that seek to review, update, or design national pesticide legislation(FAO,2019).

7. CONCLUSIONS

Following the Second World War, the utilization of insecticides and plant protection chemicals has significantly increased in both industrialized and developing nations. Regrettably, all these chemicals exhibit varying degrees of toxicity, adversely affecting human health and the environment. Furthermore, many of them exhibit persistence; their degradability is significantly restricted and happens over extended periods. Soil bioremediation for their removal can be conducted with either particular or indigenous microorganisms (bacteria and fungus) or by enzymatic breakdown. Although several discoveries on soil bioremediation exist at the laboratory scale, there is a paucity of evidence regarding real-scale applications. This issue mostly arises from inadequate collaboration among research laboratories, local authorities enforcing specific soil remediation measures, and corporations engaged in the bioremediation of pesticide-contaminated soils. It would be advantageous for this cooperation to increasingly unify in order to distribute experiences and outcomes. Furthermore, the cost data are insufficient.

Regarding other contaminants, pesticide removal must consider the chemical and toxicological properties of the chemicals, while adhering to national legislation. To this end, it is essential to note that numerous countries still lack legislative measures, which is the primary obstacle to the remediation of polluted areas

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