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Pesticides Bioremediation

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Preface

Pesticide exposure is one of the foremost concerns about environmental safety worldwide. Almost 1.8 billion people are engaged in agricultural practices, with majority of them using synthetic pesticides to safeguard the food and commercial products they produce. Pesticides are used by most people commercially and for public health programs, while many others use them in their lawns, gardens, and household protection. Although efforts have been made to reduce pesticide usage by practicing organic agricultural techniques and by applying alternative pest management technologies to get rid of pests, it is imperative to find appropriate substitutes of chemical pesticides. Continued pesticide exposure from a variety of sources, such as work exposure, spray drifts, garden and home usage, food, residues in household dust, drinking water, and soil, is currently posing a severe health hazard in both developing and industrialized countries. In the process of making decisions concerning the usage of pesticides, both new and old, risk assessment remains critical.

Because of the substantial risks to human health, their use has been restricted, and alternative cleanup systems have been established for persistent pesticides at various contaminated sites. For pesticides degradation, biological techniques like biostimulation, bioaugmentation, biosurfactants, and bioremediation are accessible at polluted sites, although the last one has been proved as the most ideal approach to mitigate the hazardous effects of pesticides. In the presence of sufficient nutrition and environmental conditions, bioremediation technique uses biological agents such as microbes to break down pollutants. The nature of pollutants, properties of polluted sites, pH, and temperature are crucial factors which have an important role in the bioremediation process.

Bioremediation is an environment-friendly mechanism that involves the use of microbes (especially fungi and heterotrophic bacteria), green plants (known as phytoremediation), and their enzymes to degrade/transform hazardous pollutants into materials like water, carbon dioxide, inorganic salts, microbial biomass, and other by-products that are less hazardous than parent materials, as well as generating value-added products which are beneficial for the society. Environment Canada, USEPA, and other regulatory authorities across the world have recognized this technology and it has been proven as a viable solution for cleanup of contaminated soil, water, and sediment at multiple sites all over the world. The elimination of a broad range of noxious and hazardous contaminants from polluted sites necessitates a better understanding of various degradation pathways which is critical for human and environmental safety.

In the present volume, 19 chapters contributed by international subject professionals have been divided into three parts. Part I covers concepts and mechanisms of usage of pesticides bioremediation. Part II deals with latest tools and techniques of pesticides bioremediation, while Part III focuses on applications and global case studies of pesticides bioremediation. This volume on pesticide bioremediation will be of utmost interest to researchers, scholars, and students who are working in the realm of pesticides and bioremediation. Furthermore, this book will assist policymakers and administrative authorities around the world in making pesticide management policies using sustainable bioremediation approaches.

Researchers, academicians, industrialists, environmentalists, practicing and professional engineers, scientists, policymakers, regulatory experts, waste site managers, and students at the bachelor's, master's, and doctoral levels, as well as other enthusiastic persons who are passionately devoted to environmental conservation for sustainable development, will be benefitted immensely from this volume. The numerous strategies presented in this volume reflect the vital research and future development trends.

The volume editors would like to express their sincere gratitude to all the authors for their outstanding contributions. Going through the interesting and exciting information synthesized by the learned and diligent authors in the form of book chapters was an incredibly delightful experience. We would also like to thank editorial and production team from the Springer, particularly Mr. Herbert Moses, Project Coordinator (Books), Zachary Romano, Publishing Editor, and Aaron Schiller, Assistant Editor, for their timely and whole-hearted support.

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Abha, Saudi Arabia — Sazada Siddiqui
Gwalior, India — Mukesh Kumar Meghvansi
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Part I

Concepts and Mechanisms of Usage of Pesticides Bioremediation

Chapter 1
Impact of Organochlorine Pesticides on Soil Microflora and Soil Fertility

D. Ajitha and Linu Mathew

Abstract Microflora is the soil microbes present in the top layer of soil, along with the plant roots. They include bacteria, actinomycetes, fungi, and algae. By decomposing organic matter and adding humus, they augment the fertility of the soil. They are significant in nutrient cycling, rock and mineral weathering, and stabilizing soil aggregates. The unnecessary anthropogenic activities and inappropriate quantities of chemicals, especially organo-chorine pesticides, to increase agricultural productivity threaten the soil microflora and the healthy soil structure. Hence, a shift towards alternative cropping systems is essential for protecting the delicate ecological balance. This chapter discusses the influence of soil microflora on soil fertility, the impact of organochlorine pesticides on the soil microflora, and methods to reduce pesticide toxicity on soils.

Keywords Microflora · Organochlorine pesticides · Persistent organic pollutants · Hexachlorocyclohexane · Dichloro-diphenyl-trichloroethane · Plant growth-promoting rhizobacteria

1.1 Introduction

Soil microflora is the soil microbes present in the rhizosphere soil as an intimate part of the soil organic matter. The population of these microbes is highest in the rhizosphere soil due to the presence of growth-promoting substances secreted by plants (Bulgarelli et al. 2013). Soil microflora includes bacteria, actinomycetes, fungi, and algae, with hundreds of genera and species (Muller et al. 2016). There may be millions of soil microbes per gram of soil. They decompose organic matter and increase soil fertility by producing humus (Rangaswami and Bagyaraj 2005),

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improving the texture and structure, buffering capacity, and the soil's ability to hold water.

Additionally, they are significant in nutrient recycling, weathering rocks and minerals, and stabilizing soil aggregates. Hence, they are called the "Soil Engineers," as they play a prominent role in soil formation and ecosystem conservation (Nannipieri et al. 2003). They also detoxify the organic and inorganic pollutants in the soil.

1.2 Soil Microflora and Soil Fertility

Soil microflora is the microorganisms living in soil concerning soil fertility (Bollen 1959). They are influenced by soil moisture, soil temperature, other radiant energies, aeration of the soil, pH, food availability, biotic components, and other inhibiting influences. Soil fertility is the capability of the soil for supplying plant nutrients and the crop-producing power of the soil in a particular climate. Two types of soil fertility are recognized: active and potential (Rangaswami and Bagyaraj 2005). Active fertility is the immediately available fertility from the soil, whereas potential fertility is produced by the microbial and chemical action on soil minerals and organic matter. Soil microorganisms augment the potential fertility and make the soil alive.

1.2.1 Soil Microorganisms

The top 5 cm of the soil harbor 75% of microorganisms and comprise the bacteria, the actinomycetes, the fungi, soil algae, and soil protozoa in the order of their relative abundance (Table 1.1) (Rao 1999).

1.2.1.1 Bacteria

About one-half of the microbial biomass present in the soil is made of bacteria. Bacteria in the soil are cocci, bacilli, or spirilla; bacilli are the most common type, and spirilla is the least common (Rangaswami and Bagyaraj 2005). Most soil bacteria are heterotrophs, feeding on dead plant material and organic waste. The bacteria are good decomposers aiding in nutrient recycling by converting inaccessible nutrients to accessible and usable forms for plants.

Table 1.1 Microorganisms found in topsoil

Soil microorganisms	Number/gm in soil	Biomass	Dominate in
Bacteria—Highest in number	9–10 billion	40–500	Hardy, tolerate disturbed soil/tilled soil
Actinomycetes—10 times smaller in number to bacteria	1 billion	40–500	Hardy, tolerate disturbed soil/tilled soil
Fungi—Smaller in number, but dominate the soil biomass	70,000–1,000,000	1100–11,000	Undisturbed soil/untilled soil
Algae	1000–100,000	1–50	Undisturbed soil/untilled soil
Protozoa	100–10,000	varies	Hardy, tolerate disturbed soil/tilled soil

1.2.1.2 Actinomycetes

They are an intermediate group between fungi and bacteria and share several features with bacteria. The number and type of actinomycetes increase in decomposing organic matter. They help in humus formation by decomposing organic components resistant to bacterial degradation. (Rangaswami and Bagyaraj 2005). They can live in dry and low nitrogen soil. They produce the characteristic soil smell. Many of them are antibiotic producers.

1.2.1.3 Fungi

They are present in the soil as mycelial bits, rhizomorphs, or various spore forms. They are heterotrophs and are numerous in the surface layers of well-aerated cultivated soils (Brussaard 1997) and active in forming ammonium and simple nitrogen compounds in soil, help in soil aggregation and humus formation from raw organic residues. Mycorrhiza is a mutually beneficial relationship between some fungi and plant roots (Morton 1981). Here, the fungi supply the plant with nutrients and obtain food from the plant in return. Though many fungi are helpful, some could be harmful to soil organisms (Johns 2017). Some of their functions are:

1. Decomposers are the saprobes converting dead organic material into fungal biomass, carbon dioxide, organic acids, and other small molecules (Wilson 2018).
2. Mutualists are the mycorrhizal colonizers of plant roots. They solubilize inorganic phosphorous and make available other plant nutrients in exchange for prepared food from the plant.
3. Parasites colonize plants and other organisms, causing death and reduction in crop production.

1.2.1.4 Soil Algae

They are abundant in soils rich in water content and sunlight. They augment the water retention of soil. They are unicellular, filamentous, or colonial and capable of photosynthesis (Rao 1999). They cement soil particles together and reduce soil erosion.

1.2.1.5 Protozoa

They are unicellular life forms and abundant in the upper layer of the moist soil. They use dormant hardy cysts to weather adverse soil conditions. Some protozoa are potential biological control agents against plant pathogens and some waterborne and vector-borne human pathogens, e.g., *Entamoeba (*Johns 2017).

1.2.1.6 Soil Viruses

They are sub-microscopic and obligate parasites on other soil microorganisms like bacteria, actinomycetes, fungi, and algae. Some of the plant and animal viruses also reach the soil. They influence soil biology, soil ecology and are a potential reason for microbial deaths. Viruses are found to occur abundantly in all the areas, even where bacterial populations differ significantly (Johns 2017).

1.2.2 Role of Soil Microbes in Soil Fertility

Soil microorganisms decompose organic matter, mineralize and fix nitrogen, phosphorus, and potassium, and thereby help in plant growth, degrade toxic chemicals, suppress pathogens, and produce plant growth-promoting substances. They also stimulate plants' immune systems and activate stress responses (Reitz et al. 2015). Many of these organisms live close to other organisms in the soil rather than living independently. The different functions they perform in soil are;

1. Augmenting soil fertility, mainly by nitrogen-fixing bacteria (Bano and Iqbal 2016).

   Certain bacteria and blue-green algae live symbiotically and fix atmospheric nitrogen in the root nodules of legumes. In *Rhizobi*a-Legume symbiosis, *Rhizobia* fix atmospheric nitrogen in nodules of the legume host's roots to an available form and receive carbohydrates in return (Morton 1981).
2. Soil loosening and adding organic matter to the soil by decomposition.

   The plants absorb the nutrients released by the decomposition of organic matter. Degradation of organic matter starts by leaching out of water-soluble components followed by degradation of its structure by bacteria, fungi, and other microflora, making it soft and pliable and further decomposes. Thus, soil microflora rejuvenates the environment by maintaining the process of life, death, and decay.

3. Developing healthy soil structure: Soil microbes cement the soil by producing gummy substances (polysaccharides and mucilage) (Usharani et al. 2019).
4. Cycling nutrients: Soil microorganisms participate in biogeochemical cycles, namely, carbon, nitrogen, and sulfur cycles.
5. Locking carbon into the soil for long periods: This reduces greenhouse gas-induced climate change.
6. Biodegradation of pesticides in a slow natural process (Tarla et al. 2020).

1.3 Organochlorine Pesticides' (OCP's) Impact on Soil Microflora

Pesticides are significant in modern agriculture for increasing agronomic yield and getting good profits. They are substances used to control, kill, or repel pathogens, pests, and weeds and are termed insecticides, fungicides, bactericides, and herbicides (Tomlin 2009; Castelo-Grande et al. 2010; Tarla et al. 2020). The overuse of topsoil and the alterations in soil chemical and physical fertility upset the soil's biological fertility and productivity. The World Health Organization (WHO 1979) observes that agrochemical poisoning is increasing in developing countries (Payet 2021). The intensive, indiscriminate, and prolonged use of agrochemicals harms biodiversity, sustainability, food security, and safety. They alter the soil microbial functions, soil biochemistry, and ecological balance (Chen et al. 2001; Hagerbaumer et al. 2015).

Organochlorine pesticides (OC) are synthetic chlorinated hydrocarbon derivatives. They are highly persistent in the environment and are called persistent organic pollutants (POPs). Chemically, some of the organochlorine pesticides are Dichloro-diphenyl-trichloroethane (DDT), Dichloro-diphenyl-dichloroethane (DDD), Dicofol, Lindane, Eldrin, Aldrin, Dieldrin, Isodrin, Chlorobenziate, Benzene hexachloride (BHC), Methoxy chloro Aldrin, Chlordane, Heptachlor, Endosulfan, Isobenzan, Toxaphene, and Chloro propylate. They are highly toxic, persistent, and slow degrading. They also show low water solubility with high lipid solubility and high bioaccumulation. Organochlorines make about forty percent of all the pesticides used (Gupta 2004; Food and Agricultural Organization—FAO 2005). According to the World Health Organization (WHO 1990) study, developing nations use 80% pesticides. Low cost and the broad spectrum of action prompt these countries to use DDT, Hexa-chloro Cyclohexane (HCH), aldrin, and dieldrin (Lallas 2001; Gupta 2004; FAO 2005). High persistence and bioaccumulation make them environmental hazards (Jayaraj et al. 2016). Highly hazardous endosulfan persists moderately with a half-life of 50 days (Quijano 2002). DDT and its transformation products, namely 1,1-dichloro2,2-bis(*p*-chlorophenyl) ethylene (DDE), 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane (DDD), and 1,1,1-trichloro-2-(o-chlorophenyl)-2-(*p′* chlorophenyl) ethane (o,p′-DDT) persist still in New Zealand soil even after banning DDT in 1970 (Boul 1995; Aislabie et al. 1997). All these products of DDT and the heavy use of other pesticides cause DNA damage, changes in enzyme activity, alter membrane stability, cause acute and chronic health effects like neurological damage and endocrine disruptions (Jayaraj et al. 2016; Tarla et al. 2020). Hence, the use of these is banned by the Stockholm convention (Payet 2021). Despite the ban, many developing countries are using these OC compounds.

Soil microbial ecosystems are degraded by the indiscriminate use of organochlorine pesticides (Onder et al. 2011). OCPs contamination level and vegetation cover shape the microbial diversity and community structure in the abandoned insecticide plant sites (Sun et al. 2019). The misuse or overuse of pesticides adversely affects both the aquatic and terrestrial species, along with the microorganisms that inhabit these environments; posing a severe threat to the ecosystem (Grande et al. 1994; De Lorenzo et al. 2001; Frankart et al. 2003; Liess et al. 2005; Castillo et al. 2006; Wang et al. 2006). Continuous use of these pesticides affects the soil microflora and all other organisms that depend on them. E.g., the soil organisms like an earthworm take up DDT in the soil. When the birds ingest these earthworms, DDT enters their body and gets accumulated, finally resulting in the reduction of the avian population (Fry 1995).

The indiscriminate spraying of the pesticides across the cropping field results in more than 95% of the herbicides and insecticides reaching non-target soil microorganisms than their targeted pest species (Miller 2004). A tiny fraction (0.3%) of applied pesticides reaches the target pest, while 99.7 % go elsewhere (Pimentel 1995). They enter the environment through direct application, volatilization from applied surfaces, industrial discharge into the soil or water bodies, and landfilling with the discarded polluted wastes (Simonich and Hites 1995; Pereira et al. 2010). They affect the non-target organisms and especially the microflora of that locality. Due to their peculiar structure, OC compounds have definite physicochemical features such as persistence, bioaccumulation, and toxicity. A persistent chemical has a half-life of more than two months in water bodies and more than six months in soil sediments. The organochlorines have moderate to high persistence with a half-life of 60 days to 10–15 years. DDT, the most commonly used agriculture chemical, is highly persistent (half-life of 2–15 years) (Augustijn-Beckers et al. 1994).

1.3.1 Infiltration of Organochlorine Pesticides into the Microbial Environment

OCPs adsorb to the surface soil particles and persist for months to years without leaching down to the soil (Yang et al. 2012; Kim et al. 2014; Odukkathil and Vasudevan 2016. Doolotkeldieva et al. 2018). The organochlorine insecticides enter the soil either during the direct soil application or as runoff from sprayed leaves and stems of crop species (Hlindin and Bennett 1970; Cope 1971). They also come to the soil from the dead and decaying target and non-target organisms containing insecticides. The careless disposal of pesticides and their vessels produces localized high insecticide concentrations.

1.3.2 Biological Accumulation of Organochlorine Pesticides in the Microbial Environment

Biological accumulation is the addition of a chemical from the ecosystem into an organism. Other terms like bioconcentration, biomagnification, and ecological magnification express biological accumulation (Bevenue 1976). Kneip and Laur (1973) made a clear distinction between bioconcentration and biomagnification. Bioconcentration is the ability of the organism to accumulate a chemical from the surroundings and is expressed as a percent accumulation and concentration factor. However, biomagnification is the increased accumulation of a chemical in increasing trophic levels of a food chain.

There is only scanty information on the metabolism and accumulation of organochlorines (Lal and Saxena 1982). Accumulation mechanisms, metabolic pathways of pesticide degradation, and the enzymatic breakdown of pesticides need further clarification and elucidation. However, some microorganisms accumulate very high concentrations of OCPs. A marked difference was shown by three different species of fungi, bacteria, and actinomycetes in collecting DDT and dieldrin from water samples (Chacko and Lockwood 1967). After 4 h of incubation, 60–63% of DDT and 75% of Dieldrin were accumulated by the fungi, while *Agrobacterium tumefaciens* accrued 100% of the DDT and 90% of the dieldrin. Yeast cells accrued 94–97% of DDT (Boush 1972). In different species of algae, organochlorines get concentrated in different ratios (Rice and Sikka 1973), and bacteria show rapid accumulation of organochlorine insecticides (Lal and Saxena 1982).

1.4 OCPs and Soil Microflora and Fertility

Microbial communities play essential roles in improving the different soil processes, such as decomposition of organic matter, nutrient recycling, energy transfer through the food chain, and numerous microbe–microbe, plant–microbe, and animal–microbe interactions (Lal and Saxena 1982) and thereby maintaining balanced ecosystems and healthy soil (Yang et al. 2017). They respond rapidly to changes in the soil and thereby act as bioindicators of soil health. (Cycon et al. 2012; Panettieri et al. 2013; Wyszkowska et al. 2014). Organochlorine-microorganism interactions disturb the soil ecosystem and reduce soil fertility (Handa et al. 1999). Pesticides negatively impact soil microorganisms, soil respiration, and soil fertility (Dutta et al. 2009; Sofo et al. 2012). The exogenous applications of OCPs reduce the growth, colonization, and metabolic activities of the beneficial root-colonizing microbes like bacteria, arbuscular mycorrhiza, fungi, and algae in soil (Debenest et al. 2010; Menendez et al. 2010; Tien and Chen 2012). OCPs accumulating in the soil are toxic to decomposers, including soil bacteria and fungi, but the exact mechanism of toxicity is unknown (Wojcik et al. 2018). It was proposed that the occurrence of OCP in the soils may lead to the impoverishment of the decomposer communities, causing the extinction of soil bacteria and fungi due to the biocidal activity (Liu et al. 2008; Mertens et al. 2005; Chaurasia et al. 2013). Though the exact mechanism of the biocidal effects of OCP in the soil is not known; Liu et al. (2008) and Endo et al. (2006) hypothesized a suicidal pathway, where the OCP acquired by the decomposer organism are partially de-halogenated to more toxic products than the parent compound leading to their death.

Adsorbed OCPs on the soil organic matter influence the residue levels of OCPs in the soil (Gong et al. 2004; Zhang et al. 2006; Pateiro-Moure et al. 2008). It affects the soil pH by modifying the humus structure (Wenzel et al. 2002). It adversely affects nitrogen fixation, nitrification, and ammonification by activating or deactivating specific soil microbes and microbial enzymes (Hussain et al. 2009; Munoz-Leoz et al. 2011). For example, ammonification is higher in the presence of pesticides and causes an antagonistic action in the populations of *Azospirillum* spp. (Srinivasulu et al. 2012). A reduced or inhibitory nitrogenase activity by applying endosulfan and ϒ-HCH was also reported (Martinez-Toledo et al. 1998; Niewiadomska 2004; Niewiadomska and Klama 2005; Prasad et al. 2011). In contaminated soils with pesticide concentrations of 0.02–10 times that of field recommended doses of lindane, dichlorvos, endosulfan, and chlorpyrifos, the biochemical processes of nitrification and denitrification are diminished (Madhaiyan et al. 2006). At higher doses, pesticides often reduce the ammonification process (Cycon et al. 2010). OCP inhibited the ammonification step in bulk soils and reduced the number of microbial communities (Blondel et al. 2017). Organochlorine insecticides, especially DDT and endosulfan, are detrimental to photosynthetic autotrophs (Fries 1972; Rani et al. 2018; Shahid et al. 2021). Although OCPs did not affect the algal number, they significantly reduced the ATP detected in the algal extracts (Clegg and Koevenig 1974). The insecticides interfere with photophosphorylation in the light reaction of photosynthesis in these algae, thereby reducing ATP production and CO_2 fixation.

Pesticides may also selectively inhibit or kill certain microbes and augment others by removing competition (Hussain et al. 2009). The recurrent use of complex chemicals kills microbial life, valuable for the healthy soil ecosystem (Shang et al. 2019). Soil-dwelling microbes can be mutated by pesticides making them useless to the soil ecosystem (Aktar et al. 2009). The effect of the pesticide on the growth and survival of the beneficial microbes can be either detrimental, stimulatory, or with zero impact (Patnaik et al. 1996). The long residual effect and persistence of lindane and DDT in soil harm the microbial biomass (Singh and Singh 2005), microbial processes, and microbial enzymes (Patnaik et al. 1996). Sprayed pesticides get washed down the crop contaminating the soil and reducing soil fertility by hampering autochthonous soil flora (Wu et al. 2018; Zaller et al. 2018). DDT, methyl parathion, and pentachlorophenol can block the chemical signals needed for bacterial nitrogen fixation (Kumar 2015), thereby depleting soil nitrogen and reducing crop yields (Fox et al. 2007; Kumar 2015). Pesticide mixtures are more harmful to soil microbes. OCP pesticide spraying on virgin soils resulted in the loss of 33,397 fungal and 61,005 bacterial species (Egbe et al. 2021) with significant extinction of susceptible strains (Tejada et al. 2015; Yang et al. 2017; Doolotkeldieva et al. 2018). The reduction in Chloroflexi, Verrucomicrobia, and Nitrospirae populations and the complete extinction of Euryarchaeota, Bathyarchaeota, and Chlorobi populations in the contaminated soil indicate that these phyla are sensitive to OCPs toxicity (Demanou et al. 2006). Overuse of OCP resulted in the disappearance of Nitrospirae, providing a low nitrate value (Egbe et al. 2021). Also, OCP application resulted in the extinction of the ecologically significant phylum Glomeromycota with obligate symbionts (Lin et al. 2015). The disappearance of such sensitive microorganisms serves as a bio-indication of OCPs' pollution. The following details stress the specific mechanisms of OCP on different soil microbes.

1.4.1 Impact of OCP on Different Microbes

1.4.1.1 Bacteria

Bacteria show more sensitivity to insecticides than filamentous forms (Stojanvic et al. 2013). Many organochlorine pesticides such as aldrin, dieldrin, chlordane, endrin, and heptachlor were detrimental to bacteria at a 10,000-ppm concentration (Lal and Saxena 1982). They inhibited many Gram$^+$ stains with no effect on Gram$^-$ strains (Audus 1960). Dieldrin and heptachlor at 50 and 100 ppm reduced the growth of *Pseudomonas fluorescens* and *Streptomyces aureus* (Collins and Langlois 1968). They selectively block the electron transport chain and the cell wall or membrane components. Kepone, an organochlorine insecticide, is highly persistent in the environment (Jones and Hodges 1974; Orndorff and Colwell 1979). A field study for 2 years on Kepone 0toxicity showed that Gram$^-$ bacteria, mainly *Pseudomonas* sp., *Vibrio* sp., and *Aeromonas hydrophila*, were at risk to <1 mg of Kepone per liter (Orndorff and Colwell 1980). The destructive action of DDT, aldrin, and dieldrin targeted the structure and function of biological membranes. DDT altered the composition of fatty acids and the ratio of polar phospholipid groups in *E. coli* cell membranes (Rosas et al. 1980). Previously, in *Bacillus subtilis,* the lethal action of DDT binding to the cell membranes was reported (Hicks and Corner 1973).

1.4.1.2 Cyanobacteria

In certain cyanobacterial species, supplementing suitable nutrient salts can alleviate the toxicity of organochlorines. Increased concentrations of K_2HPO_4, Ca $(NO_3)_2$, and $CaCl_2$ assuaged the toxicity of BHC in the blue-green alga *Nostoc muscorum* (Kar and Singh 1979) suggesting the chance of BHC interacting with these to form complexes with less toxicity.

1.4.1.3 Fungi

Dieldrin and aldrin at very high concentrations of 2000 ppm had no substantial effect on fungal populations (Tu and Miles 1976). Nevertheless, high soil concentration of endrin altered soil microbiota (Bollen and Tu 1971). Organochlorine insecticides inhibited cell division in *Saccharomyces cerevisiae* (Nelson and Williams 1971). Aldrin interfered with the oxidative enzymes and inhibited the metabolism of pentoses, hexoses, and tricarboxylic acid cycle intermediates in *Rhizobium* sp (Juneja and Dogra 1978).

1.4.1.4 Algae

Even high concentrations of BHC did not upset the algal population (Vance and Drummond 1969). Organochlorine insecticides in aquatic environments destroy sensitive zooplanktons and thereby cause phytoplankton blooms by removing competition and predation. Organochlorine insecticides inhibited algal photosynthesis (Wurster Jr. 1968; Bowes and Gee 1971; Mosser et al. 1972a, b; Cole and Plapp Jr. 1974). Even the lowest concentration of DDT distorted the chloroplasts in *Nitzschia delicatissima* (MacFarlane et al. 1971).

1.4.1.5 Protozoans

Protozoans are the most resistant microorganism to DDT. DDT at one ppm did not show any toxicity on *Euglena gracilis, Paramecium bursaria*, and *P. multimicronucleatum* and concentrated DDT to 99–900 folds (Gregory et al. 1969). DDT concentration of 100 ppm did not affect the growth of *E. gracilis* (Poorman 1973). But, several protozoans, including amoebae and flagellates, were killed by 5 and 50 ppm DDT (MacRae and Vlnckx 1973). In three ciliate protozoans, *Stylonychia notophora* (Lal and Saxena 1980), *Blepharisma intermedium*, and *Tetrahymena pyriformis* (Lal and Saxena 1979), low concentrations of DDT, up to 1 ppm, neither affected the morphology nor cell division. But, at high concentrations of 50 and 100 ppm, DDT was inhibitory to cell division. *Stylonychia notophora* treated with 100 ppm DDT revealed many nuclear morphology changes, like deep incisions, chromatin loosening, and macronuclear fragmentation (Lal and Saxena 1980).

In a nutshell, organochlorine insecticides interfere with membrane permeability, photosynthetic machinery, oxidative metabolism, nucleic acid, and protein synthesis. They alter the plasma membrane architecture and change its lipid composition; thus, compromising cell permeability and cellular physiology (Lal and Saxena 1982).

1.4.2 Synergism of OCP on Soil Microflora

Applied pesticides may act as an energy source to some microbial groups by increasing their number, growth, and interference in the soil ecosystem (Gill and Garg 2014). Certain strains of microbes are exclusive to the OCP-contaminated soil. These strains invade adjacent environments by human activities. For example, applied endosulfan amplified bacterial biomass by 76% and fungal biomass by 47% (Xie et al. 2011). About 63,474 fungi and 38,212 counts of bacteria were exclusive to the OCP impacted soil (Egbe et al. 2021). OCP contaminated soil showed prominence of Proteobacteria, Actinobacteria, Firmicutes, and Bacteroidetes (Doolotkeldieva et al. 2018). Some prominent representatives in the OCP contaminated soil include *Bacillus* (Kafilzadeh et al. 2015; Kumar et al. 2014), *Burkholderia cepacia* (Hussain et al. 2007), and *Rhodanobacter lindaniclasticus* (Nalin et al. 1999). Both α- and β-endosulfan degradation was reported in *Bacillus subtilis* and *B. circulans* enriched cultures (Kumar et al. 2014; Kafilzadeh et al. 2015).

Enterobacteriaceae capable of mineralizing and tolerating OCPs occurred abundantly in the OCPs' impacted soil (Egbe et al. 2021). These bacteria can resist organochlorine toxicity and use pesticides for their growth (Phugare et al. 2013; Wang et al. 2019; Ekram et al. 2020; Ramya and Vasudevan 2020). Long-term exposure to organochlorines may lead to the emergence and evolution of resilient microbes with pesticide degrading and detoxifying genes. The facultative anaerobe *Enterobacter* sp can degrade pesticides without forming any toxic by-products (Ekram et al. 2020; Ramya and Vasudevan 2020). Also, *Klebsiella* sp is one of the dominant bacteria present in pesticide-contaminated soils (Wang et al. 2019), degrading endosulfan competently (Seralathan et al. 2015). *Escherichia/Shigella* spp. are also crucial in OCPs' metabolism (Kulkarni and Kaliwal 2018; Sirajuddin et al. 2020). *E. coli* strains degrade lindane, acetofenate, and other organochlorines (Kulkarni and Kaliwal 2018; Sirajuddin et al. 2020). Bradyrhizobiaceae, Acidobacteriaceae (Cederlund et al. 2014; Lu and Lu 2018), and Rhodospirillaceae present in the OCP polluted soil help in tolerating pollutants and degrading OCPs and improve the soil fertility (Jeffries et al. 2018) indicating the ecological importance of these in nutrient recycling and other changes in the agricultural soil (Shettigar et al. 2012; Jeffries et al. 2018). Bradyrhizobiaceae species with the nif-H sequence in water-stressed paddy soil with elevated CO_2 and a high dose of N_2 (Kumar et al. 2020) can fix nitrogen and utilize organic compounds for growth (Tikariha and Purohit 2019).

Mortierella species are slow-growing saprophytic fungi that degrade a range of toxic materials like organochlorines and thus improve soil health (Kataoka et al.

2010; Clemmensen et al. 2015). *Mortierella elongata* hydrolyzed endosulfan to endosulfan lactone (Bhandari 2017; Kataoka et al. 2010). Moreover, OCPs serve as complex organic carbon sources and increase species richness and evenness among fungi in OCP-contaminated soil (Egbe et al. 2021). Soil organic matter also affects the OCP's behavior in soils (Mishra et al. 2012). Hydrophobic organochlorine pesticides bind with soil organic matter. By increasing soil organic matter, we can supply more carbon and thus enable microbial degradation.

1.5 Alleviating Pesticide Toxicity

The unhealthy agricultural practices and the use of inappropriate quantities of pesticides for increasing agrarian productivity have resulted in a decrease in the abundance of soil microbes, threatened sustainability, and the healthy soil system (Shang et al. 2019). Accumulation, toxicity, and transport of POPs damage the soil and other ecosystems. A shift towards alternative cropping systems is essential for protecting the delicate ecological balance of soil and biodiversity. Some treatment methods are outlined below to minimize the adverse effects of DDT and other OCPs.

1.5.1 Biopesticides

They are natural biochemical substances derived from naturally occurring products. They can be derived from microbes (microbial pesticides) or plants. They are significant in pest management, act as an eco-friendly alternative to chemicals, and minimize soil contamination without harming the soil microbes (Meena et al. 2020). They also ensure good soil health, environmental stability, and ecological balance and improve the nutrient uptake efficiency of plants (Gupta and Dikshit 2010).

1.5.1.1 Microbial Pesticides

Biopesticides made from microorganisms specific to target pests do not harm the environment and other soil microbes and offer a better and good ecological solution (Gupta and Dikshit 2010). The most commonly used microbial pesticides are *Bacillus thuringiensis* (Bt), Baculoviruses, and *Trichoderma*. *Bacillus thuringiensis* is being used against moth larvae of plant pests (Meena and Meena 2016). Baculoviruses are target-specific to the lepidopteran pests of cotton, rice, and vegetables (Alam 2000). *Trichoderma* and *Trichoderma*-based products work best against soil-borne pathogens (i.e., root rot) and control rots and wilts in dryland crops such as pulses (Gupta and Dikshit 2010). Entomo-pathogenic nematodes (EPN) (*Heterorhabditis* sp. and *Steinernema* sp.) are potent against insect pests belonging to Diptera, Coleoptera, Lepidoptera, and Orthoptera, and other soil-inhabiting insects (Sharma et al. 2011). They are safe and easy to apply. However, limiting factors such as the high cost of production, reduced shelf-life, moisture, temperature, and UV sensitivity prevent their broader application (Lacey and Georgis 2012).

1.5.1.2 Plant-Based Biopesticides

They are the specific compounds produced from plants that stimulate or subdue diverse soil microbes (Neal et al. 2012). Examples include plant growth-promoting rhizobacteria (PGPR) *Pseudomonas fluorescence* which benefits plants like tomatoes (Sood 2003). Neem cake oil offers much-required nutrition for soil microbes, augments soil physico-chemistry, and controls wide ranges of pests (Gopal et al. 2007). Insecticides like azadirachtin have been recognized as effective anti-fungal (Govindachari et al. 2000) and antimicrobial (Coventry and Allan 2001).

1.5.2 Bioremediation

Bioremediation uses living organisms, mainly microbes, to biodegrade and detoxify harmful chemicals from the environment. This method was effectively used to reclaim OCPs, DDT, HCH, and PCBs contaminated soils and sediments (Mansouri et al. 2017; Sadiq et al. 2018; Vergani et al. 2019).

1.5.2.1 Microbial Bioremediation

Microbial pesticide remediation is cost-effective and thermodynamically reasonable (Parte et al. 2017). Under favorable conditions, microbes use pesticides as carbon and sulfur sources and electron donors. Bioremediation results in the complete mineralization of the pesticides to H_2O and CO_2 without building up any intermediates. Microorganisms enzymatically convert the pollutants to fewer toxic products in a suitable environment for growth and microbial activity (Lacey and Goettel 1995; Vidali 2001). Surfactant Tween 80 encouraged *Pseudomonas aeruginosa* to remove 94% endosulfan at pH 8.5 by producing less toxic endodiol and endosulfan sulfate (Jayashree and Vasudevan 2007). Similarly, *Stenotrophomonas maltophilia* (85.5%), *Citrobacter amalonaticus* (56.7%), and *Acinetobacter Iwoffii* (80.2%) degraded endosulfan (Ozdal et al. 2016).

Although HCHs are degraded under aerobic and anaerobic conditions, the pesticides are more persistent under aerobic conditions (MacRae et al. 1984). Organic materials such as straw and glucose had a stabilization effect on degrading HCH (Zhao et al. 2020). Also, the marine bacterium - *Paracoccus sp.* DDT-21 consumed DDT as a nutrient source (Rashed et al. 2021). *Streptomyces sp.*—strain 885 successfully degraded DDT and can be used for remedying DDT-contaminated soil (Ito et al. 2021).

1.5.2.2 Bioremediation by Earthworms

Earthworms enhanced DDT removal from soils by speeding up the biological degradation (Xu et al. 2021). Earthworm cast enables complete degradation of DDT, improves soil properties, and stimulates the growth of indigenous microorganisms. Ten new DDT degrading bacteria genera (*Streptomyces, Streptacidiphilus, Dermacoccus, Brevibacterium, Bacillus, and Virgibacillus*) were found in the drilosphere soil, which cleaves the DDT ring structure. *Bacillu*s and *Dermacoccus* are essential in the dechlorination of DDTs, and bioremediation of DDT-contaminated soils.

1.5.2.3 Phytoremediation

Phytoremediation is cleaning organic and heavy metal pollutants by plants and rhizosphere microbes (Ali et al. 2013; Dixit et al. 2015; Jan and Parray 2016); an efficient, inexpensive, and eco-friendly method of environmental restoration. The success of phytoremediation is determined by soil contaminants and the plants' ability to take up these from the soil. Rissato et al. (2015) assessed the capacity of *Ricinus communis* L to degrade various organic pollutants like HCH, DDT, heptachlor, and aldrin. They found that this plant could efficiently remove 25–70% of various organic pollutants. *Saccharum officinarum* (sugarcane) and Candida exhibited enhanced lindane removal from contaminated soil (Salam et al. 2017). Also, sunflower (*Helianthus annuus*) could take up the contaminants from the environment and hence be used for phytoremediation of organic and heavy metal pollutants (Ojuederie and Babalola 2017).

1.5.3 Microbial Biodegradation of Pesticides

Removal of DDT from the soil is necessary since its degradation products accumulate in the primary metabolites. DDT biodegradation in the soil is slow, and several strategies are proposed for enhanced degradation in situ. One such mechanism is the microbial degradation of DDT. By adding DDT metabolizing microbes (Fungi and bacteria) to contaminated soil and supplying suitable environmental conditions, DDT can be efficiently degraded (Aislabie et al. 1997). Other promising biodegraders are ligninolytic fungi and chlorobiphenyl degrading bacteria (Aislabie et al. 1997). Soil pre-treatment by flooding, the addition of organic matter, and microbial inoculum enhance DDT degradation by augmenting the microbial access to the pollutant. However, little is understood about the biodegradation of DDE, which is the primary residue in soils. Both aerobic and anaerobic microorganisms can degrade HCH (MacRae et al. 1984). The inoculation of Bacillus sp. PRB101 showed maximum degradation of endosulfan in the soil after 120 days of inoculation (Rani et al. 2019). This result indicated that plant growth-promoting bacteria effectively remediate endosulfan contaminated soil thereby enhancing plant biomass production.

The degradation of organochlorine compounds is through two major pathways:- anaerobic reductive dechlorination and aerobic dehydrochlorination. Many bacterial genera like *Klebsiella* (Kwon et al. 2005), *Pseudomonas* (Barragan-Huerta et al. 2007), and *Staphylococcus* (Sonkong et al. 2008) carry out such reactions. Many fungi can also degrade organochlorines with basidiomycetes showing more resistance than others (Machado et al. 2005; Rigas et al. 2005). A *Trichoderma harzianum* strain degrade OCPs through an oxidative mechanism (Katayama and Matsumura 1993). DDT degradation using brown rot fungi (BRF) has a low degradation rate needing prolonged incubation. By adding 10 ml of P*seudomonas aeruginosa* into the BRF fungi *Daedalea dickinsii* culture, the highest biodegradation of DDT was possible (Rizqi et al. 2021). Table 1.2 outlines the different microorganisms involved in the degradation of organochlorine pesticides.

1.5.4 Education to Farmers, Distributors, and Other Stakeholders

Farmers are the leading risk group of pesticide toxicity. Other susceptible groups are formulators, loaders, mixers, production workers, and agricultural farm workers. Educating farmers, distributors, industry, policymakers, and other stakeholders on the indiscriminate use of pesticides is critical in decreasing harm to humans and the environment (Meena et al. 2020). They must be aware that pesticides' judicious and discriminatory use is vital because the overuse of these chemical pesticides can bring about several health problems. Also, the continued use of such chemical pesticides may make the soil barren and lifeless.

1.6 Conclusion

Pesticides are hazardous compounds to the environment, soil microflora, and human health because of their persistence. They negatively affect microbial functions, diversity, population composition, and biochemical activities. Pesticides affect crop yield and cause an imbalance in the ecosystem by reducing soil fertility. Indiscriminate use of pesticides affects crop production and alters the food chains and ecosystems. Some reviewers claim that the adverse effects of organochlorine insecticides on microorganisms are due to the high rate of insecticide application.

Table 1.2 Microorganisms capable of degrading OCP (+ sign indicates the capability of pesticide degradation)

Microorganisms	DDT	DDE	DDD	Aldrin O	Eldrin O	Dieldrin	Endosulfan	PCP	1,4-dichlorobenzene	Lindane	Heptachlor O	Toxaphene O
Bacteria												
• *Pseudomonas sp.*	+			+	+	+			+		+	+
• *Aerobacter aerogenes*	+											
• *Alcaligenes eutrophus*	+											
• *Sphingobacterium sp.*	+											
• *Micrococcus sp.*	+										+	+
• *Arthrobacter sp*	+						+	+				+
• *Bacillus sp.*	+						+				+	+
• *Pseudomonas aeruginosa*	+						+					
• *Burkholderia cepacia*							+					
• *Flavobacterium sp.*								+				
• *Sphingomonas paucimobilis*										+		
• *Streptomyces sp.*	+									+		
• *Klebsiella sp.*							+					
• *E. coli*										+		
Fungi												
• *Trichoderma viride*	+										+	+
• *Penicillium miczynskii*	+											
• *Penicillium raistrickii*	+											
• *Aspergillus sydowii*	+											
• *Trichoderma sp.*	+		+									
• *Bionectria sp*	+											
• *Aspergillus niger*							+					

Microorganisms	DDT	DDE	DDD	Aldrin O	Eldrin O	Dieldrin	Endosulfan	PCP	1,4-dichlorobenzene	Lindane	Heptachlor O	Toxaphene O
• *Pleurotus ostreatus*										+		
• *Ganoderma australe*										+		
• *Phanerochaete chrysosporium*		+										
• *Phlebia sp.*											+	

(References: Wedemeyer 1967; Matsumura et al. 1968; Patil et al. 1970; Stanlake and Finn 1982; Crawford and Mohn 1985; Spain and Nishino 1987; Bumpus et al. 1993; Nadeau et al. 1994; Kamanavalli and Ninnekar 2003; Pesce and Wunderlin 2004; Rigas et al. 2005; Bhalerao and Puranik 2007; Benimeli et al. 2008; Fang et al. 2010; Ortega et al. 2011; Xiao et al. 2011; Rani et al. 2019)

However, it is now apparent with the advancements in pesticide technology that even lower doses of insecticides at standard rates may have antagonistic effects. For maintaining sustainability, the use of such pesticides should be replaced using biofertilizers and biopesticides. Bioremediation and biodegradation are also the best methods to combat these OCPs in the soil. Also, pesticide use can be reduced by culturing vigorous and resistant plants, maintaining native species that are resistant innately to native pests, and promoting pest predators like frogs and birds. Awareness among the common public is essential to reduce the lasting ill-effects of using these pesticides. To conclude, the swelling world demand for quality food requires developing an ecologically sound strategy for sustaining a “live soil.”

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Chapter 2
Phytoremediation of Environmental Matrices Contaminated with Photosystem II-Inhibiting Herbicides

Katarína Kráľová and Josef Jampílek

Abstract Excessive use of agrochemicals, including photosystem II (PS II)-inhibiting herbicides, especially after 1950, resulted in significant contamination of environmental matrices. Although some of these photosynthesis-inhibiting herbicides, including atrazine or simazine, have been banned in many countries due to their endocrine disrupting activities, their residues from agricultural field runoff persist mainly in sediments and can be released in aquatic environments where they can adversely affect non-target species. Phytoremediation is an inexpensive environmentally friendly method that uses diverse types of plants to decontaminate soils and aquatic ecosystems from inorganic and organic contaminants. This chapter provides a comprehensive overview focused on the phytoremediation of substrates contaminated with PS II-inhibiting herbicides using grasses, aquatic plants, seaweeds and seagrasses, algae and cyanobacteria, woody species, crops, and transgenic plants. The mechanism of action of PS II-inhibiting herbicides and the development of plant resistance to these herbicides are described. The beneficial impact of microbial species on the degradation of herbicides by microbial species in the rhizosphere is discussed, and the removal of herbicides from the soil using electrokinetic-assisted phytoremediation is briefly mentioned.

Keywords Algae · Atrazine · Crops · Macrophytes · Photosystem II Herbicides · Phytodegradation · Rhizodegradation · Transgenic plants · Trees

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Abbreviations

AMR	Ametryn
ATP	Adenosine triphosphate
ATZ	Atrazine
BCF	Bioconcentration factor
CAT	Catalase
Chl	Chlorophyll
CYA	Cyanuric acid
Cys	Cysteine
DDA	Desethyldeisopropylatrazine
DEA	Desethylatrazine
DIA	Desisopropylatrazine
DOM	Dissolved organic matter
GST	Glutathione-*S*-transferase
HA	Hydroxyatrazine
HXZ	Hexazinone
IC_{50}	Herbicide concentration that is required for 50% inhibition
ISO	Isoproturon
LAC	Laccase
MTZ	Metribuzin
NADPH	Nicotinamide adenine dinucleotide phosphate, reduced
PAH	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PET	Photosynthetic electron transport
Pheo	Pheophytin
PQ	Plastoquinone
PRO	Prometryn
PS	Photosystem
RC	Reactive center
ROS	Reactive oxygen species
SIM	Simazine (SIM)
SNP	Nitroprusside
TBR	Terbutryn
TBZ	Terbuthylazine
TF	Translocation factor
WOC	Water oxidizing complex

2.1 Introduction

Intensive use of effective herbicides to achieve improved yields in the second half of twentieth century was accompanied with increasing contamination of environmental matrices with these toxic compounds. However, due to mobility of herbicides in environmental matrices, they can be transported to places distant from their application. For example, 32% of U.S. water bodies contained atrazine (ATZ; 6-chloro-*N*-ethyl-*N′*-(propan-2-yl)-1,3,5-triazine-2,4-diamine) in an average amount of 0.17 μg/L (Beaulieu et al. 2020a). Moreover, the amounts of herbicides in water markedly fluctuate between seasons and reflect their spatial and temporal use, whereby sediment can function as a principal secondary emission source, particularly for the historic-use pesticides including ATZ, simazine (SIM; 6-chloro-*N*,*N′*-diethyl-1,3,5-triazine-2,4-diamine), and isoproturon (ISO; 1,1-dimethyl-3-[4-(propan-2-yl)phenyl]urea) (Cui et al. 2020). Therefore, it is important to ensure effective removal of herbicides residues from environmental matrices near their application and for this purpose phytoremediation techniques are frequently used (Moeder et al. 2017; Gikas et al. 2018; Qu et al. 2018; Wang et al. 2018; Aguiar et al. 2020b; Prosser et al. 2020; Wang et al. 2021; Perez et al. 2022). These environment friendly green methods use the ability of plants to take up herbicide from contaminated substrates and allocate it in the tissues of plant organs. Plant using enzymes, can transform herbicides to degradation products within plant tissues and by releasing the exudates can improve microbial activity and promote biochemical transformations in the soil. Moreover, mycorrhizal fungi and the microbial consortia associated with the root surface increase mineralization at the root/soil interface (Schnoor et al. 1995).

Runoff loss of herbicides from crop fields can be significantly reduced by grass hedges (Wang et al. 2018) and considerable reduction of the mobility of pesticides and nutrients can be achieved by vegetated buffers (Prosser et al. 2020). Buffer strips are vegetation areas located in the direction away from a source of pollutants or a plume or along a waterway (i.e., riparian corridors). On the other hand, implementing of filter strips connected with displacement of cropland and grassed waterways may reduce yields and profits (Abimbola et al. 2021). The ability of vegetated ditches to remove organic pollutants and contaminants originating from domestic sewage and agricultural runoff was discussed by Moeder et al. (2017). A vegetal filtering system composed of short-rotation willow crops suitable for remediation of pesticide-contaminated groundwater was described by Lafleur et al. (2016) and for removal of contaminants, also grass and grass with poplar buffer strips were found to be suitable (Caron et al. 2010; Franco and Matamoros 2016). In floating treatment wetlands used for removal of contaminants from surface water bodies, the vegetated mats are floated on the surface of water and roots situated in the water column remove the contaminants (Shahid et al. 2018; Hwang et al. 2021). For effective remediation of waters contaminated with compounds of agricultural origin also constructed wetlands (CWs) can be used (Gikas et al. 2018; Papadopoulos and Zalidis 2019; Zhao et al. 2019). However, for removal of emerging organic pollutants, hybrid CWs, which combine vertical flow CW, horizontal flow CW, and free water surface CW are suitable (Ilyas et al. 2021).

Besides aquatic plants (Qu et al. 2017, 2018, 2020; Li et al. 2019a; Papadopoulos and Zalidis 2019; Qu et al. 2020; Vieira et al. 2021a; Perez et al. 2022) and woody species (Fiore et al. 2019; dos Santos et al. 2018, 2020; Kumar et al. 2019; Yao et al. 2019) used for remediation of pesticide-contaminated areas, application of grasses (Mimmo et al. 2015; Del Buono et al. 2016; Sun et al. 2016; Khrunyk et al. 2017; Sanchez et al. 2017; Pannacci et al. 2020; McKnight et al. 2022) and transgenic plants (Vail et al. 2015; Azab et al. 2016, 2020; Zhang et al. 2017a) was found to be effective. Because herbicides similarly to other toxic contaminants frequently adversely also affect the development, growth, and performance of non-target plants, the plant species suitable for phytoremediation purposes must be tolerant to herbicidal contaminants present in soils and waters. On the other hand, algae (Kabra et al. 2014; Yang et al. 2019; Hu et al. 2021), cyanobacteria (González-Barreiro et al. 2006; Campos et al. 2013; Breda-Alves and Fernandes 2021), seaweeds (Rodrigues et al. 2018; Ojemaye et al. 2020), and seagrasses (Gao et al. 2017, 2019; Wilkinson et al. 2017), which can serve as indicators of fresh and marine water contamination with herbicides, can be applied also as effective phytoremediators capable not only absorb the herbicides from aqueous medium but also transform them to less toxic metabolites. However, considering the higher persistence of herbicides in the sediments, it is necessary to monitor, whether the content of herbicides in edible seaweeds do not exceed the permissible levels.

It could be mentioned that beside killing unwanted vegetation such as weeds, the herbicides can be absorbed also by crops, i.e., non-target plants (Jiang et al. 2020; Ju et al. 2020; Pintar et al. 2020; Wang and Liu 2020; Zhang et al. 2021), and therefore to ensure food safety consistent surveillance of their contents in crops is necessary also at application of wastewater containing herbicides for irrigation (Pico et al. 2019) and at application of excessive amounts of herbicides in greenhouses. Comparison of ATZ contents in greenhouse (from not detectable levels to 137 ng/g) and open-field agricultural soils (from not detectable levels to 134 ng/g) in China showed higher ATZ levels of greenhouse soils and even in 60% of the greenhouses the ATZ levels were considerably higher than in the open-field soils in their vicinity (Dou et al. 2020).

Photosystem (PS) II-inhibiting herbicides showing adverse impact of photosynthetic processes include phenylcarbamates, pyridazinones, triazines, triazinones, phenylcarbamates, pyridazinones uracils, amides, uracils, nitriles, ureas, benzothiadiazinones, nitriles, and phenylpyridazines (WSSA 2011).

Triazines are usually generally used as pre- and post-emergence herbicides and they are able to control both grasses and broad leaf weeds in many numerous agricultural crops (LeBaron et al. 2008). The main representative and most commonly used herbicide of this group is ATZ with estimated global annual consumption of 70,000–90,000 tons, whereby about 5% of its amounts applied in agriculture move into water bodies via surface runoff or leaching (Hou et al. 2017; Szewczyk et al. 2020). According to la Cecilia and Maggi (2016), the half-life ($t_{1/2}$) of ATZ biodegradation in surface water is 10–105 days. Douglass et al. (2014) reported that $t_{1/2}$ of ATZ mineralization in water was estimated in the range from 7 days to 5 years.

Moreover, ATZ herbicide and its degradation products can be desorbed from sediment (where it persists longer than in water) and be released into water (Boithias et al. 2014). Because ATZ, SIM, ISO, and prometryn (PRO; 6-(methylsulfanyl)-*N*,*N*'-di(propan-2-yl)-1,3,5-triazine-2,4-diamine) were found to show endocrine disrupting activities (Orton et al. 2009; Zorrilla et al. 2010; Hrouzková and Matisová 2012; Park et al. 2014; Grasselli et al. 2018; Harper et al. 2020; Hayes et al. 2020; Horak et al. 2021; Rohr 2021), their use in European Union was banned. For example, the European Union banned the use of ATZ in 2004 because groundwater levels exceeded the limits set by regulators (European Commission 2004), which resulted in effective reduction of ATZ in coastal waters (Nödler et al. 2013), and thereafter ATZ was replaced by terbuthylazine (TBZ; *N*-*tert*-butyl-6-chloro-*N*'-ethyl-1,3,5-triazine-2,4-diamine). However, residues of ATZ in environmental matrices and environment contamination caused by its permanent use in many countries outside European Union require efficient techniques for their removal, including phytoremediation and phycoremediation. Rohr (2021) focused on the history of ATZ and analyzed a smear campaign supported by huge funds, lawsuits, investigative reports, and research manipulation to satisfy economic, political, or ideological issues that were accompanied by ethically questionable decisions by responsible authorities and should be avoided in the future to protect human and environmental health.

This chapter provides a comprehensive overview focused on phytoremediation of substrates contaminated with photosystem II (PS II)-inhibiting herbicides using grasses, aquatic plants, seaweeds and seagrasses, algae and cyanobacteria, woody species, crops, and transgenic plants, including mechanism of action of these herbicides, and beneficial impact of microbial species on degradation of herbicides in the rhizosphere. Structures of PS II-inhibiting herbicides discussed in this chapter are shown in (Fig. 2.1).

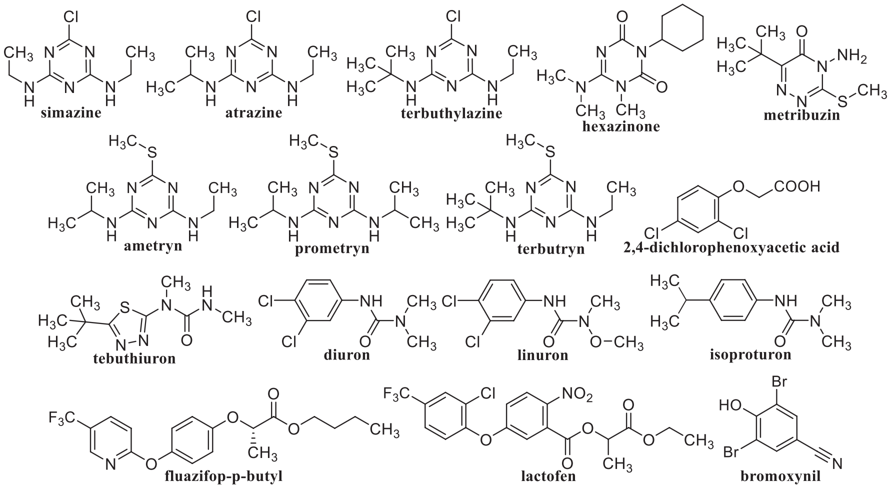


Fig. 2.1 Photosystem II-inhibiting herbicides

2.2 Photosystem II-Inhibiting Herbicides

According to classification of herbicides based on their mode of action given by the Weed Science Society of America (WSSA), PS II inhibitors include Group 5 (phenylcarbamates, pyridazinones, triazines, triazinones, uracils), Group 7 (amides, ureas), and Group 6 (benzothiadiazinones, nitriles, and phenylpyridazines) (WSSA 2011).

2.2.1 Mechanism Mode of Action of PS II-Inhibiting Herbicides

Photosystem II (PS II) is a membrane protein supercomplex situated in the thylakoid membranes of photosynthesizing organisms that uses light energy for catalyzing oxidation of water and reduction of plastoquinone (PQ). Redox components involved in the light-driven electron transport from H_2O to the PQ pool following redox components of PS II are involved: the water oxidizing manganese cluster (WOC), the amino acid tyrosine (Y_z) situated on the D_1 protein on the donor side of PS II, the reaction center chlorophyll of the PS II reaction center (RC; P_{680}), pheophytin (Pheo), and two plastoquinone molecules, Q_A and Q_B (Fig. 2.2). After absorption of photons charge separation between P_{680} and Pheo occurs, creating P_{680}^+/Pheo$^-$. Oxidation of water is driven by oxidized primary electron donor P_{680}^+, which oxidizes Y_z situated on the D_1 protein on the donor side of PS II, and four Mn ions occurring in WOC undergo light-induced oxidation as well. On the acceptor side of PS II electron is transported from Pheo$^-$ to Q_A functioning as an one-electron acceptor the Q_A site. From Q_A protein, the electron is transported to another plastoquinone molecule, Q_B (plastoquinone molecule acting as a two electron acceptor), which is loosely bound at the Q site to D_1 protein, and after two photochemical turnovers of the RC it unbinds from RC as fully reduced and protonated, and diffuses in the hydrophobic core of the membrane. The Q_B-binding site will be thereafter occupied by an oxidized PQ plastoquinone molecule (Whitmarsh 1998; Whitmarsh and Govindjee 1999; Barber 1999, 2016; Barber and Tran 2013).

PS II-inhibiting herbicides inhibit photosynthetic electron transport (PET) at the acceptor side of PS II via binding to the niche of the redox-active quinone Q_B, which is situated on the D_1 protein. Consequently, PET from Q_A to Q_B is inhibited and production of adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADPH), which are indispensable for the fixation of CO_2, is ceased, which results in plant growth inhibition. Due to PET inhibition, Q_A cannot be reoxidized, which contributes to stimulated formation of chlorophyll (Chl) in the triplet state. Triplet excited chlorophyll (^{3}Chl*) can transfer excitation to the O_2 in ground state generated from the water splitting reaction during photosynthesis, whereby singlet oxygen ($^1O_2$), which is a very harmful reactive oxygen species (ROS), is formed. Due to chain reaction of lipid peroxidation and oxidation of

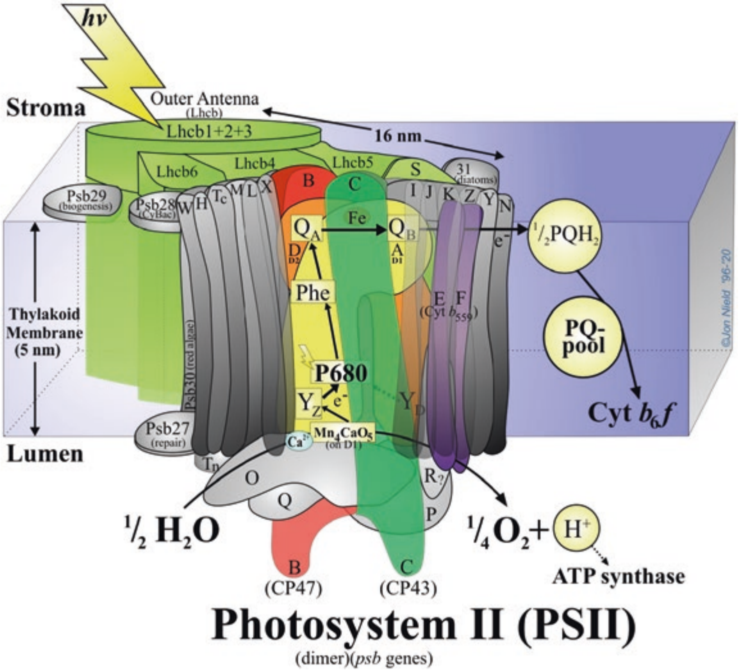


Fig. 2.2 Structure of photosystem II

proteins, which can be initiated by both ^{3}Chl* and $^1O_2$, loss of assimilation pigments (Chls and carotenoids) and damage of membranes is observed. At binding of phenolic herbicides the formation of ^{3}Chl* and subsequently generating of $^1O_2$ is stimulated to a greater extent than by binding of triazine and urea herbicides, resulting in increased efficiency of photodamage (Rutherford and Krieger-Liszkay 2001). Although Q_B is displaced by all PS II-inhibiting herbicides from its binding site, binding site of these herbicides is not identical to the binding site of the secondary quinone, Q_B, but there is a significant special overlap. ATZ and diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) bind to 34 kDa protein, while phenolic herbicides bind to 43–51 kDa PS II RC reaction center proteins (Oettmeier et al. 1982; Oettmeier 1985).

Takahashi et al. (2010) investigated structures of phenolic herbicides and their binding sites in the Q_B pocket of PS II and based on docking calculations found that deprotonated bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) binds to D_1-His_{215} at the CO group, in contrast to the protonated form of bromoxynil and diuron that bind without an interaction with D_1-His_{215} to the opposite side of the pocket. Based on the finding that in the dark, ATZ noncompetitively inhibits the binding of HCO_3^- to the PS II complexes, it was suggested that besides of a high-affinity ATZ binding site per PS II complex situated in Q_B niche on the reducing side of PS II, there are also a specific low-affinity herbicide binding site, although light eliminates the inhibiting effects of ATZ on bicarbonate binding (Stemler and Murphy 1985).

Diphenylcarbazide, which is known to supply electrons at the donor side of PS II in Y_z intermediate, was reported to displace ATZ and metribuzin (MTZ; 4-amino-6-*tert*-butyl-3-(methylsulfanyl)-1,2,4-triazin-5(4*H*)-one) from their binding site in the Q_B pocket (Purcell et al. 1991; Borse et al. 2000).

2.2.2 Development of Plant Resistance of Plants to PS II-Inhibiting Herbicides

Long-term application of large amounts of PS II-inhibiting herbicides resulted in the development of weed resistance to these agrochemicals. It could be mentioned that the D_1 polypeptide protein is encoded by the *psbA* chloroplast gene and is highly conserved in photosynthesizing organisms not only in vascular plants but also in algae and cyanobacteria. The resistance to PS II-inhibiting herbicides is related to associated mutations in the *psbA* gene, leading to an amino acid exchange in the D_1 polypeptide (Q_B binding protein) (Trebst 1991). In vascular plants a single amino acid substitution of serine (Ser) to glycine (Gly) at position 264 in the D_1 protein causes the resistance to ATZ (Hirschberg et al. 1984; van Rensen and de Vos 1992). On the other hand, rapid detoxification of ATZ in tolerant crops results from glutathione-*S*-transferase (GST) activity. In MTZ-resistant wild radish beside the known Ser_{264}-Gly mutation also higher level of ^{14}C-MTZ metabolism was observed, resulting in reduced translocation of ^{14}C in the plants (Lu et al. 2019a). At the presence of Ser_{264}-Gly mutation, resistance against ATZ is connected by abolishing H-bonds. However, Lu et al. (2019b) also investigated an ATZ-resistant wild radish population, which displayed a novel Phe_{274}-Val substitution, and these plants were moderately resistant to ATZ, MTZ, and diuron; the Phe_{274}-Val substitution was supposed to affect indirectly hydrogen bond formation between the herbicides and Ser_{264} residue, resulting in a resistance against these PS II-inhibiting herbicides. When investigating the mechanism of ATZ resistance in *Amaranthus tuberculatus* from Nebraska it was found that *psbA* gene did not exhibit known point mutations associated with ATZ resistance, but in the resistant plants, conjugation of ATZ mediated by GST was faster than in ATZ-susceptible plants, suggesting that metabolism-based resistance to ATZ was predominant (Vennapusa et al. 2018). Novel methyltransferases enhancing detoxification and degradation of ATZ residues to less toxic compounds in *Oryza sativa* rice plants were identified by Lu et al. (2016).

In *Sisymbrium orientale* L. plants from near Horsham (Victoria, Australia), two resistant populations were found showing a 311- and 315-fold higher resistance to ATZ than susceptible population and based on the sequencing of the chloroplast *psbA* gene it was found that this was related to a missense mutation of Ser_{264} to glycine in both populations. However, these *S. orientale* populations showed no resistance to diuron (Dang et al. 2017). Antonacci et al. (2020) considering the structure of D_1 protein of the PS II of green alga *Chlamydomonas reinhardtii*, designed in silico a novel 50-mer biomimetic peptide in the region of D_1 protein from the residue 211–280, which enabled ATZ binding with residues of three amino acids, Ser_{222}, Asn_{247}, and His_{272} via three H-bonds.

2.3 Removal of Contaminants by Physicochemical Methods Versus Phytoremediation

For pesticide removal several physicochemical methods can be used (e.g., Marican and Durán-Lara 2018; He et al. 2019). Methods based on physical processes are, for example, the use of adsorbents such as biochar (Gamiz et al. 2019; Suo et al. 2019; Mandal et al. 2021), activated carbon (Gonzalez et al. 2020; Pimenta et al. 2020; Vieira et al. 2021b), zeolites (Kucherova et al. 2018; Toledo-Jaldin et al. 2018; Rad and Anbia 2021), polymeric materials (Ronka 2016a, b; Romita et al. 2019; Baigorria et al. 2021), etc. Chemical treatments use various agents to improve the extraction of harmful compounds such as pesticides to less toxic or no toxic compounds via chemical reactions. Chemical treatments involve advanced oxidation processes (Babu et al. 2019; Zhou et al. 2019; Esquerdo et al. 2020; Garrido-Cardenas et al. 2020; Ghavi et al. 2021), O_3/H_2O_2 oxidation (Chen et al. 2020; Rekhate and Srivastava 2020), UV-H_2O_2 oxidation (de Oliveira et al. 2019), photocatalysis (Kaur and Kaur 2021; Kelly et al. 2021; Saravanan et al. 2021), Fenton reaction (Sangami and Manu 2017a, b; Dolatabadi et al. 2021), photodegradation (Liu et al. 2016; Shawky et al. 2020), or ultrasound-assisted remediation (Castelo-Grande et al. 2017). On the other hand, phytoremediation technologies using plants to decontaminate environmental matrices represent a green, inexpensive, and environmentally friendly solution based on the ability of plants to remove, break down, or immobilize contaminants and pollutants, and are applied to remediate contaminants and pollutants from soils, sediments, sludges, groundwater, surface water, or wastewater (Sun et al. 2016; Dong et al. 2016; Yadav et al. 2016; Akhtar et al. 2017; Dhanwal et al. 2017; Qu et al. 2017; Schwitzguébel 2017; Ribeiro et al. 2019. Papadopoulos and Zalidis 2019). The most important phytoremediation techniques include: (i) phytoextraction, (ii) rhizofiltration, (iii) phytostabilization, (iv) phytodegradation, (v) rhizodegradation, and (vi) phytovolatilization (Fig. 2.3) (Pascal-Lorber and Laurent 2011; Yadav et al. 2016; Dhanwal et al. 2017; Masarovičová and Kráľová 2018; Bhat et al. 2020; Kanwar et al. 2020; Tonelli et al. 2020; Kristanti, et al. 2021).

Phytoextraction (also known as phytoaccumulation) is the removal of contaminants from soil and water by plant roots and their allocation to shoots. Non-biodegradable contaminants, such as toxic metals accumulated in the shoots, can then be harvested, and thus definitively eliminated from the environment (Sheoran et al. 2016; Teofilo et al. 2020).

Rhizofiltration uses the absorption, concentration, and precipitation of contaminants by the roots and is suitable for the remediation of contaminated aquatic ecosystems using aquatic or terrestrial plants. In contrast to phytoextraction, contaminants are not transferred to the shoots, and once saturation is achieved, the plants are harvested by roots (Han et al. 2021; Kristanti et al. 2021).

Phytostabilization uses the adsorption of contaminants on the surface of the roots and thus prevents their migration; consequently, migration of contaminants by wind and water erosion and as well as leaching and dispersion of the soil are restrained

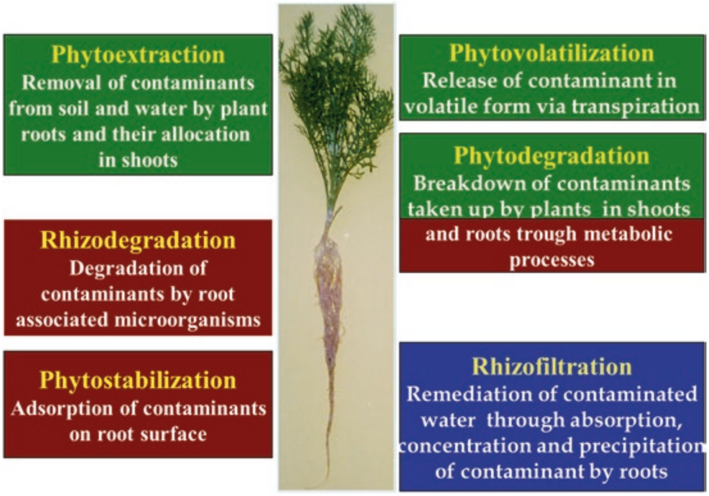


Fig. 2.3 Different kinds of phytoremediation techniques

which indicates a favorable impact of the plant cover on the surface of contaminated soils. Thus, plants grown on contaminated soil have favorable impact on the environment (Radziemska et al. 2017; Schachtschneider et al. 2017). Phytodegradation (also known as phytostimulation and phytotransformation) eliminates organic contaminants taken up by plants by their decomposition in root and shoot tissues through metabolic processes. Plant enzymes including peroxidases, phenoloxidases, nitroreductases, or esterases rise the polarity of contaminants by inserting functional groups (e.g., –OH groups) and further increase of the polarity achieved by conjugation with plant biomolecules leads to reduced toxicity (He et al. 2017; Qu et al. 2018).

Rhizodegradation (also known as phytostimulation) is the break down of organic contaminants by root-associated microorganisms. The microbial activity of these microorganisms, which consume organic pollutants as a source of energy and nutrition and can degrade them into non-toxic or less harmful compounds, is supported by exudates released by plant roots (Dominguez et al. 2020; Sivaram et al. 2020).

Phytovolatilization is the release of contaminants (either in their original form or after metabolic modification) by a plant in a volatile form via transpiration into the atmosphere, whereby the contaminants could be in their original or metabolized form (Limmer and Burken 2016; Zhang et al. 2020). In addition, plants capable of absorbing huge quantities of water can prevent spreading of contaminated wastewater to neighboring environment through hydraulic control (Lewis-Russ et al. 2009; Yadav et al. 2010; Danielescu et al. 2020; Ciampi et al. 2021) and restoring infertile areas with planting of resistant plant species that effectively cover the soil (phytorestoration), which can inhibit transfer and migration of contaminated soil particles with bound contaminants and prevent soil erosion caused by wind as well as surface water runoff, can be used for ecosystem restoration (Lin et al. 2007; Burges et al. 2018; Pandey et al. 2020).

For evaluation of the plant bioremediation ability, the bioconcentration factor (BCF), known also as bioaccumulation factor, i.e., defined as the ratio of the contaminant concentration in plant dry mass (μg/g d.m.) to its concentration in the soil (μg/g soil) or external solution (μg/mL) is used. On the other hand, the translocation factor (TF) corresponds to the ratio of contaminant concentration observed in the shoots to this in the roots and reflects the effectiveness of plants in translocating contaminant from roots to the above-ground part of plants (Tu and Ma 2002; Deng et al. 2004; Masarovičová et al. 2010a).

Recently, several comprehensive review papers related to phytoremediation were published, which were focused, for example, on the use of phytoremediation for removal of organic pollutants (Tripathi et al. 2020), polycyclic aromatic hydrocarbons (PAHs) (Gabriele et al. 2021; Kumar et al. 2021), polychlorinated biphenyls (PCBs) (Jing et al. 2018), organic pollutants such as explosives in impacted military ranges (Fayiga 2019), or pharmaceuticals and personal care products (Nguyen et al. 2019), decontamination of pesticide-contaminated areas (Kumar et al. 2019; Tarla et al. 2020), use of invasive plants (Prabakarana et al. 2019; Singh et al. 2021) or transgenic plants for removal of heavy metals (Ibañez et al. 2015; Gunarathne et al. 2019; Prasad 2019), use of natural and artificial soil amendments improving phytoremediation effectiveness (Poonam Kumar 2019) or utilization hairy root cultures for phytoremediation purposes (Majumder et al. 2016; Moola et al. 2021).

In summary, environmentally friendly phytoremediation techniques are less invasive and require less equipment compared to physicochemical methods, are inexpensive, can be used for various types of contaminants, and their use prevents the natural environment. On the other hand, there are certain disadvantages associated with the use of phytoremediation, such as incomplete prevention of pollutant leaching to groundwater, impaired plant performance/survival in highly toxic substrates, dependence on climatic conditions and soil properties, risk of bioaccumulating harmful contaminants entering the food chain, and the long time required for effective, though not always complete removal of contaminants (Tonelli et al. 2020; Masarovičová and Kráľová 2012, 2017, 2018).

2.4 Degradation of Herbicides by Microbial Species

Sene et al. (2010) summarized the findings related to degradation of ATZ by isolated microbial species/and microbial consortia and focused attention on the development of techniques applied for microbial removal of ATZ in natural environments using microbial species. Wan et al. (2021) analyzed the content of triazine herbicides, ATZ, TBZ, SIM and their degradation products, desethylatrazine (DEA), desisopropylatrazine (DIA), desethyldeisopropylatrazine (DDA, also known as didealkylatrazine), hydroxyatrazine (HA), and desethylterbuthylazine in surface

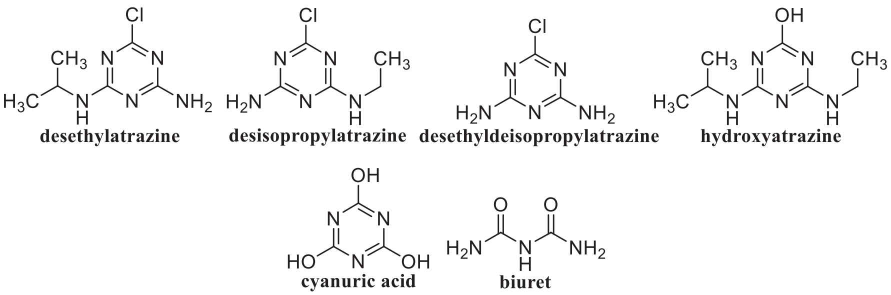
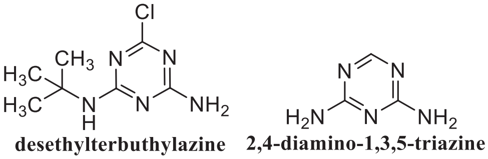


Fig. 2.4 Degradation products of atrazine

Fig. 2.5 Degradation products of terbuthylazine (desethylterbuthylazine) and prometryn (2,4-diamino-1,3,5-triazine)



water from northern Vietnam. In the samples of lake water, the chlorotriazines with total content of 49.3 ng/L were found to be the major herbicides in the samples of lake water; the content of ATZ and its metabolites (in ng/L) in these samples decreased as follows: 11.0 (DIA) > 10.9 (ATZ) > 4.98 (HA) > 3.56 (DEA) > 1.85 (DDA). Chlorotriazines and their degradation products (the total content of 164 ng/L) were also evaluated as major pesticide contaminants in river water; the content of ATZ and its metabolites (in ng/L) in these samples decreased as follows: 116 (ATZ) > 21.3 (HA) > 11.7 (DIA) > 8.50 (DEA) > 5.88 (DDA). The structures of ATZ degradation products are shown in Fig. 2.4 and the structure of TBZ degradation product desethylterbuthylazine is shown in Fig. 2.5.

The rhizodegradation by *Inga striata* and *Caesalphinea ferrea* tree species contributed to more rapid degradation of ATZ residues resulting in elimination of adverse impact of ATZ to herbicide-sensitive plants. In the rhizospheric soils of tree species *Mycobacterium*, *Bradyrhizobium*, *Conexibacter*, *Rhodoplanes*, *Solirubrobacter*, , *Streptomyces*, *Geothrix, Gaiella*, *Geothrix*, *Haliangium,* and *Nitrospira* species were found to be predominant and rhizosphere soils contained also some ATZ degradation genes (Aguiar et al. 2020a).

Although soil microbial communities practically are not affected by herbicide treatment in the long-term, it is desirable to design multi-site microbiological field studies involving multiple locations; for effective herbicide degradation, microbial mixed cultures should be evaluated; and the attention should also be paid to coexistence of multiple microbial species (along with their identification) on a single resource, which may ameliorate the degradation potential of the herbicide.

2.5 Vascular Plant Species and Algae Used for Phytoremediation of PS II-Inhibiting Herbicides

2.5.1 Grasses

Grasses have extensive root system enabling effective absorption of water and nutrients and their highly branched (fibrous) roots stabilize the soil and prevent erosion. Due to this large root system the grasses are suitable candidates for phytoremediation purposes, and in addition, they can also effectively metabolize or degrade organic contaminants, including herbicides (Khrunyk et al. 2017; Sanchez et al. 2017; Panja et al. 2018; Ma et al. 2020; Liu et al. 2020a; Pannacci et al. 2020; Phouthavong-Murphy et al. 2020; McKnight et al. 2022).

Sui and Yang (2013) investigated bioaccumulation of ATZ and content of ATZ residues in the soil in three ryegrass cultivars cultivated in soil containing 0.8 mg/kg ATZ. They found that the presence of plants pronouncedly reduced ATZ residue in soil, and ATZ content in the rhizosphere was also considerably lower compared to non-rhizosphere soil. Although ATZ suppressed the activities of some enzymes in soil, including urease, polyphenol oxidase, invertase, and acid and alkaline phosphatases, in the presence of tested ryegrass cultivars they were successfully activated. Among investigated ryegrass cultivars, Changjiang II cv. was found to be the most tolerant against ATZ, which was reflected not only in superior growth characteristics, but also in higher Chl content and lower damage caused by oxidative stress compared to Abode and Jiawei cultivars. All three cultivars accumulated more ATZ in shoots than in roots. Abode and Jiawei cultivars accumulated ca. 2.70 mg/kg in shoots and 0.58 mg/kg in roots, which corresponds to BCF_{shoot} of 3.41 and TF of 4.66. On the other hand, the BCF_{shoot} and TF values for the most tolerant Changjiang II cv. were lower, ca. 1.9 and 3.9, respectively.

Three prairie grasses, switchgrass (*Panicum virgatum* L.), Yellow Indiangrass (*Sargassum nutans*), and big bluestem (*Andropogon gerardii*) grown three weeks on sterilized sand or in hydroponic solution supplemented with ^{14}C-labeled ATZ were investigated by Khrunyk et al. (2017) for their ability to remove ATZ. ATZ uptake by *P. virgatum* and *A. gerardii* from hydroponic medium achieved ca. 40% of the ^{14}C contained in hydroponic solution and 20–33% in sand cultures, suggesting that these species are suitable for phytoremediation purposes. On the other hand, *S. nutans* was characterized with low ATZ uptake from hydroponic medium. Prevailing ATZ amount absorbed by investigated grasses from sand culture underwent degradation to metabolites, whereby increasingly enhanced ATZ degradation from sand to roots and leaves was observed, and in the leaves 60–80% of detected ^{14}C belonged to metabolites; whereas desisopropylatrazine (DIA) was found to be the main ATZ metabolite in roots, higher amount of DDA observed in leaves indicated further metabolism in this plant organ.

An experiment performed with *P. virgatum* seedlings cultivated in sand containing 10 μg ATZ/g showed that 7 days after treatment ATZ metabolites were detected in leaves, but not in the sand and roots, suggesting that this plant can degrade ATZ

(Murphy and Coats 2011). Albright et al. (2013) treated switchgrass-soil column system with 16 ppm ATZ and found that up to first 2 weeks of the experiment ATZ was detected in both soil and seedlings, however, by day 21 of the experiment, its level did not reach the limit of detection. Whereas DEA and DDA metabolites were detected during the experiment, the presence of DIA could not be verified. In another experiment, using treatment with 4 ppm ATZ solution, the researchers detected DEA and DIA metabolites already one day after treatment, while DDA and cyanuric acid (CYA) were observed later, and HA metabolite was not detected. The increase in the portion of ATZ metabolites was accompanied with decreasing levels of ATZ.

Lin et al. (2008) investigated ATZ uptake, phytodegradation, and detoxification in the rhizosphere using orchardgrass (*Dactylis glomerata* L.), tall fescue (*Festuca arundinacea)*, timothy *(Phleum pretense*), smooth bromegrass (*Bromus inermis*)*,* and switchgrass *(P. virgatum)* grasses. In the presence of grasses, ATZ occurring in soil showed by 20–45% higher biological degradation or chemical hydroxylation of ATZ compared to control. Switchgrass was able to degrade >80% of ATZ soil residues to less toxic metabolites, and 25 days after herbicide application to transform 47% of these residues to hydroxylated metabolites characterized with lower mobility. In the tissues of *P. virgatum* and *F. arundinacea* the hydroxylated metabolites were detected as predominant ATZ degradation compounds, while as the main degradation products in cool-season species *D. glomerata* L., *P. pratense,* and *B. inermis N*-dealkylated metabolites were estimated. The warm-season species *P. virgatum*, showing not only high tolerance to ATZ but also powerful ATZ degradation capacity, was evaluated as a suitable grass to be used in riparian areas to diminish ATZ toxicity and mobility. Among seven plants (*D. glomerata* L., *B. inermis* Leyss., *F. arundinacea* Schreb., *Desmanthus illinoensis*, *P. virgatum* L., *Lolium perenne* L., and *Tripsacum dactyloides*) the best efficiency for stimulation of ATZ degradation in the rhizosphere showed *T. dactyloides* (eastern gamagrass), which was able to degrade 90% ATZ in its rhizosphere compared to 24% observed in soil without plants; the other tested species considerably enhanced ATZ degradation as well. Correlation was found between ATZ dealkylation and enhanced activities of β-glucosidase and dehydrogenase enzymes as well as hydrolysis of fluorescein diacetate. The tested plants, especially eastern gamagrass, were evaluated as species suitable to be incorporated into vegetative buffer strips for efficient ATZ removal, supporting degradation of the herbicide moved therein by surface runoff (Lin et al. 2011). The degradation of ATZ and SIM in herbicide-contaminated soil was faster with planted *Pennisetum clandestinum* compared to unplanted soil, achieving approx. 45% and 52% degradation of ATZ and SIM for 80 days, while in unplanted soil the corresponding degradation of herbicides was approx. 22% and 20%, respectively. Simultaneously, soil dehydrogenase activity and microbial biomass and soil dehydrogenase activity in soil with planted *P. clandestinum* increased about sevenfold compared to soil without plants. Moreover, the suspension of rhizosphere soil contaminated with herbicides degraded both tested herbicides in a mineral salt medium more effectively than the non-rhizosphere soil suspension (Singh et al. 2004).

Comparison of *L. perenne* and *F. arundinacea* grasses and *Hordeum vulgare* and *Zea mays* crops for removing ATZ from herbicide-contaminated soil (2, 5 and 10 mg/kg) 16 days after treatment showed that the investigated plants were able to reduce ATZ shoot concentration by 88.6–99.6% of the initial ATZ concentration compared to 63.1–78.2% reduction observed with unplanted soil. The tested plant tissues contained ATZ and its metabolites, DEA and DIA; the highest bioaccumulation of ATZ derivatives (up to 38.4% of the ATZ dose applied to soil) was observed with maize. Effective ATZ removal from soil can be associated with successful rhizosphere degradation/mineralization of herbicide by microorganisms or plant enzymes and its degradation within plants (Sanchez et al. 2017).

Sowing of ryegrass (22 kg/ha) after harvest of maize, which was treated post-emergently by ATR 500-Dow using a dose 2 L/ha, resulted in pronounced amelioration of ATZ degradation, improved agronomical properties of soil, and suppressed movement of herbicide due to rainfall. Such ryegrass intercropping strategy can considerably contribute to lower environmental contamination with ATZ in areas with intensive agronomical practices (Merini et al. 2012).

Resistant *Lolium rigidum* population collected from a triazine tolerant *Brassica napus* field from Western Australia, showing a low-level (approximately 3.0-fold) resistance to MTZ and ATZ, showed 2.3-fold greater ^{14}C-MTZ metabolism compared to susceptible *L. rigidum* plants. However, no differences were observed between sequences of the *psbA* gene of resistant and susceptible plants, and MTZ foliar uptake and translocation in both types of plants were comparable as well. MTZ resistance in *L. rigidum* can be due to enhanced MTZ metabolism involving cytochrome P_{450} monooxygenase (Ma et al. 2020).

Effective shortening of $t_{1/2}$ of PRO by 11.5 day was observed using vetiver grass (*Chrysopogon zizanioides* L.) hydroponically cultivated in the presence of herbicide for 67 days, whereby the removal of PRO followed first-order kinetics. TF value of PRO in day 67 reached a value of 0.11 (Sun et al. 2016). Switchgrass plants, which were cultivated in pots and treated with solution containing 4 ppm ^{14}C-ATZ, were after 4 days transplanted, and further 4 days were cultivated in pots with fresh sand. The amounts of parent ATZ in these plants showed a decrease, while the amounts of metabolites increased; CYA metabolite in a switchgrass was detected as well (Albright and Coats 2014).

The presence of *Pennisetum alopecuroides* (L.) considerably enhanced efficiency of ATZ degradation in laterite soils (51.46 vs. 15.22%) due to increased levels of bioavailable ATZ in rhizosphere. Both uptake of ATZ by plant roots and acropetal translocation from roots to shoots were limited. *P. alopecuroides* roots and its acropetal transfer from roots to shoots were restricted. However, ATZ speciation in rhizosphere and non-rhizosphere soil differed from each other due to decreasing pH values and organic matters in the rhizosphere (Lin et al. 2018). Italian ryegrass (*Lolium multiflorum* L.) was able to remove up to 30–40% of TBZ from aqueous solution containing up to 2.0 mg/L TBZ, although the herbicide adversely affected plant growth. Dose dependent activation of GST was observed in response to herbicide-induced stress. At exposure to 1 and 2 mg/L TBZ, ascorbate peroxidase activity was induced at the beginning of the experiment, but later showed a decrease or disappeared (Mimmo et al. 2015).

Due to the extensive root system, grasses are suitable for removing various types of contaminants, including pesticides, PAHs or heavy metals from environmental matrices. The most favorable grasses to clean soils containing organic contaminants, including herbicides, are those that are fast-growing, produce large biomass, can effectively metabolize or degrade these contaminants, and are tolerant to abiotic stresses. In addition, plant diversity, which stimulates microbial activity in soils, can also contribute to the mitigation of organic contaminants in grass soils. Thanks to the effective elimination of a wide scale of contaminants (both heavy metals and harmful organic compounds) through grasses, the multi-contaminated soils can be successfully remediated as well. Grass-planted buffer belts can effectively reduce herbicide runoff from fields.

2.5.2 Aquatic Plants

Macrophytes are aquatic plants growing in or near water, which colonize many different types of aquatic ecosystems, including lakes, wetlands, rivers, marine environments, etc. They are classified in three classes: floating, emergent, and submerged macrophytes. While floating macrophytes live exclusively on the surface of water bodies; and emergent macrophytes are attached with roots to the substrate occurring at the bottom of water bodies, but their leaves grow to or above the water surface; submerged macrophytes are steadily permanently submerged in water (Ekperusi et al. 2019). Mechanisms and applications of phytoremediation in engineered wetlands were overviewed by Zhang et al. (2010). Macrophytes belong to plant species frequently used for efficient decontamination of aqueous environment from herbicide residues (Akhtar et al. 2017; Li et al. 2019a; Papadopoulos and Zalidis 2019; Qu et al. 2017, 2020; Vieira et al. 2021a).

2.5.2.1 Freshwater Macrophytes

Qu et al. (2017) who investigated ATZ distribution and its phytoremediation by *Potamogeton crispus* and *Myriophyllum spicatum* in lake sediments found 6-fold higher ATZ absorption by sediments compared to soils; sediments planted with these submerged macrophytes achieved over 45 days ATZ removal >90% compared to 77.2 ± 2.12% observed with unplanted sediments. *P. crispus* and *M. spicatum* also significantly reduced the $t_{1/2}$ value of ATZ dissipation estimated in unplanted sediment (14.30 days) to 8.60 and 9.72 days, respectively, suggesting that these plant species are suitable to be used for remediation of ATZ-contaminated sediments. Qu et al. (2020) used sediments (unplanted as well as planted with *P. crispus* and *M. spicatum* macrophytes) from two lakes, Tangxunhu Lake (TL) and Honghu Lake (HL), contaminated with 2.0 mg/kg ATZ, and investigated the factors affecting the fate of herbicide. After incubation lasting 30 and 60 days, the TL sediments planted with *P. crispus* contained 0.61 ± 0.071 and 0.21 ± 0.05 mg/kg ATZ, while in those planted with *M. spicatum* 0.78 ± 0.087 and 0.34 ± 0.05 mg/kg ATZ was present. On the other hand, after 30 days in HL sediments planted with *P. crispus*, ATZ concentration of 0.54 ± 0.070 mg/kg was observed, while in those planted with *M. spicatum* it was 0.68 ± 0.10 mg/kg. Hence, the concentrations of ATZ in planted sediments were pronouncedly lower than 0.99 ± 0.16 mg/kg and 1.11 ± 0.14 mg/kg estimated in unplanted HL and TL sediments after 30 days. After 3 month the ATZ levels in both planted sediments were <0.040 mg/kg. Measurable levels of ATZ degradation products, HA, CYA, HA and biuret were observed from day 30 to day 60, however, after 3 months in TL sediment CYA and biuret, but in HL sediment only biuret was detected. The researchers also found that alkaline sediment showed a higher residual rate of ATZ, and ATZ concentration in the alkaline sediment interstitial water had 3-threefold higher ATZ concentration compared to this observed in acidic sediment interstitial water.

The aquatic plant *Hydrocotyle vulgaris* cultivated in hydroponic solution in the presence of 0.55 ± 0.013 mg PRO/L was able to remove up to 94.0% of herbicide in 30 days, achieving $t_{1/2}$ of PRO of 5.58 days, while the corresponding $t_{1/2}$ observed without *H. vulgaris* was 27.16 days. After 30 days the plant tissue contained ca. 22% of the initial herbicide concentration and 11.7% was degraded by the plant; as degradation products of PRO in hydroponic solution 2,4-diamino-1,3,5-triazine (Fig. 2.5) and in plant tissue CYA were estimated (Ni et al. 2018).

Uptake and bioaccumulation of ATZ and linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) by two hydroponically cultivated model aquatic macrophyte species, submerged species *Echinodorus horemanii* and free-floating species *Eichhornia crassipes*, were studied by Pi et al. (2017). The estimated whole-plant uptake rate constants for ATZ were 90.0 ± 8.3 L/kg and 38.4 ± 2.9 L/kg per day using *E. horemanii* and *E. crassipes*, respectively, whereas for linuron the whole-plant uptake rate constants were 76.2 ± 5.9 L/kg per day (*E. horemanii*) and 129 ± 9.4 L/kg per day (*E. crassipes*), respectively. On the other hand, elimination rate constants of ATZ and linuron in *E. horemanii* were 0.25 ± 0.02 and 0.35 ± 0.03 per day, while in *E. crassipes* the corresponding values achieved 0.25 ± 0.02 and 0.32 ± 0.02 per day, respectively. The steady state bioconcentration factors (BCF) of ATZ in leaf, root, and whole plant were 319 ± 23.3, 30.3 ± 2.5, and 259 ± 18.3 L/kg for E. *horemanii*, and 138 ± 12.5, 56.9 ± 4.3 and 106 ± 8.4 L/kg for *E. crassipes*, while those of linuron were 244 ± 19.6, 40.9 ± 3.0 and 214 ± 15.4 L/kg for *E horemanii*, and 222 ± 18, 432 ± 32.4 and 307 ± 21.7 L/kg for *E. crassipes*.

Potential of water lettuce (*Pistia stratiotes* L.) for phytoremediation of ATZ-contaminated waters was investigated by Vieira et al. (2021a). In plants exposed to 150 mg/L ATZ for 24 h enhanced ROS levels due to oxidation stress caused damages to cell membranes, increased the rate of electrolyte leakage in leaves, had adverse impact on photosynthesis, reduced the levels of assimilation pigments, and decreased CO_2 assimilation rate by ca. 55.81%. The estimated 24 h IC_{50} value was 123.89 μg/L, and the ATZ toxicity was pronouncedly alleviated by addition of 0.05 mg/L of sodium nitroprusside (SNP), a NO donor (IC_{50}: 199.93 μg/L). SNP also considerably improved *P. stratiotes* growth rate, which was suppressed by ATZ. Increased tolerance of water lettuce plants to ATZ in the presence of SNP was reflected also in higher uptaken ATZ amounts (8.0 vs. ca. 4.3 µg/g fresh weight) and higher BCF (28.8 vs. 55.2) and TF (0.17 vs. 0.9). In contrast to beneficial impact of SNP on ATZ stressed leaves, in the roots the combine treatment of ATZ and SNP resulted in an increase of mitotic index, suggesting that NO stimulated cell division, likely as a defense response to ATZ toxicity, aimed to replace the roots destroyed by herbicide with the formation of new root cells, and thus to ensure to the maintenance of root function. Addition of SNP clearly improved the efficacy of the phytoremediation of ATZ-contaminated aqueous environment.

ATZ amount absorbed by *M. spicatum*, a cosmopolitan species that primarily colonizes eutrophic waters, was 18.29-fold higher than the ATZ amount in sediments, the equilibrium being achieved after 15-day incubation, and ATZ concentration in plant achieved 30.67 ± 4.10 mg/kg. However, at prolongation of the exposure to 60 days the levels of herbicide in the plants decreased, suggesting that the degradation of ATZ exceeded its uptake by plant. Moreover, phytodegradation of ATZ in *M. spicatum* to HA, DEA, HA, CYA, DDA, CYA and biuret was observed. On day 15, in *M. spicatum*-grown sediment considerably higher levels of HA, CYA and biuret were observed than in unplanted sediment, suggesting that the plant stimulated ATZ degradation and removal through rapid dechlorination. The levels of CYA even pronouncedly exceeded those observed in unplanted sediment during the whole incubation period of 60 days; during this period DIA, DEA, and DDA were not detected in all the sediments during this period. Rhizosphere microorganisms contributed to ATZ degradation, whereby *M. spicatum* growth contributed to the increase of dominant sediment microbial populations, from which 41.08-63.43% were *Proteobacteria*. Considering that among the genera of ATZ-degrading bacteria (*Acetobacter*, *Pseudomonas*, *Clostridium,* and *Burkholderia*) *Acetobacter* was predominant, it can be supposed to be responsible for rhizodegradation of ATZ (Qu et al. 2018).

In an experiment lasting 2 months, ATZ was eliminated faster in pots, in which submerged macrophytes, *M. spicatum* and *P. crispus* were cultivated than in unplanted pots, whereby ATZ was converted predominantly to DDA and HA. Submerged macrophytes are favorable as phytoremediators because they can absorb ATZ, resulting in remediation of the contaminated sediment and water (Li et al. 2019a). Bouldin et al. (2006) investigated ATZ uptake and accumulation in hydroponically cultivated *Juncus effusus* (perennial herbaceous flowering plant) and *Ludwigia peploides* (floating primrose-willow) at concentrations, which were estimated based on calculation using recommended field applications, and considering a 5% runoff model from a 0.65-cm rainfall event on a 2.02 ha field. After 8 h and 24 h, *J. effusus* absorbed by roots 75.4 and 86.8% ATZ, respectively, and the total ATZ uptake by plant after 8 days achieved 14697.1 µg/kg; herbicide distribution throughout the plant was as follows: 37% (adsorbed), 32% (roots) and 32% (upper biomass). On the other hand, ATZ uptake from hydroponic solution by *L. peploides* after 8 h was distributed as follows: 30.2% (adsorbed), 40.4%, (roots) and 29.4% (upper biomass), and after 48 h plant upper biomass contained 4980.2 µg ATZ/kg.

Lemna gibba and *Azolla caroliniana* plants hydroponically cultivated in the presence of 10.0 mg/L ATZ were able to remove ATZ from the solution; in the removed amounts achieving 0.016 and 0.018 mg ATZ/g per gram of fresh mass, respectively, probably due to ATZ adsorption by dead plant material, because high herbicide doses were toxic and caused chlorosis and necrosis (Guimaraes et al. 2011).

Investigation of short-term accumulation of ATZ by *Typha domingensis*, *Sagittaria lancifolia*, and *Echinochloa pyramidalis* from a wetland model system showed that the plant roots accumulated 40% of herbicide, while 30% were accumulated in soil and 10-20% in water. Beside the applied ATZ concentration, the accumulation was found to depend on the plant species. At treatment with 30 ppm ATZ, the accumulated amounts of ATZ in roots of tested plants were ca. 7.5 mg/kg for *E. pyramidalis*, and ca. 10 mg/kg for *T. domingensis* and *S. lancifolia*, respectively (Cejudo-Espinosa et al. 2009). *Typha latifolia* L. in constructed wetland microcosms efficiently remediated TBZ herbicide, whereas increasing levels of its degradation products (desethylterbuthylazine and DIA) were detected in surface water. Between the investigated plant densities of 10 and 30 rhizomes/m^2, the higher plant density contributed to a more efficient reduction of herbicide (7.3 vs. 23.4%); the $t_{1/2}$ value related to the rate of reduction of herbicide was achieved within 30 days compared to the 61 days observed with lower plant density. The accumulated TBZ in *T. latifolia* foliage was 2.96-fold higher than in the roots (3219.5 vs. 1088.6 ng/g) (Papadopoulos and Zalidis 2019).

Although all three types of macrophytes can be used to remove herbicides from aquatic environments contaminated with herbicides, for sites with highly contaminated sediments, submerged and emerging aquatic plant species are preferred that are anchored with roots to the substrate occurring at the bottom of the water bodies and can degrade herbicides persisting in the sediment; consequently, the herbicides occurring in sediment cannot be released back into the water. However, it is desirable to minimize the entry of herbicides into rivers and lakes by avoiding overuse of herbicides and by implementing of vegetated buffers, vegetated ditches, etc., pronouncedly reducing the loss of herbicide runoff from crop fields.

2.5.2.2 Seaweeds and Seagrasses

Seaweeds and seagrasses are marine macrophytes forming the predominant part of the photosynthesizing biomass in coastal habitats. For the coastal ecosystem, a great risk represents industrial discharge and agricultural runoff, resulting in accumulation of harmful organic contaminants. Seaweeds and associated microbiomes can play a crucial role in remediation of aquatic ecosystem (Haynes et al. 2000; Alam 2021; Barot and Kumar 2021). For example, *Sargassum* spp. can be utilized as ecological filter for elimination of organic and inorganic pollutants (Lopez-Miranda et al. 2020), and bioremediation potential of biomass of these brown seaweeds can be used for remediation of coastal ecosystems (Saldarriaga-Hernandez et al. 2020). The bioaccumulation of organochlorine pesticides in seaweeds decreased in the order of *Sargassum wightii* (Pheophyta) > *Gelidiella acerosa* (Rhodophyta) >

Gracilaria verrucosa (Rhodophyta) > *Ulva lactuca* (Chlorophyta) (Sundhar et al. 2020). *Laminaria* sp. (brown seaweed) was able to remove and degrade phenanthrene and pyrene in its tissues via the enzyme-oxidation process (Wang and Zhao 2007), and green seaweed *Ulva rigida* removed polychlorinated biphenyls PCBs contained in sediments (Cheney et al. 2014).

Seaweeds could also be used for the remediation of the environment contaminated with toxic metals and serve as indicators of heavy metal contamination, because the metal content accumulated in seaweeds often correlates with its content in surrounding seawaters and sediments (Malea and Kevrekidis 2014; Chalkley et al. 2019; Sun et al. 2019a; Bonanno et al. 2020; Jampílek and Kráľová 2021).

Investigation of marine seaweeds *Ulva* sp. and *Codium fragile* grown in the near shore marine environment of an urban setting (Camps Bay, Cape Town, South Africa) for their potential to accumulate SIM and ATZ showed BCF (L/kg) values for SIM of 20,141 (*Ulva*) and 20,822 (*Codium*), respectively; while for ATZ the estimated BCF values were 11,423 (*Ulva*) and 14,899 (*Codium*), respectively. As both seaweeds showed BCF > 5000 L/kg, they could be considered as bioaccumulative. Whereas concentration of both herbicides in the marine sediment was approx. 24 ng/g, the concentrations of SIM achieved 84.2 ng/g d.w. in *Ulva* and 87.0 ng/g d.w. in *C. fragile;* the concentrations of ATZ were ca. 24 ng/g d.w. in *Ulva* and 28.2 ng/g d.w. in *C. fragile.* It could be emphasized that consumption of edible seaweeds originating from herbicide-contaminated environment can adversely affect human health. The evaluated hazard quotients reflecting the non-carcinogenic effect due to long-term exposure to herbicides were 0.2 for ATZ (for both seaweeds), while for SIM they achieved values of 4.7 (*Ulva*) and 4.9 (*Codium*), respectively, suggesting that SIM can pose adverse health effects. The carcinogenic risk assessment also confirmed pronouncedly higher risk of SIM compared to ATZ (0.110 vs. 0.011 for *Ulva* and 0.114 vs. 0.015 for *Codium*) (Ojemaye et al. 2020).

Carafa et al. (2009) implemented, calibrated, and validated a bioaccumulation model to predict concentrations of ATZ, SIM, and TBZ in the macroalga *U. rigida*, and compared simulated data with experimental data obtained from samples originating from the Sacca di Goro lagoon (Northern Adriatic). This model was able to predict properly the concentrations of herbicides detected in *U. rigida.*

Rodrigues et al. (2018) studied the spatial and temporal occurrence of the pesticides, including ATZ and TBZ herbicides in the River Mondego estuary (Portugal), and determined their amounts in surface water, and sediment, as well as in macroalgae (*Ulva* sp., *Gracilaria gracilis*, *Fucus vesiculosus, Gracilaria gracilis*, *Ulva* sp.) and aquatic plants (*Zostera noltii, Spartina maritime, Scirpus maritimus, Spartina maritime*, *Zostera noltii*). Bioaccumulated ATZ in *G. gracilis* achieved a value of 20 ng/g and bioaccumulated TBZ in *Ulva* sp. was 149 ng/g d.w. TBZ herbicide was detected in *Ulva* sp. in August, suggesting a seasonal impact; a spatial gradient concerning this herbicide was also observed. It could be mentioned that bioaccumulated amounts of TBZ in *Ulva* estimated in two sampling stations (108 ng/g and 149 ng/g d.w., respectively) exceed the maximum residue levels for algae (50 ng/g) established by Commission Regulation 149 of the European Parliament and of the Council (2008). On the other hand, in three tested aquatic plants the pesticides exceeding quantification limits of respective method quantification limits were not detected.

Seagrasses, the flowering plants grown in marine environment are also endangered by harmful contaminants, which can accumulate in their tissues (Olisah et al. 2021). Concentrations of herbicides are usually highest near seaside and in the vicinity of seagrass meadows, showing no tolerance to PS II herbicides. Chronic exposure of seagrasses to these herbicides causes a decline in photosynthesis and results in reduced growth and survival (Flores et al. 2013; Negri et al. 2015; Wilkinson et al. 2015a, b). The transport of these herbicides through the leaf and hydrophobic semi-permeable cell membrane to reach their side of action is more facile for herbicides showing higher lipophilicity compared to less lipophilic ones (e.g., hexazinone) (Wilkinson et al. 2015a). Consequently, the phytotoxicity of individual PS II herbicides to seagrasses significantly differ each from other and, for example, diuron was found to exhibit approx. 8-fold higher potency than ATZ (Flores et al. 2013).

Eelgrass (*Zostera marina* L.) is the most distributed seagrass in temperate waters in coasts of both the Pacific and Atlantic oceans in the Northern Hemisphere. Exposure of *Z. marina* L. to ATZ (1, 3 and 10 μg/L) for one month reduced its photosynthetic efficiency, increased the N content and reduced C:N ratio of leaf tissue. Whereas the levels of carbohydrates as well as intermediates of tricarboxylic acid cycle (glucose, sucrose, mannose, and maltotriose) were reduced, the levels of γ-aminobutyric acid increased, which can be related to the oxidative stress generated by the PET inhibition in PS II caused by ATZ. At exposure to ATZ also the levels of 1-aminocyclopropane carboxylic acid, which functions as a signaling molecule, were enhanced (Gao et al. 2019). Pollution by diuron and nitrate was reported to increase the sensitivity of *Z. marina* seagrass to infections with *Aplanochytrium* sp. and *Labyrinthula zosterae* causing seagrass wasting-type disease, resulting in a decline of seagrass meadows (Hughes et al. 2018). Increased phytotoxic impact on the tropical seagrass *Halophila ovalis* was also observed at its exposure to diuron at temperatures differing from the thermal optimum (31 °C) for photosynthetic efficiency (Wilkinson et al. 2017). Similarly, co-exposure of the *Z. marina* to high temperatures ($\geq$31 °C) and ATZ resulted in more harmful impact to eelgrass than treatment with individual stressors (Gao et al. 2017).

Although concentrations of triazine herbicides ranging from <10 to 440 ng/L, which were observed in a tropical coastal area in China (the northeast coast of the Island Hainan), do not present acute toxic impact on seagrass beds, at long-term chronic exposure combined with rising sea surface temperature, damaging effects on seagrasses could not be excluded (Dsikowitzky et al. 2020). Although seaweed and seagrass play a key role in remediation of coastal aquatic ecosystems by accumulating heavy metals and accumulating/detoxifying harmful organic compounds, including herbicides from agricultural runoff, careful levels of toxic compound residues need to be closely monitored, especially for consuming species of seagrass and seaweed, which must not exceed the maximum permitted levels. The selection of the most appropriate species of seaweed/seagrass for certain contaminated sites must be made on the basis of their remediation efficiency with respect to the predominant contaminants. Planting coastal forests with efficient species of phytoremediators could also make a significant contribution to reducing the entry of herbicides into coastal aquatic ecosystems.

2.5.3 Algae and Cyanobacteria

Algae are photosynthesizing organisms living in all aquatic ecosystems (freshwater, saltwater, and brackish water) and producing ca. 50% of all oxygen on Earth. As primary producers, they represent the basic level of aquatic ecosystem trophic pyramid (Chapman 2013). Many synthetic pollutants and toxic metals present in marine and freshwater environment adversely affect algae at both cellular and molecular levels, ultimately resulting even in their death, which might have dramatic consequences on the remaining ecosystem. On the other hand, algae can accumulate or degrade contaminants and can therefore be used to phytoremediation; and they purify a contaminated aquatic environment via degradation, immobilization, adsorption, bioaccumulation, and co-metabolism (Masarovičová et al. 2010b; Kumar and Singh 2017; Kráľová et al. 2019; Usmani et al. 2022; Kráľová and Jampílek 2021). Besides pesticide removal, algae and cyanobacteria can remediate wastewater and remove nutrients from municipal and industrial sources (Subashchandrabose et al. 2013; Pacheco et al. 2015; Brar et al. 2017; Yu et al. 2019; Liu and Hong 2021; Mohsenpour et al. 2021), and they can contribute to restoring of salt-affected environmental matrices as well (Li et al. 2019b; Rocha et al. 2020; Vo et al. 2020; Gao et al. 2021; Mohseni et al. 2021). Metabolic mechanisms responsible for the removal of pesticides by microalgae and methods used to improve this removal ability were discussed by Nie et al. (2020).

In *Chlorella vulgaris* algae exposed to ATZ for 4 and 8 days, it was found that the herbicide damaged RC of PS II, and inhibited PET at the oxidizing and reducing sides of PS II, and can influence absorption, transfer, and utilization of light energy (Sun et al. 2020). *Cyanobacterium Microcystis novacekii* grown in WC culture medium supplemented with ATZ was able to remove 27.2% ATZ from the culture supernatant, and low level of degradation (<9% at a dose 500 μg ATZ/L) suggested efficient ATZ bioaccumulation by cyanobacterium. At tested ATZ doses (50–500 μg/L), the culture medium did not contain ATZ metabolites, and *Microcystis novacekii* also showed superb tolerance to ATZ reflected in IC_{50} (96 h) of 4.2 mg/L, suggesting that this cyanobacterium could be used for remediation of herbicide-contaminated surface waters (Campos et al. 2013). On the other hand, *Scenedesmus obliquus* and *Microcystis aeruginosa* exposed to ATZ for 6 days practically did not reduce ATZ concentration in culture medium and ATZ degradation by these species was also negligible.

At exposure to ATZ, the BCFs related to algal dry mass for green algae decreased as follows: 324.1 ± 10.7 (*Pediastrum* sp.) > 175.4 ± 7.4 (*Chlamydomonas* sp.) > 172.7 ± 11.7 (*Chlorella* sp.) > *Scenedesmus quadricauda*, while for diatoms they decreased in the following order: 45.5 ± 2.7 (*Synedra radians*) > 42.2 ± 1.9 (*Synedra* *acus*) > 40.9 ± 2.2 (*Cyclotella gamma*), and 8.0 ± 0.9 (*Cyclotella meneghiniana*); higher BCFs were found to be associated with enhanced ATZ sensitivity. Similarly, ATZ accumulation in green algae, Chlorophyta (5.43–12.73 ng/mg) was found to be considerably higher than in diatoms (5.43–12.73 ng/mg vs. 0.33–1.69 ng/mg). High correlation was found between algal cell biovolume and surface area and ATZ accumulation effectiveness of algal cells. Despite considerably higher ATZ concentrations levels in the algal cells compared to that observed in medium, ATZ removal from solution by algae was only 1–3% (Tang et al. 1998).

González-Barreiro et al. (2006) reported that cyanobacterium *Synechococcus elongatus* exposed to 0.25 and 0.75 μM ATZ in culture medium was able to remove 80 and 70% ATZ, respectively, from the medium at 12 h and similarly, this cyanobacterium exposed to terbutryn (TBR; *N*-*tert*-butyl-*N*′-ethyl-6-(methylsulfanyl)-1,3,5-triazine-2,4-diamine) removed >80% of this herbicide from solution at 12 h of exposure. The maximum accumulated amounts of tested herbicides were 9 μmol ATZ/g d.m. observed after 12 h of culture, and 12 μmol TBR/g d.m. after 18 h of culture. On the other hand, the maximum accumulated amounts of these herbicides by *C. vulgaris* were 11 μmol ATZ/g d.m. (after 12 h) and 12 μmol TBR/g d.m. (at 18 h of culture). Whereas ATZ and TBR did not affect algal cell viability in *C. vulgaris,* the viability of *Synechococcus elongatus* in the presence of TBR showed a strong decrease but the herbicide was maintained in cells and was not released to medium suggesting that cells were no viable. Consequently, it can be assumed that in contrast to *C. vulgaris*, which maintained their cellular integrity, *S. elongatus* lost it.

At exposure of *Chlamydomonas mexicana* algae to 10, 25, 50, and 100 μg/L ATZ for two weeks, reduction of herbicide concentration in medium by 41%, 30%, 18%, and 20% was observed, suggesting ATZ accumulation by algal cells. At day 6 of exposure to 10, 25, 50, and 100 μg/L ATZ, herbicide bioaccumulation of 0.41, 0.39, 0.62, and 0.52 μg/g fresh weight of cells was observed, however with prolongation of exposure, after 14 days 36%, 25%, 14%, and 16% ATZ degradation was observed. Consequently, despite adverse impact of ATZ on the growth of *C. mexicana*, due to its ability to accumulate and simultaneously also degrade this herbicide, this algal species is a good candidate for remediation of ATZ-contaminated water. It could be mentioned that at low ATZ concentration (10 μg/L) the content of polyunsaturated fatty acids in *C. mexicana* decreased, likely due to protective adaptation of microalga, but at high herbicide concentrations showed an increase, suggesting cellular damage (Kabra et al. 2014).

In the presence of 5 and 50 μg/L ISO, the cultures of green algae *Chlamydomonas reinhardtii* bioaccumulated it in algal cells with BCFs of ca. 280 and 50, respectively, while at exposure to 25 μg/L ISO, the BCFs estimated on day 1 and 6 of cultivation were ca. 30 and 135.7, respectively. *C. reinhardtii* was also able to degrade ISO, whereby at exposure to 25 μg/L and 50 μg/L ISO for 3 days, the algae degraded 6.3 and 15.1% of herbicide accumulated in algal biomass, suggesting that the ratio of ISO degradation showed an increase with increasing bioaccumulated herbicide amount. However, it could be mentioned that the application of increasing concentration of ISO resulted in increasing inhibition of algal growth and increased the level of oxidation stress, which was accompanied by up-regulation of several genes encoding antioxidant enzymes and increased levels of thiobarbituric acid reactive substances (Bi et al. 2012). Jin et al. (2012) investigated bioaccumulation and catabolism of PRO in *C. reinhardtii* using PRO concentrations ranging from 2.5 to 12.5 µg/L. The BCF values decreased with increasing herbicide concentration from ca. 750 to ca. 210 at 2.5 and 12.5 µg/L PRO, respectively, and the highest accumulated amount of 1.47 mg/kg fresh weight was observed on day four of the exposure. After incubation also lower amounts of PRO were estimated in medium with algal cells compared to control. On day 5, PRO accumulated in algal cells showed a decrease <50%, suggesting simultaneous accumulation and degradation of herbicide.

Beaulieu et al. (2020b) reported that current national environmental guidelines and standards cannot sufficiently prevent unfavorable impact of PS II-inhibiting herbicides, ATZ and diuron, at environmentally relevant concentrations on phytoplankton cultures and communities. Hu et al. (2021) performed photocatalytic degradation of ATZ lasting 60 min, resulting in degradation of 31.4% of ATZ, providing DIA, DEA, and DDA degradation products, and then the researchers cultivated *C. vulgaris* algae in such diluted degraded solutions containing 40 µg/L and 80 µg/L of ATZ as well as its degradation products DIA, DEA, and DDA; after 8 days, 83.0% and 64.3% ATZ removal was estimated. *Chlorella* sp. cultivated in degraded ATZ solution was characterized with lower removal efficiency and growth rate compared to that of pure ATZ solution having the same concentration. Pronouncedly lower values of performance index on absorption basis observed with algae cultivated in degradation ATZ solution compared with pure ATZ indicated possible inhibitory impact of degradation products on *C. vulgaris*. Both ATZ and its degradation products inhibited photosynthesis in *C. vulgaris*; they reduced light absorption, inhibited PET, and caused a decrease in utilization of light energy via energy dissipation.

The assessed total concentrations of ten triazine herbicides of 6.61 nmol/L, which exceeded the "no observed effect concentrations" for phytoplankton in the Bohai Sea and the Yellow Sea in (China), were assessed as 6.61 nmol/L, and inhibited fluorescence intensity of Chl*a* in *Phaeodactylum tricornutum* Pt-1 by 13.2%, which corresponded approximately to the toxicity caused by ATZ dose of 14.08 nmol/L. ATZ remarkably disturbed multiple metabolic pathways related to photosynthesis and carbon metabolism, which can adversely affect the primary productivity of coastal waters. Based on BCFs estimated for ATZ, which were in the range of 69.6-118.9, it could be supposed that herbicide contamination can have negative impact on marine food web and eventually endanger the seafood safety (Yang et al. 2019).

At exposure of living *C. vulgaris* to 2 µg/L mixture of ATZ and ISO for one hour using stirring, the biosorption efficiency of 85.60–88.15% was observed, although at application of lyophilized algal biomass it achieved even 96-99%. However, in long-term study lasting 5 days, the growing algae were able to remove up to 96.5% and 95.7% of SIM at the initial herbicide SIM concentrations of 2 µg/L and 10 µg/L, respectively; effective removal of ATZ and ISO exceeding 90% was observed as well. The bioremoval of herbicides in the short-term experiment of 60 min occurred likely by biosorption, while in the long-term experiment combine mechanism of herbicide removal can be supposed, involving biosorption as well as metabolization of ATZ and its degradation mediated by algae (Hussein et al. 2017).

Several species of algae cannot only effectively accumulate heavy metals but can also degrade toxic herbicides and can therefore be used to remediate herbicide-contaminated waters. The growth of some algae, although they accumulate herbicides, is adversely affected and algae may die before they metabolize the herbicide to less toxic metabolites, which can pose a danger to the marine food chain. Therefore, species of green algae and cyanobacteria that are more resistant to herbicides and have an effective detoxification mechanism are suitable for application in herbicidal/contaminated waters.

2.5.4 Woody Species

Fast-growing trees commonly used in short-rotation coppicing could be effectively used for phytoremediation of soils containing inorganic and organic contaminants, whereby tree planting is also beneficial for land restoration (Masarovičová and Kráľová 2017, 2018; Gomez et al. 2019; Kanwar et al. 2020). Fast-growing tree species such as poplars and willows characterized by high water use can reduce mobility of contaminants and stabilize the contaminated substrate. Moreover, they can stimulate degradation of organic contaminants via root exudates and promote microorganisms present in the rhizosphere (Marmiroli et al. 2011; Robinson and McIvor 2013; Coninx et al. 2017). Ability of *Populus nigr*a L. to detoxify chloroacetanilide herbicides *via* glutathione conjugation was reported by Komives et al. (2003). Fast-growing woody species producing high biomass yields in a short period could also be used for effective phytoremediation of heavy metal-contaminated areas (Marmiroli et al. 2011; Liu et al. 2013; Masarovičová and Kráľová 2017, 2018; Abdelsalam, et al. 2019; El Rasafi et al. 2021; Nissim et al. 2021; Qu et al. 2021). Potential for the phytostabilization of heavy metals such as Cu, Cr, Ni, Cr, Cu, and Pb in the riparian zone of the Sava River showed also *Ulmus glabra* Huds, which transported most of the accumulated Cu and Zn to the leaves (Mataruga et al. 2020).

Uptake, hydrolyzation, and dealkylation of ATZ to less toxic metabolites by poplar using ^{14}C-ATZ were investigated by Burken and Schnoor (1997) who found that ATZ metabolism occurred roots, stems, and leaves of poplar plants, and increased residence time in tissues contributed to more complete metabolism. When poplar cuttings were exposed to herbicide for 50 days, in leaves only 21% of the ^{14}C label was detected, and after 80 days, this portion decreased to 10% of the ^{14}C label. Although *Populus* sp. was mostly investigated as an effective phytoremediator of metal-contaminated soils, the ability of poplar cuttings to take up, hydrolyze, and dealkylate ATZ to metabolites showing lower toxicity was reported also by Chang et al. (2005). These researchers found that ATZ metabolism in plant organs advanced with the prolongation of the residence time in the tissues. Hybrid poplar (*Populus deltoides x nigra*, DN34) can be considered as an appropriate tree species for remediation of ATZ-contaminated soils . The faster degradation of ATZ in rhizosphere soil than in non-rhizosphere soil can be associated with higher abundance of bacteria in the rhizosphere microenvironment of hybrid poplar, while in non-rhizosphere microenvironments ATZ showed adverse impact on the microbial biomass (Yao et al. 2019).

Brazilian trees species *Calophyllum brasiliense, Eremanthus crotonoides, Calophyllum brasiliense*, *Inga striata*, *Hymenaea courbaril*, *Inga striata*, and *Protium heptaphyllum* were tested on their ability for phytoremediation of soil contaminated with ametryn (AMR; *N*-ethyl-6-(methylsulfanyl)-*N*'-(propan-2-yl)-1,3,5-triazine-2,4-diamine) and hexazinone (HXZ; 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione), whereas *C. brasiliense* and *H. courbaril* were found to be tolerant to both herbicides, and *P. heptaphyllum* showed tolerance only to AMR. On the other hand, *E. crotonoides*, *I. striata*, and *P. heptaphyllum* did not survive when exposure to HXZ. Comparison of mean AMR residual found in control soil without plants (9.0 ng/g) and in soils with planted trees 80 days after application of herbicides showed 57.7 ng/g for *H. courbaril*, 14.23 ng/g for *P. heptaphyllum*, 5.02 ng/g for *I. striata*, 2.24 ng/g for *C. brasiliense,* and 2.42 ng/g for *E. crotonoides*; mean HXZ residual in soil was 14.35 ng/g for *C. brasiliense* and 20.87 ng/g for *H. courbaril*, while for the control a concentration of 11.89 ng/g was detected. As the best tree species suitable for remediation of soils containing the above-mentioned PS II herbicides, *C. brasiliense* was evaluated (dos Santos et al. 2018). dos Santos et al. (2020) investigated tolerance to ATZ and remediation potential of some trees (*Inga edulis* Mart., *Myrsine gardneriana* A.DC., *Schizolobium parahyba* (Vell.) Blake. *Myrsine gardneriana* A.DC., *Schizolobium parahyba* (Vell.) Blake, *Toona ciliata* M. Roem., *Trichilia hirta* L., and *Triplaris americana* L.) irrigated monthly with ATZ solutions (1000 g/ha) and found that saplings of *M. gardneriana*, *I. edulis*, *S. parahyba*, *T. ciliate*, *S. parahyba*, and *T. hirta* tolerated ATZ, while intoxication was observed in *S. parahyba* and *T. americana*. Treatment with ATZ enhanced the biomass for *T. hirta*, impaired growth and biomass in *T. americana* but did not affect these characteristics in the rest of tested plants. Common riparian forest species, *Cecropia hololeuca* Miq and *Trema micranta* (L.) Blum grown in soil microcosms and treated with ATZ at the bottom of the microcosm using a dose corresponding to a 1/10 of the field-recommended dose, were able to take up 45% (*C. hololeuca*) and 35% (*T. micrantha*), respectively, from the applied herbicide.

ATZ was bioaccumulated mainly by thick, fine roots, and leaves, and higher ATZ mineralization was observed in planted microcosm compared to that without plants (102 vs. 1.2%) (Bicalho and Langenbach 2012). Among investigated riparian forest species, *C. hololeuca* and *T. micranta*, which were cultivated in microcosms supplemented with ^{14}C-tebuthiuron (1-(5-*tert*-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea), seedlings of *C. hololeuca* showed high survival and high herbicide uptake of 45±5%, in contrast to *T. micrantha*, which was characterized with low survival rate and not even a half uptake (45±5% vs. 20±7%) and low survival rate.

High radioactivity estimated in the first fallen leaves of *C. hololeuca* but low radioactivity levels in fallen leaves at the end of the experiment suggested that plant detoxified the contaminant by discarding it via leaf fall. While after 78 days only 0.9% of the applied herbicide was mineralized in both species and no metabolites were detected, it can be concluded that tebuthiuron is not easily biodegradable and persists in the environment for long time (Bicalho and Langenbach 2013). *C. hololeuca* and eucalyptus were able to remediate ATZ-contaminated soils (Red-Yellow Latosol and Quartzarenic Neosol soil), while *Hymenaea courbaril* was effective phytoremediator in the Quartzarenic Neosol soil. In these experiments eucalyptus was found to be the most tolerant species to ATZ (Heemann et al. 2018).

Short-rotation willows were successfully used to filter/degrade ATZ and ethylene urea occurring in groundwater flowing out of an apple orchard, and concentrations of herbicides in the willow plots were lower than in the control, while concentration of DEA metabolite was higher in the willow plots (Lafleur et al. 2016).

Whereas a riparian 60 m woody buffer zone consisting predominantly of trees with a height of 15–20 m such as *Anadenanthera colubrina*, *Sebastiania commersoniana*, *Anadenanthera colubrina, Vernonia discolor*, *Jacaranda puberula*, *Syagrus romanzoffiana*, *Jacaranda puberula*, *Ilex theezans*, *Cedrela fissilis, Ocotea porous*, *Ocotea odorifera*, and *Tabebuia alba* was able to remove fluazifop-*p*-butyl (butyl (2*R*)-2-(4-{[5-(trifluoromethyl)pyridin-2-yl]oxy}phenoxy)propanoate) lactofen (1-ethoxy-1-oxopropan-2-yl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate) and fluazifop-*p*-butyl (butyl (2*R*)-2-(4-{[5-(trifluoromethyl) pyridin-2-yl]oxy}phenoxy)propanoate) herbicides to non-detectable levels, for ATZ a residual level of 0.3 μg/L was detected (Aguiar et al. 2015). *Caesalpinia ferrea*, *Cedrela fissilis*, *Schinopsis brasiliensis,* and *Handroanthus serratifolius* forest species were found to be not appropriate for removal of ATZ and 2,4-dichlorophenoxyacetic acid herbicides at conditions simulating riparian region near cultivated lands, while *Inga marginata*, which was tolerant to ATZ, was able to reduce its amounts in the soil (Fiore et al. 2019).

As above-mentioned, fast-growing trees are not only excellent phytoremediators of soils contaminated with heavy metals, but can also effectively degrade toxic organic contaminants, including herbicides, to less toxic compounds. A riparian forest buffer zone consisting mainly of trees can effectively reduce herbicide contamination in soils and the efficiency of decontamination can be increased by co-planting suitable grasses. Woody plants, such as willows and poplars, which can reduce the mobility of contaminants in soils, can stimulate the degradation of organic contaminants by root exudates; promote microorganisms present in the rhizosphere, and phytometabolize a significant part of the herbicide in their shoots. As a result, harvesting the above-ground part of willows several times during the season can increase the efficiency of phytoremediation and emphasize that these species can be successfully used to rehabilitate multi-contaminated soils containing heavy metals in addition to herbicides; in addition, the harvested biomass can subsequently be used for energy production.

2.5.5 Crops

Although herbicides are used to control the unwanted vegetation, they can also negatively affect growth and performance of crops. In addition, herbicides can be accumulated/degraded by herbicide tolerant crops cultivated on herbicide-treated areas. To avoid adverse impact of herbicides or their metabolites accumulated in edible parts of crops, their rigorous monitoring focused on the compliance with the permissible limits of herbicide content is necessary (Dong et al. 2016; Pecev-Marinkovic et al. 2019; Singh et al. 2020).

Analysis of spatial and temporal distribution of triazine herbicides in soils of agricultural regions of Liaoning (China) showed predominant occurrence of ATZ, SMZ, PRO, DEA, and DDA. However, despite a high prevalence, these herbicidal compounds were present at relatively low concentration. Maximum ATZ concentration in the soils was 73.80 μg/kg and maximum estimated ATZ content in maize was 12.52 μg/kg (Wang and Liu 2020).

Inoculating of *Pennisetum americanum* (L.) K. Schum with *Pseudomonas chlororaphis* PAS18 producing indole-3-acetic acid enhanced its tolerance against ATZ and attenuated ATZ toxicity, which was reflected in reduced ATZ accumulation in plants. While at application of 20 and 100 mg/kg ATZ the herbicide concentration in plant roots with inoculating strain was 0.74 ± 0.12 mg/kg and 1.77 ± 0.19 mg/kg, respectively, compared to 1.09 ± 0.11 mg/kg and 3.40 ± 0.33 mg//kg in roots without inoculation, in leaves of plants with inoculating strain, ATZ concentration achieved ca. 1 mg/kg at treatment with 20 mg/kg ATZ and was lower than that estimated in leaves of plants without inoculation. However, at application of 100 mg ATZ/kg, the leaf concentrations of both inoculated and non-inoculated plants contained only a little higher and comparable ATZ levels. The beneficial effect of *P. americanum* inoculation with *P. chlororaphis* PAS18 was reflected also in enhanced Chl content, increased activity of superoxide dismutase, and increased *psbA* gene expression, thereby improving the repair of the damaged PS II. Moreover, PAS18 strain regulated the flux of Ca^{2+} in inoculated plants and in this way also regulated the defense of the plant against stress induced by ATZ (Jiang et al. 2020).

In wheat plants hydroponically cultivated in the presence of 10 mg/L ATZ, the herbicide concentrations in plants organs increased within 6 h, and then decreased; at 48 h they achieved 2.86, 2.49 and 1.86 mg ATZ/kg in leaves, stems, and roots, respectively, suggesting upward translocation potential of ATZ. After 48 h, the BCFs of ATZ related to leaves, stems and roots were 0.424, 0.369 and 0.27 L/kg, respectively. During the first 12 h the $TF_{stem/root}$ and $TF_{leaf/stem}$ showed an increase with prolongation of the treatment up to 1.34 and 1.11, respectively, and then remained stable. The ATZ translocation was supported primarily by the relatively steady transpiration of tested wheat *Triticum aestivum* plants. ATZ concentration in root organelles pronouncedly exceeded ATZ concentration in the soluble fractions and was only insignificantly higher than that in cell wall. Higher ATZ adsorption by fresh roots compared to dead roots suggested that the ATZ root uptake occurred primarily via the symplastic pathway, and it was acropetally translocated. ATZ allocated predominantly in aerial plant part, which can threaten the product safety of wheat (Ju et al. 2020).

Glomus caledonium, an arbuscular mycorrhizal (AM) fungus, affected ATZ accumulation and metabolism in *Z. mays* plants grown and cultivated in soil contaminated and supplemented with 0.5, 2, and 5 mg/kg ATZ. Roots of mycorrhizal plants accumulated 132.4-260.5% more ATZ than non-mycorrhizal roots, whereby with increasing ATZ dose the accumulated ATZ concentration in both root types increased. On the other hand, at application of 0.5, 2, and 5 mg/kg ATZ, the accumulated herbicide concentration of inoculated shoots showed a decrease by 57.2, 31.3, and 55.5%, respectively, and thus, the shoots accumulated the lowest ATZ amount at application 2 mg/kg ATZ. Whereas in both soils (without and with *G. caledonium*) DEA and DIA metabolites were not detected, using ATZ dose of 5 mg/kg, their concentrations in mycorrhizal colonized roots were 2.6-and 3.8-fold higher compared to non-inoculated roots. Hence, *G. caledonium* contributed to improved ATZ degradation in roots. After harvest of maize plants the residual ATZ concentrations in soil considerably decreased with mycorrhizal treatment compared to non-inoculated treatment (73.7% vs. 31.4% at treatment with 2 mg/kg ATZ) (Huang et al. 2007).

Liu et al. (2017) investigated break down and accumulation of AMR in soils and in *T. aestivum*, *Zea mays*, *Lolium perenne*, and *Medicago sativa* plants. AMR concentration in rhizosphere soil of 4 tested species was lower than in non-rhizosphere soil, and represented 33.4% (alfalfa), 38.0%, (ryegrass), 55.4% (wheat), and 72.8% (maize) of that observed in non-rhizosphere soil, suggesting that in rhizosphere soil higher amounts of herbicide are degraded or absorbed by plant roots from soil. BCFs related to roots decreased in the order 2.876 (alfalfa) >2.193 (wheat) > 1.562 (ryegrass) > 0.500 (maize), while BCFs related to shoots decreased as follows: 2.172 (alfalfa) > 1.593 (wheat) > maize (0.330) > ryegrass (0.305). The TF value of 5.122 estimated for ryegrass was considerably higher than TFs of other plants (1.276 for alfalfa, 1.382 for wheat and 1.517 for maize). Thus, it can be supposed that ryegrass has a powerful degradation mechanism for AMR in roots and shoots, and its particularly high TF compared to other 3 tested plant species indicates potential of this plant to be used for AMR removal from soils. Moreover, it could be mentioned that the concentrations of low molecular weight organic acids such as citric acid, malonic acid, and malic acid (low molecular weight organic acids) in soils planted with ryegrass exceeded those observed with other tested plants. It can be supposed that exudation of organic acids from plant roots induced by AMR also remarkably contributed to the degradation of the herbicide. In ryegrass plants treated with AMR pronouncedly higher activities of catalase (CAT), laccase (LAC) and GST were observed compared to untreated plants, whereby a 28.84- and 6.16-fold increase of CAT activity in ryegrass *L. perenne* root and shoot over the control was observed. It can be supposed that similarly to findings reported for ATZ (Zhang et al. 2014), GST in ryegrass played a role involved in the degradation mechanism of AMR; in *L. perenne*, LAC can be involved in a defense or detoxification mechanism as well.

Rice mutants Osmet1-1/2, which was defective in the genomic CG DNA methylation, accumulated considerably less ATZ than the corresponding wild-types, and numerous differentially methylated loci, which were associated with activation of genes responsible for degradation of ATZ in rice plants, were detected. Based on the finding that demethylated loci OsGTF, OsHPL1, and OsGLH, which were expressed in eukaryotic yeast cells, reduced ATZ concentration in the medium by 48%, 43%, and 32%, respectively, it can be concluded that for the removal of ATZ in *Oryza sativa* plants activation of the loci mediated by ATZ-induced hypomethylation is responsible (Ma et al. 2019). ATZ uptake by rice plants and its degradation in plants were affected by abiotic stresses such as presence of arsenate or phosphate deficiency, which generated oxidative stress. In the presence of arsenate an increase of H_2O_2 content to 110-285% was accompanied with increased ratios of degradation products in shoots. Similarly, also in phosphate-deficient systems at low ATZ levels, considerable increase of H_2O_2 contents as well as in the ratios of DIA and DEA in shoots was observed (Chen and Su 2018).

During phytoremediation of ATZ-contaminated soil using *Pennisetum americanum* lasting 28 days, the plant was able to adjust soil, environment, and bacterial properties; rhizosphere soil of *P. americanum* was characterized with enhanced urease activity, CAT activity, and the content of water-soluble organic carbon content. Bacteria (*Rhizobium*, *Paenibacillus*, *Rhizobium*, *Mycoplana,* and *Sphingobium*) improving soil nutrient cycling and degradation of organic contaminants were only observed in rhizosphere soil (Cao et al. 2018).

Application of Triton X-100 surfactant and dissolved organic matter (DOM) reduced sorption and enhanced desorption of ATZ in soil and considerably stimulated ATZ mobility in soil and ATZ concentration in leachate of the soil column. ATZ accumulation in both roots and shoots of *Z. mays* L. plants cultivated in soil supplemented with 1.0 mg ATZ/kg and watered (relative water content of 60%) showed an increase with increasing surfactant concentration, while increasing amount of DOM was reflected in reduced ATZ levels (Tian et al. 2019).

Due to the possible accumulation of herbicides in the plant organs of crops intended for human or animal consumption, it is always necessary to estimate whether the non-metabolized amounts of herbicides and their degradation metabolites in the consumable plant organs do not exceed the permitted limits. On the other hand, crops which have an effective degradation mechanism for various herbicides, for example, through the exudation of organic acids from plant roots can be successfully used for remediation of matrices contaminated with herbicides. Unmetabolized amounts of herbicides allocated in roots of plants can be definitively removed after harvest of crops by plough-up.

2.5.6 Other Plants

Eremanthus crotonoides and *Inga striata*, which were used for phytoremediation of soils containing up to double concentration of ATZ recommended commercial dose, showed lower photosynthesis rate and fixation of CO_2 compared to uncontaminated soil, and were characterized with reduced physiological variables. However, these plants were able to reduce ATZ residues in soil, suggesting that they, when planted on ATZ-contaminated soil, can function as a filter preventing the entry of higher herbicide amounts into watercourses (Aguiar et al. 2020b).

In pots sprayed with 22.5 g/L ATZ before transplanting 15 days old *Amaranthus hybridus* and *Corchorus olitorius*, decreased ATZ concentration in soil from 4.66 mg/L (after 2 weeks of plant growth) to 1.96 mg/L at plant harvest after 2 months. BCF factors suggested effective ATZ uptake from soil by roots. In *C. olitorius* the highest BCFs were observed for the applied ATZ dose 90 g/L, reaching maximum value at day 15, and showing a strong decrease within the following period up to harvest. For *A. hybridus* the decrease of BCF with increasing time was moderate. The TFs were <1 in *A. hybridus*, suggesting higher ATZ accumulation in roots, while the TFs >1 estimated for C. *olitorius* indicated higher ATZ accumulation in leaves. The minimum ATZ concentrations detected in consumable leaves ranged from 0.22 mg/g d.m. in *A. hybridus* to 0.99 mg/g d.m. in *C. olitorius*, whereby the concentration of 0.22 mg/g d.m. corresponds to 19.8 mg/kg of wet mater and is >39000-fold higher than the tolerable daily intake of ATZ (0.0005 mg/kg). Consequently, it is necessary to exclude the use of ATZ at cultivation of these plants with edible leaves (Houjayfa et al. 2020).

Zhang et al. (2016) identified transcriptome involved in ATZ detoxification and degradation in alfalfa (*Medicago sativa)* plants. At exposure to ATZ considerable up-regulation of several genes encoding glycosyltransferases, glutathione *S*-transferases, glycosyltransferases, or ABC transporters, and differentially expressed genes involved in oxidation-reduction, conjugation, oxidation-reduction, and hydrolysis for of ATZ degradation were observed, indicating that for degradation and detoxification and degradation of ATZ in *M. sativa* alfalfa different pathways could be responsible.

At cultivation of *Canna indica* cultivated in nutrient solution containing 0.5 mg/L PRO, shortening of the dissipation half-life by 17 days was achieved compared to that without *C. indica*, and potential degradation of herbicide occurred between days 10 and 16 (Sun et al. 2019b). Inoculation with the arbuscular mycorrhizal fungus *Funnelliformis mosseae* mitigated the adverse impact of ATZ on growth, biomass, and Chl content of *C. indica*, and reduced the oxidative stress induced by herbicide. After exposure of untreated *C. indica* plants to ATZ for 14 days, 20.5–55.3% ATZ removal was observed, while at inoculation with *F. mosseae* it raised to 35.6–75.1% (Dong et al. 2017). Thiols-related protein genes from alalfa *Medicago sativa* plant, which were exposed to environment containing ATZ residues, were highly up-regulated, and most of differentially expressed genes was involved in regulation of responses to stresses; the detoxified forms of ATZ in plants were ATZ-thiols conjugates, cysteine (Cys) *S*-conjugate, ATZ-HCl+Cys (cysteine (Cys) *S*-conjugate), being the most important metabolite. Whereas under ATZ stress some conjugates were observed not only in alfalfa but also in rice plants, it can be supposed that both plants can share some detoxification mechanisms and pathways and that in detoxification of ATZ the low molecular weight thiols play a decisive role (Zhang et al. 2017b).

After 24 h of exposure of *Arabidopsis thaliana* plants to different doses of ATZ, HA and DEA and HA it was found that their root-level contamination affected early plant growth and development, whereby the involvement of distinct mechanisms showing direct impact on respiration and root development was suggested. Consequently, besides PS II also additional target points for these compounds could be assumed (Alberto et al. 2017). Improved phytoaccumulation of ATZ by *A thaliana* using sucrose amendment was described by Sulmon et al. (2007). Under natural conditions exposure of *Acorus calamus* and *Iris pseudacorus* to 4 mg/L ATZ did not affect their growth but the growth of *Lythrum salicaria* showed a decrease. These three plants were able considerably reduce ATZ concentration in a cultivation solution compared with solution without plants. In the hydroponic system the contribution of the plants/microbial populations to the degradation of ATZ was 76.6%/5.4% for of *I. pseudacorus*, 65.5%/11.4% for *L. salicaria* and 61.8%/17.4% for *A. calamus* (Wang et al. 2012).

The herbicidal nanoscale formulation of ATZ encapsulated in poly(ε-caprolactone), which was foliar applied to *Brassica juncea* plants, adhered to the leaf and penetrated into mesophyll tissue and was transported directly through vascular leaf tissue and into cells causing degradation of chloroplasts (Bombo et al. 2019). It could be mentioned that nanosized ATZ formulations can exhibit the same or higher herbicidal effect at lower applied dose than bulk herbicides, and thus, they contribute much less to environmental contamination (de Oliveira et al. 2015; Preisler et al. 2020). In general, plants suitable for phytoremediation of areas contaminated with herbicides must be sufficiently tolerant to the herbicides to be removed, and due to the effective detoxification mechanism, their consumable plant parts must be free of herbicide and its toxic metabolites. In addition, inoculation with appropriately selected microbial species/microbial consortium is favorable for increased herbicide degradation in soil and plant tissues.

2.5.7 Transgenic Plants

Transgenic plants contain artificially inserted gene/genes, whereby the new transgenic DNA targets the nucleus of the plant cell. Such genetically modified plants are characterized with insect resistance, herbicide tolerance, they are not sensitive to abiotic stresses, show resistance against plant diseases, ensure high yield, and can be used also for remediation of polluted environment (Rani and Usha 2013; Verma 2013; Fasani et al. 2018; Boechat et al. 2021; Sharma et al. 2021; Ojuederie et al. 2022). According to Maestri and Marmiroli (2011), for production of transgenic plants suitable for phytoremediation several approaches are possible such as (*i*) transformation with genes from mammals, bacteria, etc.; (*ii*) transformation with genes from other plant species; and (*iii*) overexpression of genes from the same plant species (Maestri and Marmiroli 2011).

Current findings related to engineered transgenic plants, which can be used in decontamination of environmental matrices contaminated with organic pollutants and heavy metals, were summarized by Fasani et al. (2018) and Boechat et al. (2021), whereby the researchers focused also on the ability of the rhizospheric microorganisms in maintaining diversity and functions in plant-soil ecosystem. In a chapter focused on the utilization of transgenic plants in phytoremediation of environmental matrices contaminated with toxic metals and metalloids, Gunarathne et al. (2019) also paid attention to the risks associated with their use. Because plants did not dispose the catabolic pathway enabling them completely degrade the herbicides, their potential ability for remediation of these harmful herbicides can be enhanced by transferring the genes involved in xenobiotic degradation from microbes/ or other eukaryotes to plants (Eapen et al. 2007). ATZ degradation with transgenic plants has been reviewed by Dhankher et al. (2011).

Whereas actual weed management uses pre-emergence herbicides with residual activity to ensure absence of weeds in the field already before crop establishment, due to increasing occurrence of resistant weed populations the selection of suitable herbicide sensitive to weed population is challenging. Therefore, the use of genetically modified crops possessing multiple herbicide-tolerant traits enabling application mixtures of herbicides, which would be toxic to conventional crops, can be considered as favorable (Liu et al. 2020b).

Transgenic plants of *A. thaliana* plants expressing CYP1A2 gene exhibited considerable resistance to SIM supplemented into growth medium or applied in form of spray on plant leaves and the herbicide treatment with SIM did not affect both primary root length and rosette diameter and primary root length. The transgenic *A. thaliana* plants showed tolerance up to 250 μmol/L of SIM, while wild type of *A. thaliana* plants was strongly injured already at treatment with >50 μmol/L SIM. Consequently, these transgenic *A. thaliana plants* expressing CYP1A2 gene can be used as potential phytoremediator for phytoremediation of SIM-contaminated environmental matrices (Azab et al. 2016).

Engineered rice plants overexpressing glycosyltransferase l (ARGT1), which is responsible for transformation of ATZ residues in plants, exhibited considerably higher tolerance to ATZ than the wild type. At exposure to 0.2-0.8 mg/L ATZ these engineered rice plants showed higher biomass and remarkably higher Chl content (36-56%) and lower membrane damage (up to 69%) and ATZ content in the grains (by 30-40%) than the wild type. In this transformed line 8 ATZ metabolites formed in Phase I reaction and 10 conjugates formed in Phase II reaction were detected, from which three ATZ-glycosylated conjugates were identified first time (Zhang et al. 2017a).

Introduction of the human cytochrome P_{450} CYP1A1 gene into *O. sativa* rice plants ensured them tolerance to 8.8 μM ATZ and 50 μM SIM and both herbicides were metabolized by the transgenic plants more rapidly compared to control plants.

Kawahigashi et al. (2005) performed small-scale experiments, in which the residual SIM and ATZ amounts in cultivation medium containing CYP1A1 transgenic achieved only 12.3 and 43.4% and 12.3% of SIM and ATZ amounts observed in control cultivation medium. On the other hand, residual amounts of ATZ and SIM in the medium when non-transgenic rice plants were used achieved 68.3 and 57.2% of the control. Transgenic rice plants with introduced human cytochrome P_{450} CYP1A1 gene were able to eliminate 1.3-fold and 1.4-fold more ATZ and SIM from the soil than the control plants.

Vail et al. (2015) studied the biodegradation of ATZ by transgenic grasses (tall fescue, perennial ryegrass, and switchgrass) (*Festuca arundinacea, Lolium perenne*, and *Panicum virgatum*) and *Medicago sativa* alfalfa expressing a modified bacterial ATZ chlorohydrolase gene (*p-atzA*). Resistance of plants cultivated on agar or in hydroponic solution to ATZ showed correlation with the levels of gene expression and ATZ degradation. Due to expression of *p-atzA* in transgenic *F. arundinacea*, ATZ was transformed into HA and other ATZ metabolites. The advantage of transgenic plants is more rapid metabolization of herbicides compared to control plants, and by combined transgenic plant-microbe remediation system herbicide removal efficiency can be considerably enhanced. In addition, to planting appropriate plant species, such as transgenic grasses, on herbicide-contaminated area that provide efficient biodegradation of herbicides, cultivation of transgenic crops characterized by rapid biotransformation of herbicides can help reduce environmental contamination by herbicides. However, it can be mentioned that many people avoid consumption of transgenic crops.

2.6 Electrokinetic-Assisted Phytoremediation

Electrokinetic-assisted phytoremediation, i.e., combination of low intensity electric fields and plants is an environment friendly method that can be used to remove pollutants from contaminated soils (Rodriguez et al. 2022). Sanchez et al. (2020) investigated electrokinetic-assisted phytoremediation of ATZ-polluted soils (2 mg/kg) in a mesocosm scale experiment lasting 19 days with continuous application of direct current electrical field (0.6 V/cm) without changing polarity and using *Lolium perenne* L. weed as model plant. The final distribution of water and ATZ in the soil was affected by electro-osmosis, gravity, and plant roots, and ATZ accumulated predominantly in the cathode section. In electrokinetic-assisted phytoremediation the removal of ATZ occurring by biochemical degradation was strongly improved in the presence of *L. perenne* plants achieving ATZ removal yield of 61.01% compared to 40.20% observed with unplanted soil.

The application of an electric field of 2 V/cm applied each 2 h during a period of 4 h a day and with the use of periodical polarity inversion (each 2 h) to ATZ-spiked soils (5 and 10 mg/kg), in which *Z. mays* plants were cultivated, slightly reduced the biomass of plants, and pronouncedly increased the ATZ accumulation as well as accumulation of main ATZ metabolites in plant tissues, achieving enhancement of

ATZ removal up to 36.5% compared to the phytoremediation process without application of electric field (Sanchez et al. 2018). Enhanced ATZ removal from soils and considerably enhanced ATZ accumulation in *L. perenne* (predominantly in shoot biomass) were also observed with continuously applied electric field (1 V/cm; 24 h per day); ATZ half-life value in the soil decreased significantly compared to control (5.4 vs. 8.4 days) as well (Sanchez et al. 2019).

2.7 Conclusion

To feed the increasing human population, efficient agricultural management using effective herbicides is essential to achieve high crop yields for safe food products. However, the benefits of using effective herbicides to provide improved crop yields are accompanied by the negative impact of persistent residues of toxic herbicides or their metabolites in environmental matrices on non-target organisms. PS II herbicides have been used extensively worldwide since the second half of the 20th century, but as the endocrine disrupting properties of simazine and atrazine have been confirmed, many countries, including the EU, have banned their use. On the other hand, some other herbicides from the PS II herbicide group have been largely replaced by others which show a different mechanism of action. However, residues of these herbicides and their metabolites in soils and sediments pose a permanent environmental risk and can also contaminate aqueous ecosystems. Therefore, their removal from environmental matrices is most desirable. In addition to methods using physical processes or chemical treatments to remove herbicides, microbial-supported phytoremediation is an excellent green, ecological, and inexpensive tool to significantly reduce residues of these herbicides in agricultural soils and waters. Strict adherence to regulations prohibiting the use of certain herbicides and monitoring of their residues in the environment is highly desirable. However, there are still countries, including some developed countries, which, for example, due to the excellent herbicidal activity of atrazine, continue to use it despite proven adverse health effects. In addition, the sale of banned herbicides with adverse effects on non-target organisms and human health from countries where they are banned to developing countries should also be stopped. Reduced contamination of environmental matrices with synthetic herbicides can also be achieved by applying their nanoscale formulations showing a comparable or better herbicidal effect than their bulk counterparts. However, prior to application, all nanoscale herbicidal formulations must be inspected for possible toxic effects on non-target organisms and appropriate rules for their use must be adopted. Due to the ongoing climate change, which may affect the bioavailability of herbicides to living organisms and increase the herbicide runoff from fields into rivers and lakes, in addition to careful monitoring of herbicide content in environmental matrices, their permanent and effective removal from soils and surface waters is desirable. In addition to the known active plant species, which function as phytoremediators, the search for other plant and microbial species suitable for phytoremediation of environments contaminated with toxic synthetic herbicides as well as the use of transgenic plants can increase the effectiveness of this environmentally friendly green technique in cleaning contaminated soils and waters.

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Chapter 3
Fipronil Microbial Degradation: An Overview From Bioremediation to Metabolic Pathways

Maricy Raquel Lindenbah Bonfá, Caio César Achiles do Prado, Francine Amaral Piubeli, and Lucia Regina Durrant

Abstract Fipronil is an insecticide that is widely used in several crops such as soybeans, corn, and sugar cane. Although it is used in a few countries, it has been banned due to its toxicity in some European countries such as France, Italy, Germany, and others. There are some papers describing fipronil degrading microorganisms and their applications in bioremediation. The bacterial enzymes and, consequently, the genes responsible for the oxidation or reduction of this compound have not been described yet, as it is the case for other pesticides. Thus, this chapter will present all the available information on fipronil biodegraders, bioremediation cases, and the metabolic pathways involved on its biodegrading. In addition to exploring the molecular, omics, and analytical methods necessary to elucidate, in the near future, the metabolic pathways and enzymes are responsible for the degradation of fipronil.

Keywords Pesticide · Biodegradation · Enzymes · Omics approach

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3.1 Introduction

Pesticides are widely used in large productive areas where monocultures are affected by pests and weeds. In this context of traditional production, there is a dependence on these compounds to increase agricultural productivity. However, indiscriminate use is often observed both from the point of view of the concentration and of the type of the pesticide used. As an example, we can mention countries such as Brazil, which still use products that are banned in several European countries, for instance, the insecticide fipronil.

This xenobiotic compound is also recalcitrant and has been shown to be toxic, causing both acute and chronic effects (Gibbons et al. 2015; Ali et al. 2016). The European Union has prohibited the use of fipronil on agricultural crops due to the toxicological and ecological risks of the compound and its metabolites. China has completely prohibited its use since 2009 (Li et al. 2020)

Although the toxic effects of fipronil have already been extensively studied in target and non-target organisms (Ali et al. 2016), research on the microbial biodegradation and behavior of this compound in the environment are limited (Zhu et al. 2004; Masutti and Mermut 2007; Kumar et al. 2012; Mandal et al. 2013, 2014; Uniyal et al. 2016a, b; Wolfand et al. 2016; Gajendiran and Abraham 2017; Cappelini et al. 2018; Abraham and Gajendiran 2019; At et al. 2019; Bhatti et al. 2019; Prado et al. 2021; Bhatt et al. 2021a, b).This chapter will address both the basic aspects of the molecule and its short- and long-term toxic effects, as well as the aspects of the molecule's biodegradation, metabolite formation, and known metabolic pathways. In addition, there is a lack of information on the description of the enzymes that is involved in the oxidation, reduction, and hydrolysis of the molecule. For this reason, the methods used for the study of the metabolic pathways will be described, highlighting the most recently applied omics studies.

Understanding the degradation pathways of fipronil is extremely important, since the metabolites formed as fipronil-sulfide, fipronil-sulfone, fipronil desulfinyl, and fipronil amide are more toxic than the parent compound. So far, the bacteria described as biodegrading fipronil oxidize or reduce the compound, as will be described in the chapter. The two fungi described to date as fipronil degraders produce other metabolites, probably because they have different enzyme pathways that are being elucidated.

It is interesting to note that although there are a greater number of studies with fipronil biodegrading bacteria, there is still no inference of enzyme complexes implicated in the metabolic pathways. Knowledge of the enzymes involved in a biodegradative process is important as more effective degradation can be induced through the application of systems biology and metabolomics tools. In addition, for bioremediation processes, immobilized enzymes can be used directly at the contaminated site. From the point of view of the evolution of omics tools, it would not be as complex today as in the past to describe the enzymes responsible for the transformation of fipronil and its metabolites as in the past. Transcriptomics and proteomics provide possible ways for the definition of the complete metabolic pathway of fipronil degradation, as we see for other toxic pesticides such as atrazine, which is described in the Kegg database (Kanehisa and Goto 2000).

This chapter will address the current state of research taking place in the area of microbially assisted fipronil degradation and the integrative role of omics approaches in describing new pathways.

3.2 Fipronil

Discovered in 1987 by Rhône-Poulenc Agro Company (now Bayer Corpscience) and registered in 1996 in the United States. Since 2003, the active ingredient fipronil has been under the control of BASF (Badische Anilin & Soda Fabrik), a leading German chemical company in the pesticide market (Gunasekara et al. 2007). Used in the agricultural system of regions with tropical and subtropical climates, fipronil has a great potential for action, acting on a wide range of insects and even arachnids. Representing the group of insecticides of the phenylpyrazole family, fipronil over the years has won the agricultural market, being used on various crops such as cotton, soybean, rice, potato, and especially on corn and sugarcane crops. The use of fipronil aims to form a barrier against insect attack on crops, thus reducing damage to growers (Baldaniya et al. 2020).

Fipronil (molecular formula $C_{12}H_4Cl_2F_6N_4OS$) and chemical name received by the International Union of Pure and Applied Chemistry (IUPAC) (RS) -5-amino-1-[2,6-dichloro-4- (trifluoromethyl) phenyl] -4- (trifluoromethylsulfinyl) -1H-pyrazole-3-carbonitrile (Fig. 3.1) is presented in powder form at 20 °C, with a molecular weight of 437.1 g mol^{-1} and a density of 1.477–1.626 g mol^{-1} (Hainzl and Casida 1996). Fipronil is also highly soluble in organic media. The fluorine groups when placed in organic media increase their solubility, so the use of numerous organic solvents such as acetone is used for better homogeneity of the solution (Hidaka et al. 2015).

The large-scale ability to attack pests allows activity on several groups of plagues such as ticks, cockroaches, grasshoppers, fleas, mosquitoes, both in their larval and adult stages(Gunasekara et al. 2007). Its phenylpyrazole classification gives it the

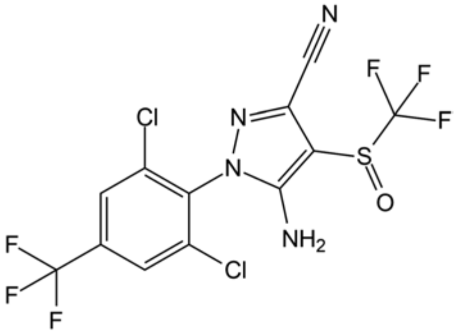


Fig. 3.1 Molecular structure of fipronil

ability to act on the central nervous system of insects, mainly in receptors of gamma-aminobutyric acid (GABA), preventing the correct flow of chloride ions, causing death, so it has great potential against insects (Cole et al. 1993).

Although fipronil is widely used on crops, it is prohibited in the European Union. The marketing prohibition was due to its high degree of toxicity, evidenced by the serious problems caused to animals that, after ingestion, were damaged by intoxication by contaminated food (Kim et al. 2020). Absorption of fipronil occurs through the intestinal tract. Contact with the agent can be through the skin, eyes, respiratory tract, or ingestion. The maximum blood concentration of fipronil occurs 4– 6 h after ingestion and its excretion occurs mainly in feces and to a lesser extent in urine (Gupta and Anadón 2018)

3.3 Toxicity

Fipronil does not present great damage to living beings in its original molecular form. However, after degradation of the molecule, its metabolites are highly toxic. One of the characteristics of fluorinated compounds is the production of metabolites more toxic than its initial compound, as is the case of fipronil-sulfone, the most toxic metabolite of fipronil (Wolfand et al. 2016).

Fipronil metabolites are highly harmful and reactive compounds. Their presence poses risks to the environment because of their high persistence due to their recalcitrant molecules, composed of cyclic carbon chains. Since the discovery of the toxicological potential to terrestrial and aquatic ecosystems, which mainly affects the quality of life of living organisms, ecotoxicological studies have become present and necessary to monitor the quality of the environment in general, especially in impacted areas (Konwick et al. 2006; Pino-Otín et al. 2020).

In line with the above, environmental studies found fipronil toxicity on non-target organisms, such as pollinating insects, mainly bees. The agent present in the seed coat, when sown or harvested, was found to cause dust, possibly causing insect intoxication. These parallel damages caused by the compound are the main problem, from an environmental point of view. It is estimated that almost 75% of all agricultural production worldwide depends on the process of natural insect insemination. Therefore, the agricultural sector may suffer losses over the years if the agricultural cultivation model is not rethought. Therefore, environmental studies have been highlighted over the years, seeking to understand and minimize the anthropogenic problems caused to the environment (Zaluski et al. 2015).

Due to insect resistance to pyrethroids, carbamates, and mainly organophosphates, which are also highly toxic to living organisms, an increase in the use of fipronil has been observed (Wang et al. 2016). However, despite having a relatively low toxicity, fipronil began to be used more and more over the years, which generated a relative accumulation of the agent in the environment, with an increase in the damage caused. Through analysis and observations of animals, plants, and microorganisms, it is possible to verify the environmental quality of the ecosystem under study (Van der Oost et al. 2003). Thus, the use of experimental models becomes extremely importance to evaluate the level of environmental impact and how it can influence the physiology of the organisms present there, being used as ecotoxicological markers of environmental quality (Van der Oost et al. 2003; Gupta and Anadón 2018). Table 3.1 shows the relationship of the toxicological potential of fipronil in some experimental models already analyzed and reported in the literature.

Table 3.1 Relationship of fipronil toxicity in non-target organisms

Organisms	Fipronil concentration	Observed damage	Reference
Japanese quail (*Coturnix coturnix Japonica*)	11.3 mg kg^{-1}	Mutagenesis; renal and hepatic toxicity	Ali et al. (2016)
Sprague–Dawley rats	4.85 mg kg^{-1}	Thyroid endocrine disruptor; thyroid and mitochondrial cytotoxicity	Ehsan et al. (2016)
Zebrafish (*Danio rerio)*	13.47 mg L^{-1}	Reduction of cell proliferation; Neurotoxicity; vascular damage	Park et al. (2020)
Chironomus riparius	0.084 μg L^{-1}	Decreased antioxidant activity; change in globin activity and expression of motor proteins, cytoskeleton, and biosynthesis	Monteiro et al. (2019)
Male albino rats	0.1–10 mg L^{-1}	Decreased antioxidant activity; increased lipid oxidation; hepatic and renal toxicity	Mossa et al. (2015)
Wistar rats	70–280 mg kg^{-1}	Decrease of the pregnancy rate; change in the estrous cycle; hormonal changes (estradiol and progesterone)	Ohi et al. (2004)
Rainbow trout (*Oncorhynchus mykiss*)	0.246 mg L^{-1}	Very high toxic	Gupta and Anadón (2018)
Bluegill sunfish (*Mola mola*)	0.083 mg L^{-1}	Extremely toxic	
Daphnia spp.	190 μg L^{-1}	Moderately toxic	
Crayfish	14-20 μg L^{-1}	Moderately toxic	
Estuarine mysids	0.14 μg L^{-1}	Extremely toxic	
Copepods (*Amphiascus tenuiremis*)	6.8 μg L^{-1}	Damage to the reproductive system; decrease reproductive rate	Chandler et al. (2004)
Male buffalo calves	0.5 mg kg^{-1}	Loss of body mass; muscle weakness; Alopecia; depression	Gill and Dumka (2013)
Nile tilapia (*Oreochromis niloticus*)	0.042 mg L^{-1}	Increasing hepatic enzymes activity; endocrine disruptor; decreased antioxidant activity	El-Murr et al. (2019)
Bee (*Apis mellifera*)	0.19 μg/bee (ingestion) 0.009 μg/bee (contact)	Behavioral changes; reduction of motor activities; paralysis and lethargy	Zaluski et al. (2015)

According to studies, it is known that aquatic ecosystems present high levels of contamination by pesticides, micropollutants, and other emerging pollutants. This is justified by the constant contact of organisms with contaminants, which can promote, in addition to the damage shown in Table 3.1, the bioaccumulation of fipronil in organisms, evolving over time to diseases and irreparable chronic damage (Konwick et al. 2006). Another factor pointed out as an increase in the incidence of aquatic pollutants is linked to the strong presence of agriculture near water bodies. As well as the influence of environmental and natural factors, such as rainfall, leaching, soil fixation, and absorption, or even the illegal disposal of untreated industrial and domestic effluents, which turns water bodies into the main recipients of these toxic compounds (Furihata et al. 2019).

The increased use of fipronil led to the need to study its mechanisms of action, its effects and environmental behavior with the purpose of maximizing and facilitating the recovery of degraded areas. Using the knowledge and tools of environmental biotechnology, the application of techniques such as bioprospecting allows the isolation of microorganisms capable of biodegrading xenobiotics in contaminated areas, and the use of bioremediation for decontamination (Kumar et al. 2011). Omics approaches, such as metagenomic analyses of contaminated soils, allow the identification of microorganisms present in a particular contaminated region (Jeffries et al. 2018). Characterization of the microbiota in particular ecosystems reveals the predominant groups and also using the Whole Genome Shotgun (WGS) method it is possible to detect which genes are related to the process of metabolism of xenobiotic compounds (Kumar et al. 2015).

3.4 Fipronil Degradation

Previous studies conducted with fipronil have shown a high persistence of the insecticide in the environment, presenting under natural conditions a half-life of up to 200 days (Wolfand et al. 2016). Environmental conditions are important factors for the degradation process of xenobiotic compounds. In general, pesticides and other xenobiotic molecules can be modified by physical processes (adsorption and sorption), chemical processes (hydrolysis and photolysis), and also biological processes (biodegradation), as shown in (Fig. 3.2) (Wolfand et al. 2016). Thus, in order to minimize the presence of toxic compounds from the environment, these strategies can be adopted for removal and/or degradation management, hoping to reduce toxicity within the affected ecosystems (Bonmatin et al. 2015).

Among the approaches for the remediation of contaminated areas, biological processes are the most widely used, due to their high degradation potential and low cost. Biodegradation is the basis of these processes and, in general, occurs naturally in the environment provided that there are microorganisms capable of metabolizing the toxic compound and favorable environmental conditions.

Over the years, procedures and techniques have been advanced and improved, with the process of biodegradation providing the development of the bioremediation

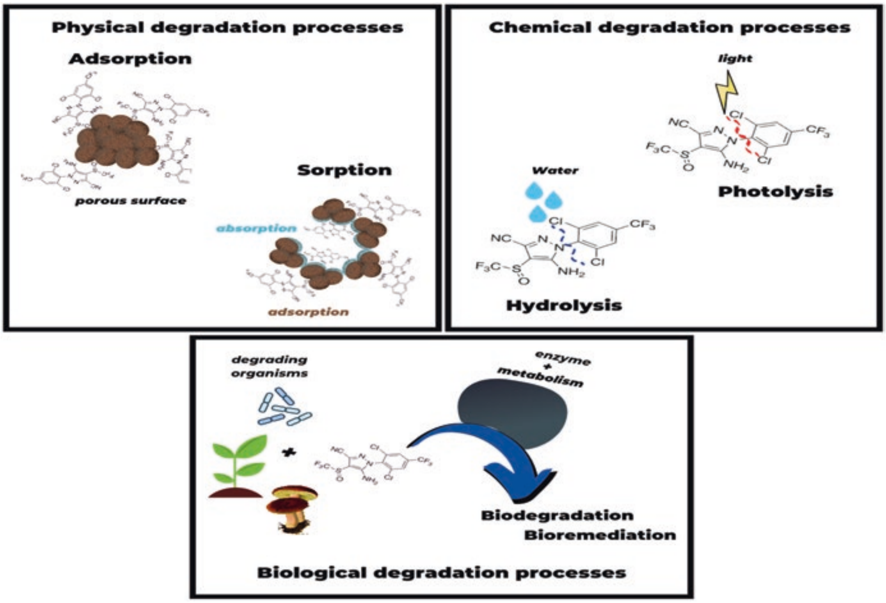


Fig. 3.2 Environmental pesticide degradation processes

technique. This technique can be applied in situ (occurs in the affected area) or ex-situ (occurs outside the affected environment). Factors such as the presence of other nutrients, pH range, humidity, climatic variations, and temperature are what will determine the time required for the degradation process of fipronil (Kumar et al. 2011). It is important to note that bioremediation is a monitored and controlled biological decontamination process. Degrading microorganisms and bioremediation techniques started to be studied subsequent to an investigation, which revealed the presence of microorganisms present in the impacted environments. These microorganisms (indigenous) were able to metabolize the toxic compounds to survive through not previously studied enzymatic devices (Kumar et al. 2011). Based on this, the study aimed at bioprospecting microorganisms with the potential to degrade xenobiotics has intensified within the scope of environmental biotechnology.

3.4.1 Bacteria Biodegradation

Fipronil, as already reported, is most toxic after initial degradation of its molecule. Studies have already identified the formation of four metabolites from the degradation of fipronil, through chemical, physical, and/or biochemical processes. Thus, the degradation pathways shown are those of photolysis (fipronil-desulfinyl), hydrolysis (fipronil amide), reduction (fipronil-sulfide), and oxidation (fipronil-sulfone)

(Fig.3.3). As mentioned earlier in this chapter, few studies report on the biodegradation of fipronil by bacteria.

The biodegradation process basically consists of stimulating the enzymatic machinery of bacteria to metabolize toxic compounds. The process of fipronil

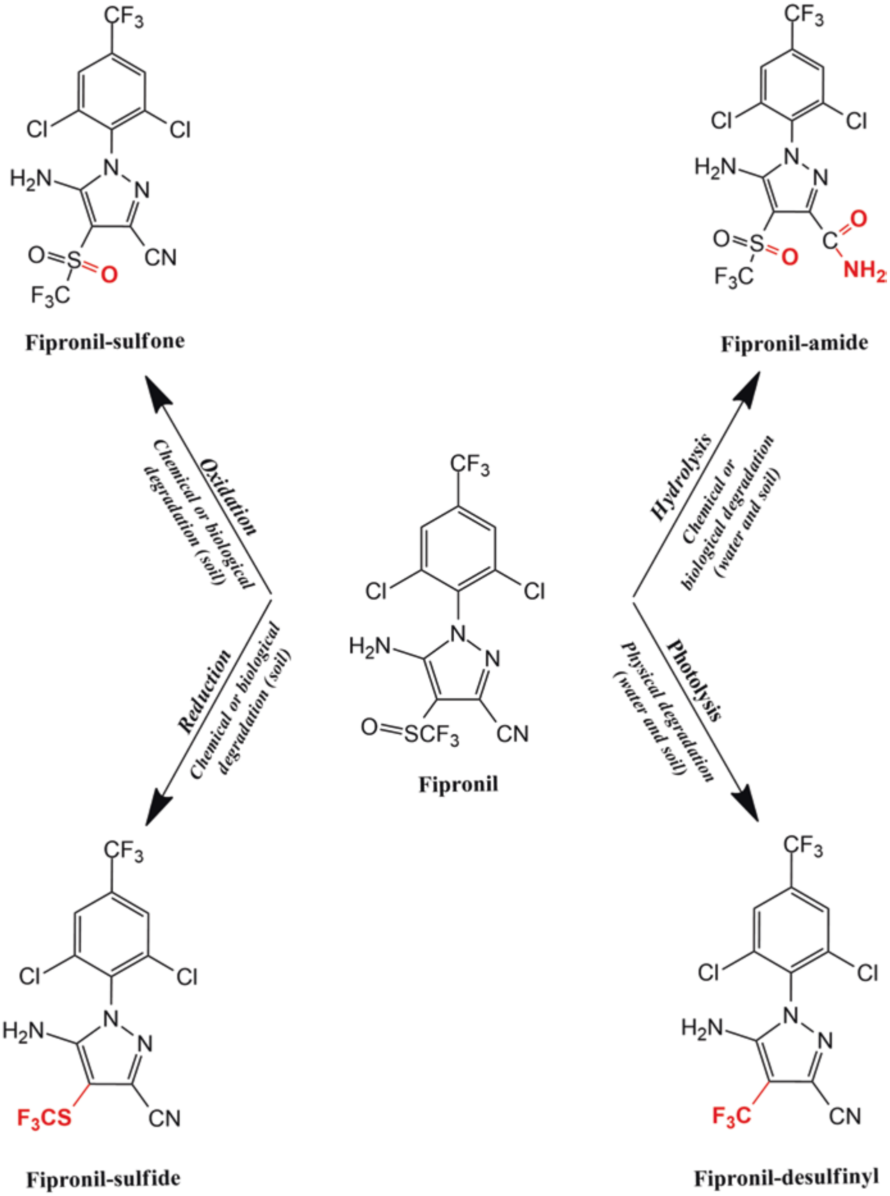


Fig. 3.3 Metabolites produced in the degradation pathway of fipronil

metabolism is still not entirely clear, but it is known that each group of bacteria has specific ways of degrading the compound. As an example, aerobic bacteria are known to have the greatest ability to oxidize fipronil generating fipronil-sulfone, while microaerophilic or anaerobic bacteria further reduce fipronil, forming fipronil-sulfide (Gunasekara et al. 2007; Gajendiran and Abraham 2017). These bacteria aim to degrade fipronil into less toxic molecules, through partial, major or total metabolization of the pesticide to mineralization, a process that results in H_2O and CO_2 (Bhadbhade et al. 2002; Abraham and Silambarasan 2014).

Studies show that the degradation of fipronil is affected by the diversity of microbiota that can be found in places that have a history of contamination by the insecticide, such as in soils of agricultural crops. The application of microorganisms in the recovery of contaminated areas has become an innovative and effective tool, which can be carried out through the use of a single microorganism or by a consortium (Pereira and Freitas 2012). Bacteria have already been shown to be natural biodegraders of toxic compounds similar to fipronil, as shown in Table 3.2. However, the biggest problem is the need for bacteria to be in direct contact with contaminants, which is not the reality of the environment, where there is a homogeneous dispersion in the soils of both contaminants and microorganisms. Some genera of bacteria have chemotaxis capacity, sensing the presence of the contaminant and going to it, either through their bacterial branched filaments, such as bacteria from the phylum actinobacteria or through the mobility of their flagella, such as diazotrophic bacteria of the genus *Burkholderia*, *Azospirillum*, *Azotobacter*, *Mesorhizobium*, *Rhizobium* among other genus (Kumar et al. 2011; Berkelmann et al. 2020)

3.4.2 Biodegradation by Fungi

Studies involving selection and analysis of degradation of fipronil by fungi are even more scarce than those involving bacteria, as shown in Table 3.2. The processes of biodegradation of the environment are mostly focused on the use of bacteria as active detoxification. However, fungi also have an excellent enzymatic machinery to perform this task. Bacteria and fungi are essential for the processes of biogeochemical cycling of organic matter in ecosystems, playing an important ecological role (Luo et al. 2017).

Fungi are eukaryotic microorganisms that have the function of degrading most old plant material, leaf litter, and tree trunks. It is important to note that the aspects of biodegradation and bioremediation are derived from biological processes that have existed in nature since forever (Kumar et al. 2011). In this way, environmental recovery practices are based on the use of microorganisms or organisms (such as plants) to metabolize toxic compounds. This capacity has already been evidenced due to the selective pressure capacity exerted by the environment itself, pressing only resistant microorganisms capable of degrading toxic compounds (Verma et al. 2014).

Table 3.2 Fipronil biodegraders

Bacteria				
Microorganism	Gram nature	Metabolism	Degradation/ concentration	Reference
Bacillus thuringiensis	G+	Aerobic	89–98% (80 mg kg^{-1})	Mandal et al. (2013)
Bacillus firmus	G+	Aerobic	100% (0.50–1.50 mg kg^{-1})	Mandal et al. (2014)
Bacillus sp. FA4	G+	Aerobic	74% (50 mg L^{-1})	Bhatt et al. (2019)
Bacillus sp. FA3	G+	Aerobic	76% (50 mg L^{-1})	Bhatt et al. (2021b)
Bacillus megaterium	G+	Aerobic	94% (0.6 g L^{-1})	Prado et al. (2021)
Bacillus cereus D2	G+	Aerobic	89% (20 mg L^{-1})	Gangola et al. (2021)
Paracoccus sp.	G-	Aerobic	50% (20 mg kg^{-1})	Kumar et al. (2012)
Stenotrophomonas acidaminiphila	G-	Aerobic	70% (50 mg L^{-1})	Uniyal et al. (2016a))
Staphylococcus arlettae	G+	Facultative aerobic	81% (10 mg L^{-1})	At et al. (2019)
Bacillus thuringiensis	G+	Aerobic	66% (10 mg L^{-1})	
Streptomyces rochei AJAG7	G+	Aerobic	100% (500 mg L^{-1})	Abraham and Gajendiran (2019)
Gammaproteobacteria	G-	Facultative anaerobic	50% (20 mg kg^{-1})	Kumar et al. (2012)
Acinetobacter calcoaceticus	G-	Aerobic	86% (50 μg kg^{-1})	Uniyal et al. (2016b)
Acinetobacter oleivorans	G-	Aerobic	89% (50 μg kg^{-1})	
Fungi				
Aspergillus glaucus AJAG1	-	Aerobic	100% (900 mg L^{-1})	Gajendiran and Abraham (2017)
Trametes versicolor	-	Aerobic	96% (800 μg L^{-1})	Wolfand et al. (2016)

G+: Positive gram nature; G-: Negative gram nature

It is known that fungi have advantages of use in bioremediation processes, when compared to bacteria. As already explained, bacteria need direct contact with the pesticide to metabolize it, but this does not apply to filamentous fungi. Unlike bacteria, which mostly have the need to absorb the xenobiotic molecule to metabolize it, filamentous fungi are able to secrete enzymes through their hyphae, reaching a greater area of contact with pesticides and other toxic compounds (Kumar et al. 2011). This fact has already been proven by comparing studies, in which the ability of fungi as *Aspergillus glaucus* AJAG1 metabolize 900 mg L^{-1} of fipronil, while bacteria like *Streptomyces rochei* AJAG7 degraded 500 mg L^{-1}.

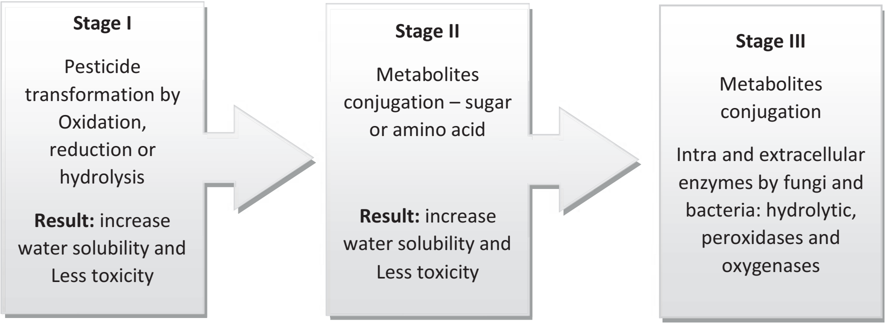
3.5 Enzymes

The transformation of toxic molecules through microbial biodegradation involves a complex metabolic process, centered on enzymes that are fundamental in this transformation. Enzymes are proteins that accelerate chemical reactions. In the case of xenobiotic compounds, i.e., that do not exist in nature, often the enzymes responsible for the transformation of the compound are enzymes that act on molecules naturally present in environments, such as phenolic compounds, lignin among others.

Bacteria and fungi are mainly responsible for the degradation of pesticides in the environment, since they have species diversity and consequently metabolic diversity. A pesticide can either be used as the main source of carbon and energy through complete mineralization of the compound, or it can be transformed through cometabolism into other molecules. Mineralization is more efficient, as it results in inorganic molecules, CO_2, and water, which are non-toxic molecules. In cometabolism, several microorganisms present in the environment are responsible for the transformation of the molecule. So, a different source of carbon is needed, since the pesticide is not used as an energy source, then the degradation of the compound is partial. In cometabolism each microorganism can be responsible for a part of this modification, culminating in a non-toxic or even nutritious product at the end of the transformation chain. The main objective of this process is to reduce toxicity to the environment. Figure 3.4 summarizes the three stages of a pesticide biodegradation process (Van der Oost et al. 2003; Ortiz-Hernández et al. 2013; Zulfiqar and Yasmin 2020). According to (Fig. 3.4) in stage I the pesticide is transformed by oxidation, reduction, or hydrolysis, which results in a compound that is more soluble in water and less toxic. The most active classes of enzyme in this stage are hydrolases and esterases and mixed function oxidases (MFO).

In stage II, the metabolites resulting from the previous phase are linked to sugars or amino acids, also resulting in more water-soluble and less toxic products. The system responsible for this stage is glutathione S-transferases (GST).

In stage III, a secondary conjugation occurs, in which fungi and bacteria produce hydrolytic enzymes, peroxidases, and oxygenases, both intra and extracellular.



Stage I

Pesticide transformation by Oxidation, reduction or hydrolysis

Result: increase water solubility and Less toxicity

Stage II

Metabolites conjugation – sugar or amino acid

Result: increase water solubility and Less toxicity

Stage III

Metabolites conjugation

Intra and extracellular enzymes by fungi and bacteria: hydrolytic, peroxidases and oxygenases

Fig. 3.4 Three stages of pesticides biodegradation by microorganisms

Table 3.3 Herbicides most used in the world and the respective classes of enzymes related to the compound biotransformation

Herbicides	Enzyme class	Reference
Glyphosate	Oxidoreductases Transferases	Pundir et al. (2017)
2,4-D (2,4-Dichlorophenoxyacetic acid	Cytochrome P-450 Oxidoreductases Hydrolases Transferases Oxygenases	Nykiel-Szymańska et al. (2018) (Pundir et al. 2017) Han et al. (2020)
Atrazine	Hydrolases	Pundir et al. (2017)
Paraquat	Transferases Oxidoreductases	Pundir et al. (2017)
Diuron	Ligninolytic enzymes Cytochrome P-450 hydrolases	da Silva Coelho-Moreira et al. (2013) Khurana et al. (2009)
Metolachlor	Oxidoreductases (hydroxylases)	Sanyal and Kulshrestha (2004)

Table 3.4 Insecticide most used in the world and the respective classes of enzymes related to the compound biotransformation

Insecticides	Enzyme class	Reference
Acephate	phosphotriesterase, paraoxonase 1, and carboxylesterase	Lin et al. (2020)
Thiamethoxam	Nitro reductase	Zhou et al. (2014)
Imidacloprid	Cytochrome P450 Oxidoreductases	Pang et al. (2020)
Bifenthrin	Hydrolysis	Chen et al. (2012), Zhang et al. (2018)
Fipronil	Ligninolytic enzymes Cytochrome P-450Laccase	Wolfand et al. (2016); Gajendiran and Abraham (2017) (Gangola et al. 2021)

Various enzymes participate in the metabolism of a pesticide, carrying out metabolic reactions such as hydrolysis, oxidation, reduction of a nitro grouping (NO_2) to an amino (NH_2), oxidation of a NH_2 group to NO_2, dehalogenation, replacement of a sulfur (S) with an oxygen (O_2), addition of a hydroxyl radical (OH) in a benzene ring, metabolism of the side chains and cleavage ring.

Although, to date, there is no consensus on which enzymes are specifically used by bacteria to degrade fipronil, Tables 3.3 and 3.4 will show the enzymes already described for biodegradation of other pesticides (herbicides and insecticides, respectively). The tables were built taking into account the most widely used herbicides and insecticides in the world (Mcdougall 2017). The EMBL Enzyme Portal tool (Pundir et al. 2017) was used when it presented data on the biodegradation of the compounds. If the tool did not return a result, searches were carried out on the basis of articles.

3.6 Partial Metabolic Pathways

Although fipronil metabolic pathways are not fully described yet, this compound is degraded by living organisms. In vivo studies have shown that mammals present oxidation as the main form of degradation, which is the reason for the elevated rate of the metabolite fipronil-sulfone found in aerobic organisms (Gupta and Anadón 2018). Analyzes exhibited modifications on microsomal liver cells showing increased activity of the cytochrome P450 complex (Wang et al. 2016).

Classified as hemeprotein type b, the P450 complex acts as a peroxisome organelle found in eukaryotes, oxidizing free radicals present in these organisms. The oxidation system acts through the dependent relationship of the substrate NADPH-cytochrome-P450 reductase and fractions of the phospholipid membrane, so that the oxidation reactions occur, as shown in Fig. 3.5 (Široká and Drastichová 2004).

Responses caused by xenobiotic substances modify the redox balance of living beings, causing damage to their homeostatic system and cellular stresses. Pollutant detoxification reactions, such as fipronil, are already known, presenting their action in two stages (I and II). In step I, the oxidation of fipronil occurs, adding an oxygen molecule to the sulfur (S) of the trifluoromethylsulfonyl group, linked to the carbon (C) "4" of the pyrazole ring, by the action of oxidative enzymes. This process occurs to make the fipronil molecule more polar, facilitating the process of metabolism and excretion from the system. The second (II) stage occurs differently when comparing animals and fungi. In animals, the detoxification process occurs through the action of catalytic enzymes such as glutathione S-transferase (GST) and N-acetyltransferase (NAT). In fungi, the process is mediated primarily by the hydroxylation of the C 3 or C 5 (meta position) of the aromatic ring, with consecutive glycosylation of the

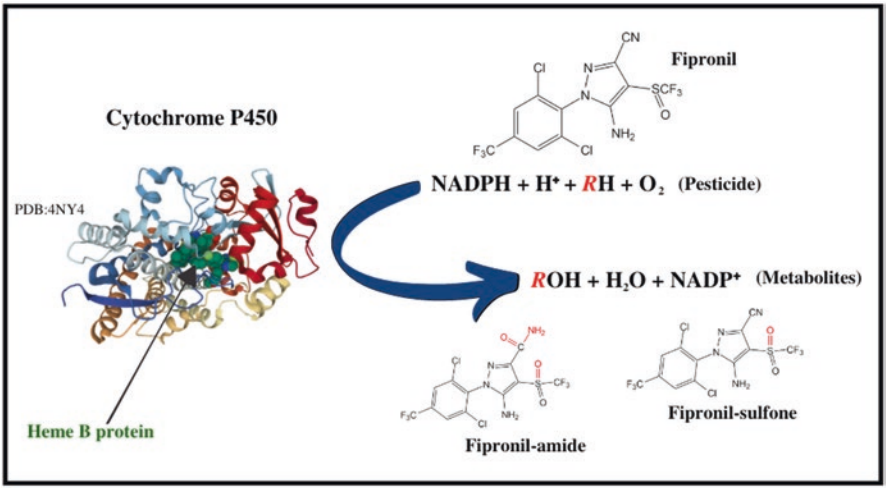


Fig. 3.5 Mechanism of action of cytochrome P450
***R*: represents the radical of the xenobiotic molecule**

added hydroxyl (Casley et al. 2007; Girvan and Munro 2016). Processes mediated by the enzymes CYP1A1, CYP3A4-A5, and CYP2B6.

The processes mediating fipronil metabolism are not yet known, but by observing the glycosylation of the fipronil molecule, it is possible to assume that it would make the molecule easier to be degraded. As already shown for fungi, they have the ability to secrete enzymes, unlike bacteria. Some enzymes involved in the process of secretion and degradation of fipronil have already been reported, such as laccases, peroxidases, among others, but none described exactly the pathway of degradation (Wolfand et al. 2016).

To date, no study has revealed how bacteria actually metabolize fipronil. However, parallel studies have shown that strains of *Bacillus thuringiensis* have the ability to metabolize compounds consisting of a benzene ring. For example, it has been reported in studies with degradation of benzo (a) pyrene via hydroxylase enzymes of the P450 complex, were controlled by the enzymes CYP450 and CYP106A2 (Lu et al. 2019). Thus, the hypothesis is that the bacteria would also be able to metabolize fipronil using the same P450 mechanisms as a possible metabolic pathway.

3.7 Methods for Studies Past, Present, and Future—Molecular, Omics, and Analytical

In this topic, examples of processes and procedures performed for the study of enzymes responsible for the degradation of toxic compounds will be described. This type of study leads to the definition of metabolic pathways and will be presented in two periods: before and after the development of omics sciences and their applications.

A widely studied pesticide due to its high toxicity is the herbicide atrazine, the publications of its metabolic degradation pathway date from studies carried out in the 1990s (Souza et al. 1995, 1996; Boundy-Mills et al. 1997) Based on the examples mentioned above, it appears that the study of a metabolic degradation pathway is interdisciplinary since it involves several areas such as microbiology, biochemistry, molecular biology, and biophysics. Figure 3.6 shows a sequence of methods and analyses that are performed to describe a single reaction within a compound's degradation pathway, and often the complete transformation of the toxic compound into CO_2 and H_2O involves numerous enzymes. In the items below, a general process used in the past for the study of the metabolic degradation pathways will be described:

A. The initial process would be to bioprospect a microorganism with the potential to degrade a toxic compound. Usually, this isolation takes place in contaminated places, or from the biological treatment of wastewaters. For the isolation, a minimal salt culture medium is used and the toxic compound is added in different

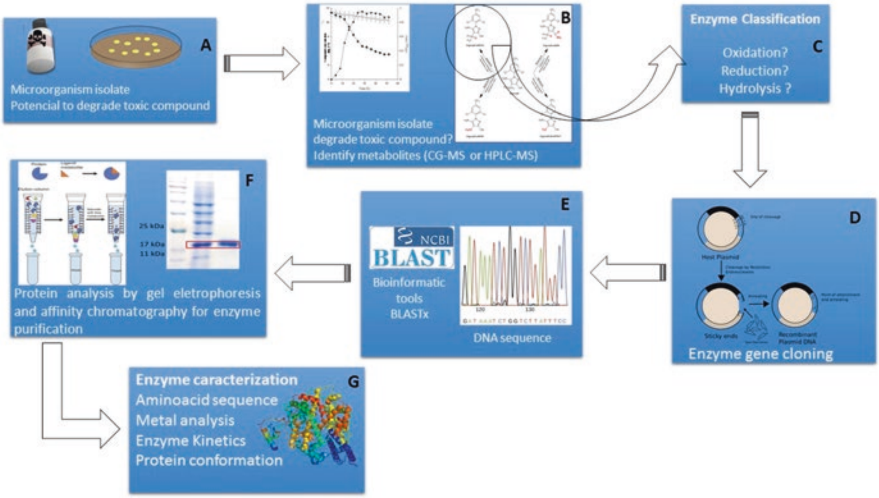


Fig. 3.6 Flowchart showing the study of new microbial enzymes responsible for the degradation of toxic compounds. This flowchart represents the studies carried out before the omics sciences.

concentrations. Another possibility is to add some minimal carbon source, since degradation by cometabolism is also possible;

B. With an isolated microorganism, several assays can be performed, such as a growth curve for several days or even months, following degradation analysis of the compound using analytical tools such as High-Performance Liquid Chromatography (HPLC) or Gas Chromatography (CG). The detection of formed metabolites is extremely important to infer which enzymatic reactions occur and a possible degradation pathway;
C. Then each enzyme will be studied separately, according to the metabolite formed, it is possible to infer the class of enzyme involved in the reaction;
D. The cloning of the gene responsible for encoding the enzyme using a library of cosmid clones has long been used. After the entire sequence of processes for obtaining the clones, the verification through the phenotype is carried out in a culture medium containing the toxic compound as an energy source;
E. Thus, clones that show growth are sequenced, and the nucleotide sequence is analyzed by bioinformatics tools such as, for example, Blastx at NCBI (National Center for Biotechnology information) (Altschul et al. 1990).
F. In addition to molecular and bioinformatics tools, it is possible to extract extra and intracellular protein from the cultured clone and perform an electrophoresis separation, extracting the target molecular weight content and then purifying it by chromatography;
G. The characterization of the enzymes, such as amino acid sequence, metal analysis, kinetics and protein conformation, can confirm the information previously found in Blastx.

This sequence of analyzes must then be performed on all clones that show growth in the different metabolites of the toxic compound, in order to propose the complete degradation pathway.

Due to the importance of analytical and molecular approaches in degradation studies, these will be discussed in more detail throughout the chapter.

3.7.1 Analytical Approaches

The presence of toxic contaminants in the environment, such as fipronil, is difficult to analyze, and is identified and quantified according to the type of environmental matrix.

There are several possibilities of analytical methods for analyzing fipronil. The use of liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) has been shown to be a technique of very high resolution and quality when in trace concentrations of fipronil 0.1–0.5 ng L^{-1} (Li et al. 2020). For analyses involving large-scale laboratory routines, cheaper techniques are indicated, such as gas chromatography coupled with tandem mass spectrometry. (GC-MS/MS). This technique has the advantage of having an affinity for volatile organic compounds used for the solubilization of fipronil, in addition to presenting high sensitivity of quantification (0.08–4.6 μg L^{-1}) and low cost for analysis (Li et al. 2019). GC-MS has the advantage of minimizing matrix effects that are often found in environmental samples. However, it is noteworthy that the LC-MS technique in general presents greater sensitivity when compared to GC-MS, but presents a high cost of maintenance and material investments of the equipment (Li et al. 2019, 2020).

3.7.2 Omics Approaches: New Insight into a Bioremediation

Bioremediation has the potential to clean up and restore contaminated environments in an economical and sustainable manner. Nevertheless, the limited information on the control of growth and metabolism of microorganisms in polluted environments provides some limitations to its implementation. However, the rapid advancement in the use of omics technologies allows a new understanding of the bioremediation techniques.

Omics approaches also allow a better understanding of the individual microorganism and also provide insight into microbial communities at the system level and finally provide information to elucidate the metabolic networks as well as the interactions between species during the mineralization process of different compounds. This section of this chapter focuses mainly on works that have used omics techniques to understand the processes that occur in microbial communities, as well as in individual microorganisms, thus understanding their metabolic interactions. In this way, using the multi-omics approach, it is possible to design new metabolic pathways and use them to build microbial strains and/or consortia for better removal of recalcitrant compounds from the environment (Laczi et al. 2020).

By the end of the last century, most of the studies related to bioremediation used pure microbial cultures obtained by conventional isolation approaches to be used for the elimination of different pollutants (Löffler and Edwards 2006). However, it has been accepted that many of the microorganisms responsible for the degradation of these compounds are not investigated using classical culture approaches (Amann et al. 1995; Oberhardt et al. 2015). This fact showed that even if a microorganism was able to degrade a compound under optimal conditions in the laboratory, the same was not observed or repeated in the field. These were examined and could be associated with the impact of ambient stressors, horizontal gene transfer, metabolites, or further uncertain constituents arising from associated microbes. In the unavailability of new generation genetic approaches, it was difficult to solve the discrepant outcomes achieved in the laboratory setting and in situ trials. In this regard, that many characteristics of traditionally isolated microorganisms may be lost in native habitat, which may be due to the specific island approaches, is well known. Moreover, a microorganism isolated as a single culture might be an unsuccessful degrader under laboratory conditions, as its pivotal synergistic partners were removed throughout isolation steps (François et al. 2016). Consequently, to aid a better understanding of the degradation capacity of microorganisms, methods able to investigate the mechanisms of the whole have been necessary to investigate the processes at the system level.

The state of the art of molecular technologies allows us to reveal even more roles, pathways, relationships, and metabolic networks. Therefore, their implementation in biodegradation has the potential to transform the bioremediation strategies (Lovley 2003). Some work that describes new degradation pathways using omics technologies as a framework, focusing mainly on metatranscriptomics will be summarized below. And the use of RT-PCR in the discovery and/or description of new degradation pathways will also be discussed.

3.7.3 Metatranscriptomics

The metatranscriptomic approach allows direct access to the transcriptome information of microorganisms able to grow or not in culture medium using mass sequencing of the components of microbial communities in targeted ambient sources. Metatranscriptomic sequencing allows random sequencing of mRNAs as a unit to understand the regulation of intrinsic processes in microbial communities. The overall process for metatranscriptomic data is illustrated in Fig. 3.7. Briefly, the first step is to extract total RNA from the sample. The RNA that presents a certain quality will be fragmented and the corresponding dataset building and testing for quality will be performed. Next, the qualified library is sequenced. The raw sequence dataset generated is used for further bioinformatics support.

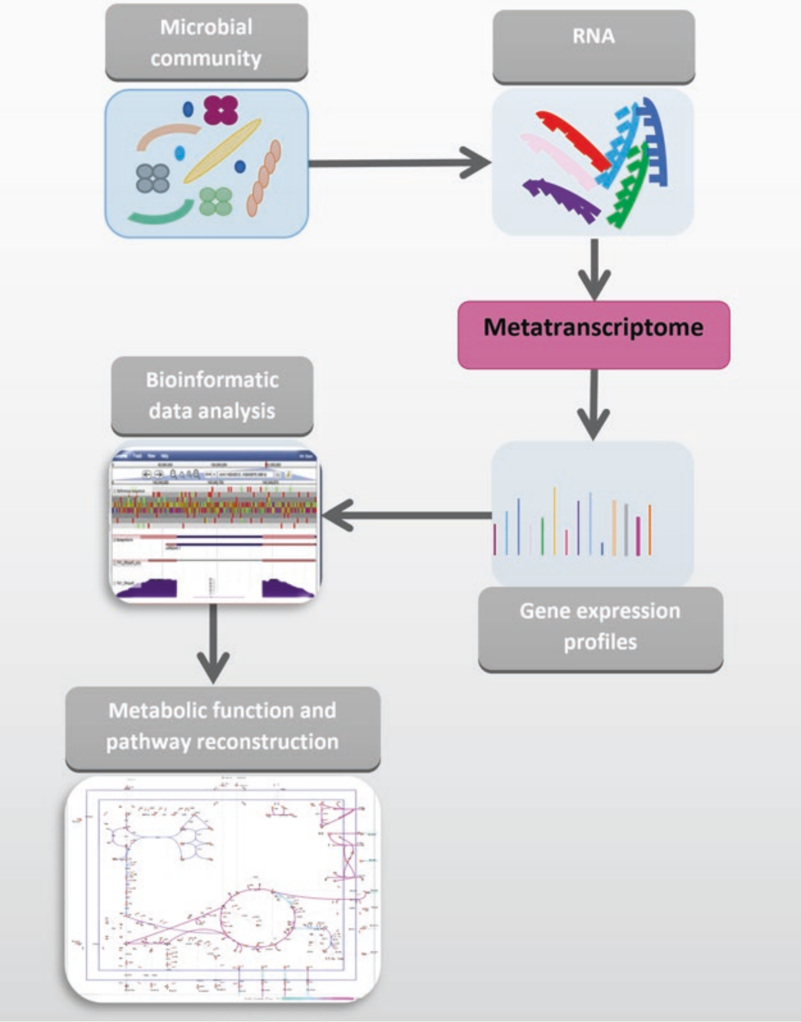


Fig. 3.7 Outline of the protocol for obtention of the gene expression patterns of the microbial populations using the meta transcriptome approach

Metatranscriptome exploration employing the next-generation sequencing techniques allows us to obtain gene expression patterns of microbial populations, revealing new insights into unknown biological systems and remedying the technical constraints associated with isolating individual bacteria. An example of this is that in a current study, Atashgahi et al. 2018 revealed the involvement of Peptococcaceae as the dominant constituents involved in early benzene degradation under anaerobic conditions using a metatranscriptomic approach. For this, the researchers used a continuous anaerobic culture that was inoculated with benzene-contaminated soil supplemented with benzene and nitrate. It was shown that the culture was composed of predominantly gram-positive microorganisms associated with Peptococcaceae (Van der Zaan et al. 2012; Van der Waals et al. 2017). Subsequently, a metatranscriptomic screen of this particular microbial assemblage was performed to select for transcripts implicated in anaerobic benzene metabolism, and a strongly transcribed gene cluster that encoded a putative anaerobic benzene carboxylase (*AbcA* and *AbcD*) and a benzoate-coenzyme A ligase (*BzlA*) was found, suggesting a pivotal role of Peptococcaceae in the anabolic degradation of benzene. At this point it is worth mentioning that subsequent attempts made to isolate benzene-degrading components from Peptococcaceae were unsuccessful, probably as they require symbiotic associations with partner species (Atashgahi et al. 2018).

In accordance with the above study, (Falk et al. 2019) performed total RNA extractions and metatranscriptomic analyses on sediments obtained near the Detroit River in a gradient of established contaminated sections with the goal of investigating relationships between contaminant grades and microbial gene transcript patterns and also diversity. Differential expression analysis at DESeq2 indicated that microbial transcripts related to methanogenesis, beta-oxygenation, and nitrate reduction were highly consistent in these contaminated sediments.

In other study (Reid et al. 2018) pioneered the reporting of in situ functional changes in freshwater microbial ecosystems through the use of metatranscriptomics, which allowed them to gain insight into gene expression with hydrocarbon-contaminated sites. For this purpose, sediments of three different sites along the Athabasca River tributaries, that have been known to contain bitumen outcrops, were selected for the metatranscriptomic analysis. Within the most relevant result, the presence of genes responsible for methanogenic activity (i.e., *mcr*) could also be involved in reverse methanogenesis. Thus, occurrence of this type of genes able to operate under methanogenic as well as methanotrophic influences suggests the necessity of an increased feature of the AOM/aerobic-MOB process, that has remained an unfruitful endeavor so far (Timmers et al. 2017). For the author, the knowledge of microbial functions in this habitat and the syntrophic relationships unraveled with the use of these new molecular approaches are becoming the new model for the study of microbial ecology and biogeochemistry in general.

Metatranscriptomics was also used to describe enzymes involved in the early steps of anaerobic benzene catabolism. In a research published by (Luo et al. 2014), cultures from microcosms derived from groundwater and soil from a gas station on cartwright Avenue in Toronto, ON, Canada were analyzed. Among other findings, abundant coverage of pathways related to anaerobic benzoate metabolism was determined, compatible to a central linkage of benzoate in the anaerobic metabolism of benzene and benzoate. In this context, gene transcripts corresponding to known or hypothesized enzymes implicated in the anaerobic metabolism of monoaromatic compounds were identified and this enabled the building of three parallel hypothesized pathways for benzoate catabolism: one found in *Azoarcus*/*Aromatoleum* spp., one identified in *Thauera* spp. (Alpha proteobacteria), and the other in obligate anaerobes (*bam* genes).

Finally, as mentioned above, clearly the next-generation sequencing that emerged in the genome and metagenome study has been effectively adapted to support gene expression studies with RNAseq and, in turn, the study of biological frameworks such as metatranscriptomics. A rapidly increase in the number of research projects, the majority of them involving differential gene expression studies aimed at getting information regarding the functional members, genes, and pathways inside a microbiome, have been undertaken in this emerging area. However, such an approach has as a disadvantage the lack of referenced sequenced genomes, and this may lead to a less than optimal fraction of reads for any given data set to be functionally or taxonomically classified. Because of this, there are ongoing endeavors to assembly metatranscriptomic data together with metagenomic data from the identical or similar sample, if available(Shakya et al. 2019). Although metatranscriptomics still needs to be improved, algorithms and tools are constantly being developed that will allow metatranscriptomics to facilitate our understanding of microbiomes and the relevant pathways involved in the metabolism carried out by microorganism of interest (Shakya et al. 2019).

3.7.4 RT-PCR Approach

In the post-genomic era, quantification of gene expression is a widely employed and relevant approach to analyze the condition of several cellular events in specific conditions. Currently, reverse transcription quantitative PCR (RT-qPCR) is widely used as the instrument to quantify nucleic acid molecules in biological and environmental samples and extensively deployed for environmental approaches in bioremediation, wastewater management, bioenergy, and others (Rossmassler et al. 2019). It is regarded as the most important medium-throughput gene expression analysis technology due to its sensitivity, precision, and fast execution (Derveaux et al. 2010). Several studies have utilized this approach to improve the knowledge about genes and pathway in different environments. Here we summarize the relevant studies where the use of reverse transcription quantitative PCR describes new genes and/or routes.

Herath et al. (2016) employed qPCR approach to elucidate the genetic machinery of *Desulfatibacillum alkenivorans* AK-01 varying the carbon source (n-alkanes C13 to C18). The authors have conjectured the two cluster of genes (two genomic loci coding for the alkylsuccinate synthase (ASS) gene) would be differentially expressed depending on the substrate used for growth. In this context, to obtain information regarding the possible co-transcription of 14 genes around assA1, RT-PCR was performed and they were able to verify that transcription occurs across 11 regions composing putative cluster 1. In addition, RT-PCR was also performed to investigate transcription in all intergenic regions surrounding assA1, and RT-PCR found that it does not have transcription in all intergenic regions downstream and upstream of Dalk 1724 and Dalk 1724, respectively. Moreover, the 12 genes that were transcribed together codify both subunits (Small and large) of a putative lao/AO ATPase, methylmalonyl-coA mutase, the activase (AssD) of ASS, a putative mmgE/prpD protein, putative ass subunits (AssB, AssC, AssA, and a MasE-like protein), a putative chaperone protein (AssE1), a hypothetical protein, and an uncharacterized protein (AssF1). Overall, these findings provided novel information on the study of upregulation of genes implicated in fumarate metabolism.

In other work (Lourdes Moreno et al. 2011) determined the sequence of a gene cluster of *Halomonas organivorans* that synthesizes genes related with phenol metabolism, in addition to the analyses of the gene arrangement, providing the first report describing the phenol catabolic genes implicated in the metabolism of phenol in halophiles. For this purpose, RT-PCR analysis was performed using *H. organivorans* cultures on medium containing benzoic acid, glucose, and phenol a carbon source. The results obtained in this study provide an ideal template for investigating the prospective use of this extremophile species in the treatment of saline sites.

Magnetospirillum sp. strain 15-1 (Meyer-Cifuentes et al. 2020), capable of degrading toluene, was used to examine the regulation of the enzyme benzylsuccinate synthase (BSS, encoded by *bss* genes), which catalyzes the major step in the anaerobic degradation of toluene. The main goal of the research was to examine the effect of both oxygen and toluene on the expression of the *bss* gene and the synthesis of BSS. The expression of BSS was also studied under nitrate-reducing conditions using various amounts of this compound. Cultures of *Magnetospirillum* sp. strain 15-1 prepared anoxically with toluene or benzoate as the only carbon source and various amounts of nitrate as electron acceptor were used to obtain cDNAs. The cDNAs of the transcribed intergenic regions of the *bss*, *tdi,* and *bbs* genes, as also a fragment of the xylR transcript, were amplified by PCR with degenerate primers. The results allowed the authors to conclude that the regulation of BSS gene expression appeared to be more complex than yet imagined. In *Magnetospirillum* sp. strain 15-1, post-transcriptional regulation of BSS synthesis might give the cells an extra regulatory overlay to better address its dynamic redox environment. Furthermore, the metabolically diverse strain 15-1 apparently has more than one regulatory component besides the established TdiRS system to control the level of *bss* and *bbs* transcription. With such information on the regulation of ISS synthesis, further enhancement of the anaerobic degradation of toluene at contaminated sites will be allowed.

A qPCR approach was employed to identify genes encoding for fumarate-related enzymes (FAE) involved in o-xylene degradation in a metagenomic culture (Rossmassler et al. 2019). Culture enriched for more than 20 years with o-xylene were used. As a starting point, metagenomic sequences of gene products were searched close to any of the previously identified FAEs. Thirty-four contigs were identified and selected for further analysis. Primers were designed to detect genes encoding for the putative FAE that were found in the metagenome. Studying these cultures post extended period with o-xylene, a novel FAE gene was identified. Sequencing and screening for the novel FAE-encoding genes were enabled by metagenomics, highlighting the utility of metagenomics to aid in the successful of novel and more accurate qPCR assay aimed at functionally targeted genes in selected mixed microbial populations. In addition, they have developed primers that targeted currently missing genes in o-xylene degradation route and showed these primers to be useful for environmental samples and also to provide supporting for study of the ability to degrade pollutants.

In conclusion, reverse transcription quantitative PCR (RT-qPCR) was used in several works for the determination of new pathways and the discovery of new genes. This approach can also be used for validation and/or as complementary techniques with high-throughput techniques (multi-omics). In short, the use of various "omics" tools has provided crucial information on metabolism and provides insight into pathways used by microorganisms that have so far been explored.

3.8 Conclusions

In conclusion to all content covered, it appears that so far there are less than 20 publications regarding microorganisms that biodegrade fipronil. Few articles reported a previous metabolic pathway. Only studies with fungi inferred the enzymes or enzyme systems involved. Thus, the need for a greater focus on the biodegradation and bioremediation of fipronil's enzymatic metabolic pathways is highlighted, mainly using molecular and omics approaches in order to obtain data regarding the degradation efficiency of the compound and the relationships between species and the environment during the biodegradation process in situ mainly. These efforts will result not only in the description of the enzyme systems involved in the degradation of fipronil but also important knowledge on how to apply these enzyme systems and/or microorganisms in the cleaning up of environments contaminated with fipronil.

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Chapter 4
Bioremediation of Cucurbitacins from Cucurbitacin Phytonematicides

Phatu W. Mashela, Ebrahim Shokoohi, Ashwell R. Ndhlala, Kgabo M. Pofu, and Dineo Raphasha

Abstract Effective microorganisms (EM) had no effect on cucurbitacin content during fermentation of cucurbitacin phytonematicides. However, under field conditions, the products have short application intervals, suggesting the post application existence of bioremediation factors of cucurbitacins. The objective of the review was to investigate the factors that could be responsible for the bioremediation process of cucurbitacins from Nemarioc-AL and Nemafric-BL phytonematicides, which are novel products serving as alternatives to fumigant nematicides. The latter had been internationally withdrawn from the agrochemical markets due to their environment-unfriendliness. Among the EM constituents used during fermentation, only *Lactobacillus* species, technically, the lactic acid bacteria, were the remaining EM after the fermentation process. *Lactobacillus* species do not release reductase enzymes, which have the potential to bioremediate cucurbitacins and therefore, the existence of extended shelf life in plastic containers. Although cucurbitacin phytonematicides have long shelf lives, after field application, the efficacy is short-lived, suggesting the existence of bioremediation factors in soil environments. In the review, we noted that due to the lipophilic properties of cucurbitacins, the products could be subjected to biosorption in lipid-rich epicuticles of nematodes. Total protein of the root-knot (*Meloidogyne* species) nematode versus increasing phytonematicide concentration exhibited negative quadratic relations to the minimum point, after which the total protein increased. After biosorption to lipid-rich epicuticle by hydrophilic part of cucurbitacins, the hydrophobic part becomes predisposed to the protein-rich subepicuticular layers, resulting in isoprenylation (protein-breakdown) and after the minimum point, farnesylation (protein biosynthesis) occurred, resulting in increase of total protein. In conclusion, ecdysozoans, which are the cuticle-bearing super phylum, represented by plant nematodes in the current review, offer potential existence of bioremediation process of cucurbitacins from cucurbitacin

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phytonematicides through biosorption, isoprenylation, and farnesylation reactions, thereby opening a frontier in bioremediation of cucurbitacin phytonematicides by these microorganisms, which are numerous in the soil environment.

Keywords Biosorption · Cucurbitacins · Ecdysozoans · Farnesylation · Isoprenylation · *Lactobacillus* species · *Meloidogyne* species · Reductase enzymes · Total protein

4.1 Introduction

Cucurbitacins occur as a class of highly oxygenated triterpenoids with tetracyclic cucurbitane nucleus skeletons: (the 19-(10 → β)-abeo-10α-lanost-5-ene (Chen et al. 2005, 2014)), within the Cucurbitaceae Family and at least five other families (Abbas et al. 2013). Although cucurbitacins have a common nucleus skeleton, the primary cucurbitacins that are biosynthesized in plants as triterpenoids are cucurbitacin B and E, each with an acetyl function at C-25 (Gry et al. 2006). More than 20 other cucurbitacins are produced from cucurbitacin B and E through one of the following chemical reactions: hydrogenation by cucurbitacin Δ^{23}_reductase, deacetylation by cucurbitacin acetylesterases, hydroxylation, dehydrogenation, and isomerization (Schabort and Teijema 1968; Dirr et al. 1986; Gry et al. 2006; Zhou et al. 2016). Generally, cucurbitacins differ from one another from hydroxylation at C-2, C-3, C-19, and C-24, the existence of a double chemical bond between C-1 and C-2 or between C-23 and C-24, the acetylation of C-25 hydroxyl groups and the presence of a ketone function at C-3 (Chen et al. 2005, 2014). The listed chemical reactions are important in explaining the potential reversal chemical processes that could enhance the bioremediation of cucurbitacins. Due to their wide-ranging biological activities, cucurbitacins have been widely investigated in pharmacological studies related to potential treatment of human diseases, particularly cancers and inflammation (Chen et al. 2005, 2014; Abbas et al. 2013; Mirr et al. 2019). In traditional medicine, cucurbitacin plant organs are widely used for treatment of various diseases (Mphahlele et al. 2012). Cucurbitacins had been recently introduced into the agriculture sector for managing plant nematode population densities as cucurbitacin phytonematicides (Mashela et al. 2017a). The latter are used as alternative to fumigant synthetic chemical nematicides, which had been internationally withdrawn from the agrochemical markets due to their degradation of ozone layer, and therefore, contributing directly to the incident of global warming (Mashela et al. 2017a).

The two cucurbitacin phytonematicides are derived from fruits of wild *Cucumis* species as crude extracts through bacterial fermentation process. The products, along with their purified active ingredients, have been widely investigated for their efficacies on suppression of plant nematodes and the amelioration of phytotoxicity on plants using the Curve-fitting Allelochemical Response Dose (CARD) computer-based algorithm model (Liu et al. 2003; Dube and Mashela 2016; Mashela et al. 2017a). The model demonstrated that most r strategist nematode species were highly sensitive to the test products, with efficacies that have relative impact effects from 90 to 100% when compared with nematode-inoculated plants without phytonematicides. The efficacies of these products were comparable to those of synthetic chemical systemic nematicides such as aldicarb and fenamiphos (Mashela et al. 2008). In contrast, the K strategist nematode *Steinernema feltia*e, widely used as a biocontrol agent of insects and worms, is tolerant to the test phytonematicides (Madaure et al. 2018), through morphological adjustment to cucurbitacin phytonematicides (Mashela et al. 2020a). Generally, r strategist nematodes are smaller, with higher reproductive rates and shorter ontogenies, whereas the opposite is true for the K strategists (Andrews and Rouse 1982). The non-phytotoxic concentration of these phytonematicides technically referred to as the Mean Concentration Stimulation Point (MCSP), along with the application interval that successfully suppressed nematode population densities, were each nematode- and crop-specific (Mashela et al. 2017a). The MCSP values ranged from 2 to 3%, whereas application intervals ranged from 14 to 22 days (Mashela et al. 2017a). Using empirically derived application frequency values for given plant cultivars, the dosage model was developed as the product of MCSP and the application frequency, which provided the total concentration of the phytonematicide applied from the initial to the final application prior to harvest. Similarly, when using second-stage juveniles (J2) of the citrus nematode (*Tylenchulus semipenetrans*) as an indicator for application interval, the findings confirmed the empirically derived values of using MCSP and nematode ontogeny, namely, approximately two to three weeks for liquid formulation and approximately eight weeks for granular phytonematicides (Mashela et al. 2017a, b).

Granular formulations of cucurbitacin phytonematicides consistently suppressed nematode population densities when assessed at eight weeks after application (Mashela 2002; Sithole et al. 2016; Mashela et al. 2017a). However, increased population densities of *T. semipenetrans* were observed when the trial was terminated at approximately 17 weeks post application of granular phytonematicides (Maile et al. 2013). In a subsequent study using liquid formulation on *T. semipenetrans*, J2 responses to Nemarioc-AL phytonematicide and aldicarb over time exhibited negative quadratic relations. In each case, after the minima were reached, J2 densities tended to have an upswing trend, suggesting the existence of density-dependent growth patterns (Mashela et al. 2017a, b). The cited observations suggested that regardless of the formulation, cucurbitacins as active ingredients of the cucurbitacin phytonematicides could undergo degradation, which could be driven by either abiotic or biotic factors. In most cases, abiotic degradation factors for soil-drenched products like phytonematicides include soil temperature, soil type, organic matter content, and/or soil pH (Jørgensen 2007), whereas biotic factors could include microbes such as bacteria and fungi (Singh et al. 2019). The biodegradation of chemicals from the environment through living entities such as microbes is technically referred to as bioremediation (Jørgensen 2007; Odukkathil and Vasudevan 2013; Canak et al. 2019). In the current study, bioremediation of cucurbitacins from the cucurbitacin phytonematicides was investigated to identify potential biological entities that serve as the bioremediation drivers, along with the potential bioremediation drivers.

4.2 Cucurbitacin Phytonematicides

Cucurbitacins are biosynthesized as secondary metabolites through either MEP/DOXP or Mevalonate pathway, which predominantly occur inside the mitochondria and serve as key component to ensure that the high-energy Acetyl-Co-A molecules do not accumulate at the entry site of the Krebs cycle, chemically referred to as the tricarboxylic acid cycle (TAC). Generally, a large number of secondary metabolites which are formed during glycolysis and the movement of the Acetyl-Co-A to TAC through the Mevalonate pathway or the D-Glyceraldehyde 3-phosphate through the MEP/DOXP pathway to form the triterpenoids are purposely removed as high-energy molecules from the primary metabolism pathway that takes Acetyl Co-A to TAC (Campbell and Reece 2005). The secondary metabolite pathway converts the high-energy Acetyl-Co-A or Glyceraldehyde 3-phosphate molecules into low-energy molecules such as cucurbitacins in a step-by-step conversion from precursor to precursor using specific chemical reactions facilitated by enzymatic activities in specific biosynthetic pathways (Chen et al. 2005, 2014). Since primary metabolism occurs in all living cells, precursors for cucurbitacins originate from all such cells, from where they are translocated to organs where low-energy cucurbitacins can be compartmentalized and used by resident plant organs in defense against herbivorous animals.

4.2.1 Sources of Cucurbitacin Phytonematicides

Nemarioc-AL and Nemafric-BL phytonematicides have A and B that represent active ingredients cucurbitacin A and B, respectively, with L depicting that the product is available as a liquid formulation. The two products are derived from oven-dried fruits of wild cucumber (*Cucumis myriocarpus*) and wild watermelon (*C. africanus*), indigenous to South Africa, with biodiversity center in Limpopo Province (Kristkova et al. 2003). *Cucumis myriocarpus* contains high cucurbitacin A ($C_{32}H_{46}O_9$) content in roots and fruit exclusively, with leaves being used as vegetable by the local people. In contrast, high cucurbitacin B ($C_{32}H_{48}O_8$) occurs in all organs of *Cucumis africanus*.

4.2.2 Preparation of Cucurbitacin Phytonematicides

Harvested fruits from the two plant species are cut into pieces and preserved through oven-drying. In medicinal plants, the materials are dried at 40 °C for 72 h in order to preserve the active ingredients (Müller and Heindl 2006). However, when fresh fruit pieces from the two *Cucumis* species were dried at 40 °C, the hyphae of the fungus that is resident on fruits of *Cucumis* species, namely, *Penicillium simplicissimum,* proliferated, resulting in rotting of the material (Mphahlele et al. 2012). The suitable temperature where *P. simplicissimum* would not thrive, which also resulted in the optimization of cucurbitacins, was derived at 52 °C for 72 h (Shadung et al. 2016). After drying, raw materials were ground separately in a Wiley mill (Thomas Scientific, Swedesboro, NJ, USA) to pass through a 1 mm sieve and stored in closed containers (Shadung and Mashela 2016). Fruits of the two plant species were separately fermented using effective microorganisms (EM) that comprised yeast bacteria, lactic acid bacteria, photosynthetic bacteria, and actinomycete bacteria, with each playing a distinct role in ensuring that the final product was of high quality. Raw materials used in the fermentation process of the two phytonematicides were summarized to enhance clarity on the inputs of the products (Table 4.1). The 20 L air-sealed plastic container had an outlet dangled in a 2 L bottle half-filled with water to allow for the escape of toxic gaseous end-products produced during the fermentation process.

4.2.3 Role of EM Components During the Fermentation Process

Fermentation refers to metabolic processes whereby organic molecules are converted into acids, gases, or alcohol in the absence of electron transport chain that requires oxygen. In simple terms, fermentation pathways regenerate the coenzyme nicotinamide adenine dinucleotide (NAD^+), which is used in cytoplasmic glycolysis to release energy in the form of adenosine triphosphate (ATP). Generally, fermentation during glycolysis yields a net of two ATP molecules, while mitochondrial

Table 4.1 Raw materials for preparation of cucurbitacin phytonematicide in a 20 L plastic container

Material	Nemarioc-AL	Nemafric-BL
Ground *Cucumis* fruits	80 g	40 g
Chlorine-free water	16 L	16 L
Sugar	100 g	100 g
Molasses	100 mL	100 mL
Effective microorganisms	100 mL	100 mL

respiration in the presence of oxygen yields the grand total of 38 ATP molecules from one glucose molecule. The organic molecules in phytonematicides include sugars in the form of purified sugars and molasses, cellulose, lignin, starch, and various other secondary metabolites, which EM constituents should biodegrade and release into solution during the fermentation process in chemical processes which are driven by various enzymes, but which are out of the scope of the current work.

Lactic acid bacteria hydrolyze the toughest materials in cell walls of plants, namely, cellulose and lignin (Madigan and Martino 2006). The final product of cellulose and lignin fermentation is lactic acid, which promotes the reduction of pH of the phytonematicide solution (Higa and Parr 1994). Yeast bacteria also reduce pH by hydrolyzing glucose to pyruvic acid through the anaerobic glycolysis pathway (Stetter 2006). The latter, without oxygen cannot proceed to Krebs cycle, the tricarboxylic acid cycle (TAC) that serves as the final electron acceptor during the enzyme-driven release of energy in the form of adenosine triphosphate (ATP) molecules, for use in biological activities. The pH of the finished liquid phytonematicides gradually decreased from 7.0 to 3.7 in 14 days after fermentation. Such conditions favor the thriving of bacteria at the expense of fungal growth (Madigan and Martino 2006). Yeast bacteria also release antimicrobial chemicals that add to the sterilization of the finished phytonematicide by preventing fungal growth that might even include the elimination of the previously described *P. simplicissimum* in cucurbitacin phytonematicides. During fermentation, the materials release copious sulfur as hydrogen sulfur (H_2S), where NAD of photosynthetic bacteria is reduced to NADH by H^+ ion from H_2S during Photosystem II (Campbell and Reece 2005). The released S is oxidized to form SO_4^{2-}, which is a lethal gas (Stetter 2006). Soon after its formation, SO_4^{2-} is reduced by $2H^+$ from H_2O molecule to form a strong acid, sulfuric acid (H_2SO_4), with highly corrosive capabilities. The Gram-positive actinomycete bacteria, which are oxygen-tolerant, have the capability to release chitinase that hydrolyzes chitin in exoskeletons of insects, insect eggs, nematode eggs, and mycelia of various fungi (Madigan and Martino 2006). Apparently, the constituents of EM have no biodegradation capabilities on cucurbitacins, for otherwise EM would not be suitable for use.

4.2.4 Unique Features of Cucurbitacin Phytonematicides

Cucurbitacin A is partially polar and slightly soluble in water, whereas cucurbitacin B is non-polar and insoluble in water (Chen et al. 2005). Both cucurbitacin A and B have high boiling points at sea level (760 mmHg = one atmosphere sea level), which occur at 731 °C and 699 °C, respectively (Krieger 2001). In contrast, at sea level, methyl bromide and Nemacur boil at 3.56 °C and 49 °C, respectively (Pesticidal Manual 1979; Windholz 1983). Generally, when *Cucumis* fruit pieces are oven-dried at 52 °C, the precursors and their related enzymes continued down their respective biosynthetic pathway, with subsequent formation of the low-energy cucurbitacins as demonstrated during the storage of raw materials of the cucurbitacin phytonematicides in sealed and unsealed plastic containers (Shadung and Mashela 2016). Similarly, containerized phytonematicides during the shelf life studies had limited degradation rate, except under chilled conditions (Mashela et al. 2020b).

4.2.5 Shelf Life of Cucurbitacin Phytonematicides

Cucurbitacin phytonematicides did not conform to the Arrhenius model, established for shelf life of various products, with product quality versus time exhibiting negative linear relations (Labuza and Riboh 1982; Steel 2004). Under chilled conditions (5 °C, 95–98% RH), Nemarioc-AL phytonematicide degraded rapidly with negligent shelf life (Mashela et al. 2020b). In most cases, cucurbitacin A breaks down rapidly into cucumin ($C_{36}H_{46}O_9$) and leptodermin ($C_{36}H_{46}O_8$) (Jeffrey 1980). However, Nemafric-BL phytonematicide with its stable cucurbitacin B versus storage time exhibited positive quadratic relations with shelf life spans of 35 weeks under chilled conditions (Mashela et al. 2020b). Under fixed tropical conditions (38 °C, 90% RH), Nemarioc-AL and Nemafric-BL phytonematicides versus time exhibited positive quadratic relations with shelf life spans of approximately 35 and 825 weeks, respectively. Extended shelf life in the two test phytonematicides were temperature-dependent, with tropical conditions being the most favorable for the storage of the products, which is well suited for use in tropical regions, where plant nematodes abound. The observed shelf life spans suggested the existence of unique features in both products when stored under tropical conditions. In contrast, with daily sampling for cucurbitacin during a 15-day period, cucurbitacin E-glycoside versus time exhibited negative quadratic trends, which were also temperature-depended (Martin et al. 2002).

4.3 Bioremediation Drivers of Cucurbitacin Phytonematicides

Bioremediation of pesticides has been defined as a process where the active ingredients are removed from the environment by microorganisms through biodegradation or biosorption processes, thereby decontaminating the environment (Ying 2018). Such processes reduce or eliminate the efficacy of the products against the target pests (Ying 2018). Historically, bioremediation factors include plants, bacteria, and fungi (Davison 2005; Kvesitadze et al. 2006; Juwarkar et al. 2010; Odukkathil and Vasudevan 2013; Singh et al. 2019), driven by factors such as microbe type, temperature, nutrition, enzymes, antimicrobial chemicals, types of chemical reaction such as the redox reactions and the size of the chemical compounds (Norris 1993; Varjani and Upsani 2017). In some cases, bacteria that release acids during bioremediation have the tendency to eliminate pathogenic fungi but could also eliminate other essential bacteria through the production of antimicrobial chemicals as by-products (Slonczewki et al. 2009; Chen et al. 2020). The focus of the current study, bioremediation factors of cucurbitacins, focused on both conventional and unconventional factors. The latter involved running short-term experiments to validate claims, which are being advanced in the study.

4.3.1 Potential Effects of Plants on Bioremediation of Cucurbitacins

Bioremediation of chemicals using plants is referred to as phytoremediation, which occurs in one of three forms, namely, phytoextraction, phytotransformation, and rhizodegradation (Vidali 2001; Kvesitadze et al. 2006). In phytoextraction, the test chemical accumulates in organs of the plant, referred to as phytoaccumulation (Kvesitadze et al. 2006). In contrast, phytotransformation and rhizodegradation each results in degradation of the chemicals without absorbing them and are technically referred to as phytodegradation (Kvesitadze et al. 2006). In living plants, cucurbitacin A was stored in fruit and roots of *C. myriocarpus,* whereas cucurbitacin B is stored in all organs of *C. africanus* plants (Jeffrey 1980). In chemical residue studies of the cucurbitacin phytonematicide in tomato production, cucurbitacin A and B were hardly detected in tomatoes or foliage of indigenous vegetable, nightshade (*Solanum nigrum*) (Dube and Mashela 2016; Shadung et al. 2017). In olives and strawberries, chemical residues of another non-polar triterpenoid, azadirachtin ($C_{35}H_{44}O_{16}$), were also not detected (Caboni et al. 2002, 2006). Generally, non-polar molecules, including glucose, cannot be transported through the bipolar membranes in the symplastic pathway of the endodermis into or out of the vascular bundle (Campbell and Reece 2005). In a tomato-cowpea or tomato-sweet stem sorghum rotation, where nematode population densities on tomato plants were managed using the cucurbitacin phytonematicides, chemical residues of cucurbitacins stimulated growth of cowpea plants (Mashela 2014) and sweet stem sorghum as successor crops (Mashela and Dube 2014). Observations in the cited two last studies suggested that phytoextraction and rhizodegradation of cucurbitacins in plants hardly occurred. Generally, the rate of bioremediation is influenced by numerous abiotic and biotic factors, including the size of the chemical compound (Varjani and Upsani 2017). Due to the large size of cucurbitacins and other triterpenoids, these chemicals probably have slower rates of biodegradation.

The two phytonematicides, when applied using empirically based concentration and application interval, did not suppress nematode population densities indefinitely, thereby necessitating the need for the establishment of the application intervals (Mashela et al. 2017a). The latter had been empirically designed in such a manner that the products would interrupt the ontogeny of the test nematode at least once, depending on the length of ontogeny of the managed nematode species. Generally, the application interval of the test phytonematicides is approximately

14–19 days for *Meloidogyne* species, which suggest the existence of cucurbitacin degradation processes in the soil as induced by either abiotic or biotic factors, or both. Plants infected by *Meloidogyne* species usually release copious concentration of amino acids into the rhizosphere, thereby modifying the rhizosphere through reducing soil pH (Wallace 1973). Acidic conditions in the rhizosphere of such plants might suppress most fungal pathogens while promoting bacterial growth, some of which might play undocumented roles in bioremediation processes of cucurbitacins.

4.3.2 Bioremediation of Cucurbitacins by Effective Microbes

At 35 weeks after storage of the phytonematicides, components of the constituents of EM from Nemafric-BL phytonematicide solution were subjected to the phylogenetic tree constructed based on maximum-likelihood analysis of 16S rRNA gene (Shokoohi 2020, unpublished data). Briefly, the South African strain of *Lactobacillus* was clustered with other *Lactobacillus* species that included *L. vini* and *L. mobilis,* along with unidentified *Lactobacillus* species (Fig. 4.1). Comparison of the 16S rRNA gene sequence of *Lactobacillus* isolates from Nemafric-BL phytonematicides corresponded with *L. mobilis* (acc. nr. AB242320) from the GenBank database at 87% similarity with 151 nucleotide differences. Besides, with *L. vini* (acc. nr. AY681132) the test strain had 87% similarity with 151 nucleotide differences. The 16S rRNA nucleotide sequence BLAST had a similarity from 85 to 87% with molecular strains of *Lactobacillus* species in the Genbank, without trace of most other bacteria that were used in the fermentation process of Nemafric-BL phytonematicide. In EM, to protect the intellectual property, the constituents of EM were provided in general terms, without providing the species names (Higa and Parr 1994). In the current study, *Lactobacillus* species, commonly called lactic acid bacteria, displayed all other components of EM, suggesting the existence of a consortium of *Lactobacillus* species in the constituents of EM. In mutant bitter Hwakesbury watermelon (*Citrullus lanatus* Thumb. Naakai (syn. *Citrulus vulgaris* Schad) study, *Bacillus* species remained as the dominant bacteria without affecting cucurbitacin E-glycoside content in the extracted solution (Martin et al. 2002).

Most bioremediation processes involve oxidation-reduction (redox) reactions, characterized by the existence of electron donors and electron acceptors (Vidali 2001). In order to enhance the understanding of why *Lactobacillus* species eliminated the other EM constituents, let us briefly review how the species achieve this feat. Fermentation is the process that includes two phases, first is the breakdown of glucose (glycolysis) to pyruvate molecules, with the net gain of two ATP and two NADH molecules in the cytoplasm of bacteria. The ATP molecules are used by *Lactobacillus* species for biological activities such as movement, feeding, and reproduction. In the second phase of fermentation, the produced NADH donates its electron in the form of H to the pyruvate molecules to convert them to lactic acids,

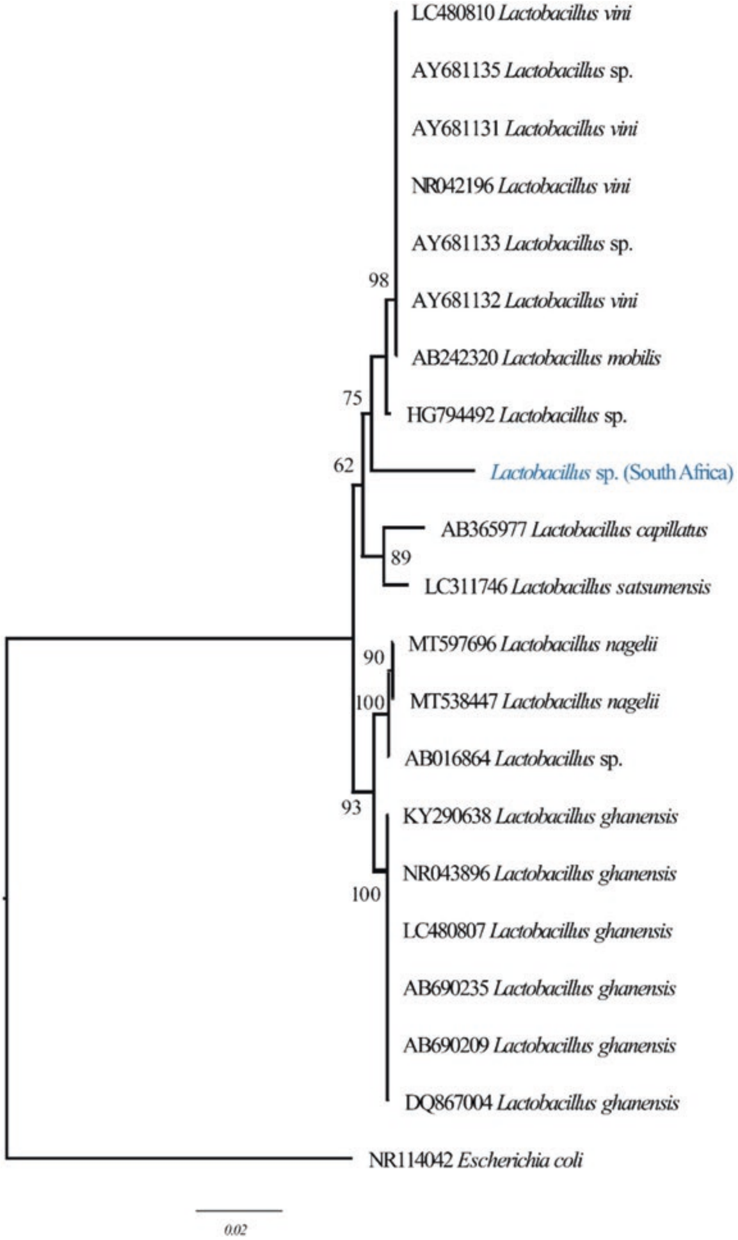

Fig. 4.1 Phylogenetic tree of South African strains of *Lactobacillus* species (blue color) derived from Nemafric-BL phytonematicide using Neighbor Joining method through MegaX software (Shokoohi 2021, unpublished data)

with NAD^{2+} being regenerated for re-use during glycolysis as an electron acceptor to allow the production of ATP to continue in the cytoplasm (Fig. 4.2).

In *Lactobacillus* species, the fermentation process had been described as being either homolactic or heterolactic fermentative process, where glucose molecules are metabolized through the phosphoketolase pathway as explained below (Vidali 2001):

$$\text{Homolactic fermentative process : glucose} + 2\,\text{ADP} + \text{Pi} \rightarrow 2\,\text{lactic acids} + 2\,\text{ATP}$$

$$\text{Heterolactic fermentative process : glucose} + \text{ADP} + \text{Pi} \rightarrow \text{lactic acids} + \text{ethanol} + \text{CO}_2 + \text{ATP}$$

Energy-wise, the homolactic fermentation process is the more efficient than the other is, since one molecule of glucose is metabolized to two molecules of lactic acids and two molecules of ATP as end-products with Pi being the phosphorus derived from the substrate. In contrast, during the heterolactic fermentation process, one glucose molecule is metabolized to one lactic acid, one CO_2, and one ATP as end-products (Vidali 2001). In addition to the formation of the released acids and hydrogen peroxide (H_2O_2), which also suppresses anaerobic bacteria except *Lactobacillus* species that are oxygen-tolerant. The latter also produce copious quantities of bacteriocins, salivaricins, and sodium butyrate, which inhibit growth of pathogenic microbes, including bacteria, fungi (Barbour et al. 2020), providing an explanation why the cucurbitacin phytonematicide is highly aseptic cucurbitacins known to be biodegraded by reductase enzymes (Ellis, 2002), but such enzymes are hardly produced by *Lactobacillus* species (Ellis 2002). Just to emphasize, in addition to other reductase-producing microorganisms (Yum et al. 1999), which are not part of the EM constituents, there could be many other bioremediation factors in the soil, which would help in the explanation of the loss of efficacy in the test products over time (Mashela et al. 2017a).

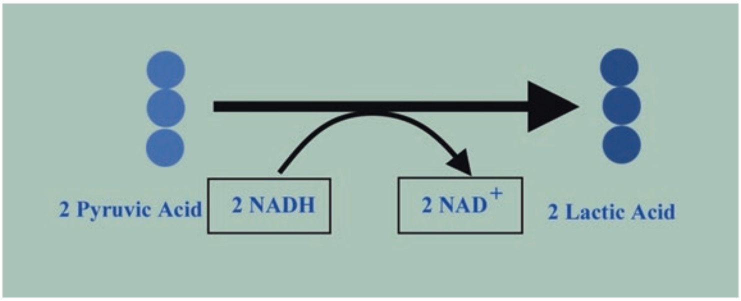

Fig. 4.2 Lactic acid fermentation uses pyruvic acid and NADH to generate NAD^+ and lactic acids, with NAD+ being reused in glycolysis to produce NADH and ATP, where ATP is used for biological activities—all in the absence of oxygen. The circles represent C atoms

4.3.3 Bioremediation of Cucurbitacins by Ecdysozoans

Ecdysozoans constitute one of the major groups within the Kingdom Animalia and include eight phyla, with the commonly reported being the Arthropoda, Kinorhyncha, Loricifera, Priapula, Onychophora, Nematomorpha, Nematoda, and Tardigrada (Ruggiero et al. 2015). Unlike other animals that build rigid skeletons using mineral elements, ecdysozoans build the cuticles as exoskeletons using organic material. Such exoskeletons are thinner and lighter than mineral skeletons, and therefore, do not require joints to allow flexibility as is the case in mineral skeletons. However, exoskeletons are sufficiently rigid to prevent growth of the body and therefore, ecdysozoans regularly shed off their cuticles, a process called ecdysis (molting), controlled by steroid hormones called ecdysteroids (Niwa and Niwa 2014). In the current work, we used the nematode cuticle to expound how ecdysozoans could play a role in bioremediation of cucurbitacins from the test cucurbitacin phytonematicides.

4.3.3.1 Nematode Cuticles

The nematode cuticle consists of four main layers, the outer layer (epicuticle), cortical layer, the collagen layer (with 4 distinct sublayers), and the hypodermal layer (Perry and Moens 2013). Only the epicuticle and median layers are shed off during the molting process (Fig. 4.3), whereas the hypodermis is used to generate the new cuticle (Schultz et al. 2014). The newly molted juvenile exits the shed cuticular layer through the stoma. The epicuticle is formed by lipids, which are coated with a glycoprotein, technically referred to as a surface coat that plays a protective role to the epicuticle. Lipids in the epicuticle enhance mobility of nematodes in aqueous solutions due to their incompatibility (Schultz et al. 2014). The collagen has four protein-rich sublayers, (a) cortical layer with insoluble proteins called cuticulins, (b) median layer with pillar-like proteins filled with gelatinous matrix, (c) basal layer with distinct soluble proteins in the form of fiber and those as dense gelatinous matrix (Fig. 4.3).

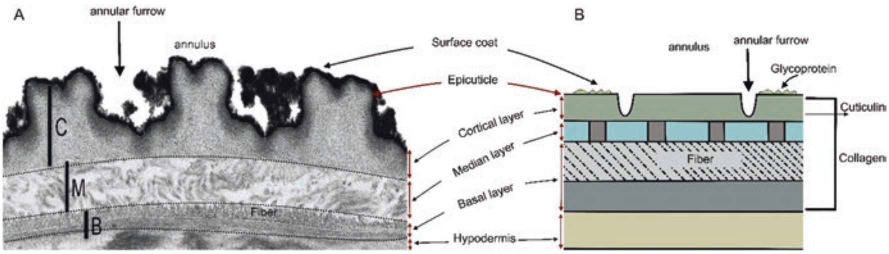

Fig. 4.3 Schematic nematode cuticle being molted (**a**) and cuticle layers (**b**) of *Caenorhabditis elegans* from transmission electron microscopy photograph (Schultz et al. 2014, improved from Shokoohi 2019)

4.3.3.2 Role of Epicuticle in Bioremediation of Cucurbitacins

Cucurbitacins are lipophilic (Van Wyk and Wink 2004), which confers them the status of being hydrophobic (Patel et al. 2009). The two properties improve the loading capabilities of cucurbitacin drugs (Patel et al. 2009). Lipids in the epicuticles have the capability of attracting cucurbitacin molecules from aqueous solutions and therefore their chemical status of being lipophilic. This attraction provides sufficient explanation why nematodes are highly sensitive to cucurbitacin phytonematicides in crude and purified forms (Dube and Mashela 2016, 2017, 2018; Dube et al. 2019). The attraction of cucurbitacins by the epicuticles removes the active ingredients of cucurbitacins from the environment, which agrees with the description of bioremediation processes (Jørgensen 2007; Canak et al. 2019). Once cucurbitacins are removed from the environment by the epicuticles, they can, due to their hydrophobic properties, further be attracted to proteins in the middle layers, which are replete with proteins, and therefore, well-suited for these roles, referred to as isoprenylation and farnesylation reactions.

4.3.3.3 Role of Subcuticular Layers in Bioremediation of Cucurbitacins

Isoprenylation is the addition of hydrophobic molecules such as cucurbitacins through the prenyl groups (3-methylbut-2-en-1-yl) to the proteins (Marshall 1993; Casey and Seabra 1996; Novelli and D'Apice 2012), whereas the addition of lipids to proteins is lipidation. The prenyl groups are important for protein-to-protein binding through specialized prenyl-binding domains. Prenylation involves the transfer of either a farnesyl or a geranylgeranyl moiety to C-terminal cysteine(s) of the target protein, using one of three enzymes, namely, farnesyl transferase, Caax protease, and geranylgeranyl transferase I (Novelli and D'Apice 2012). Importantly, farnesyl is one of the enzymes required in the biosynthesis of cucurbitacins through the MEP/DORXP pathway (Chen et al. 2005).

4.3.3.4 Evidence of Isoprenylation and Farnesylation in Nematodes

After exposing J2 of the southern root-knot nematode, *M. incognita*, to a geometric series (0, 2, 4, 8, 18, 32 and 64%) of Nemafric-BL phytonematicides for 72 h, total protein was determined using TruSpecCHNS Macro (Leo, St. Joseph, MI, USA) (Mashela and Shokoohi 2021). Briefly, data were subjected to analysis of variance using SAS software to establish the significance at 5% level probability. Prior to subjecting the data to lines of the best fit, data expressed as exponentials (2^0, 2^1, 2^2, 2^3, 2^4, 2^5 and 2) were transformed using $\log_2^x = x$ (1) to homogenize the variance (Causton 1977). Using $x = -b_1/2b_2$ relation from the quadratic relation, $Y = b_2x^2 + b_1x + c$, the minimum total protein was accrued at 4.9% (transformed data) phytonematicides. During isoprenylation, which breaks down the proteins, there was a gradual decrease of total proteins (Fig. 4.4). After the minimum, the

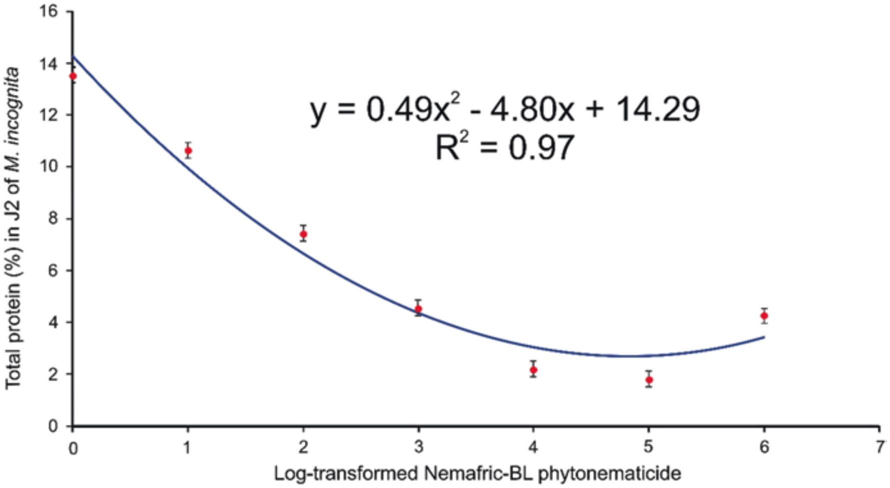

Fig. 4.4 Response of total protein to increasing concentration of Nemafric-BL phytonematicide (Mashela and Shokoohi 2021)

total protein started to increase, thereby supporting the view of farnesylation. The latter is a type of isoprenylation where a post-translational modification of proteins in which an isoprenyl group is added to a cysteine residue, which is an important process to mediate protein-to-protein interactions, thereby increasing total proteins to enable protein-to-protein membrane interactions to occur (Marshall 1993; Casey and Seabra 1996; Novelli and D'Apice 2012). Both isoprenylation and farnesylation as observed in this study supported the principles of density-dependent growth patterns, which occur when biological entities are subjected to increasing concentration of allelochemicals such as cucurbitacins (Liu et al. 2003; Mashela et al. 2017a).

4.4 Conclusion and Future Perspectives

Bioremediation processes involving secondary metabolites of phytonematicides involve various processes. Such processes require some knowledge of the biosynthetic pathways, including the precursors and enzymes involved in such processes, along with enzymes that can play a role in the reversal of the processes. *Lactobacillus* species do not produce reductase enzymes that have capabilities of hydrolyzing cucurbitacins, but the soil is replete with reductase-producing microorganisms, which could play some role in bioremediation process of cucurbitacins. In the current study, supported by empirical-evidence, we concluded that in addition to other potential bioremediation factors of cucurbitacins, the ecdysozoans play an active role in bioremediation of cucurbitacins through biosorption, isoprenylation, and farnesylation reactions due to the unique properties of cucurbitacins and cuticles.

Future studies with other cuticle-bearing organisms in the super phylum ecdysozoans would provide an essential explanation on limited persistence of cucurbitacin phytonematicides when applied under field conditions.

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Chapter 5
Following the Steps Towards Glyphosate Bioremediation. How Close Are We to Field Success?

Neli Romano-Armada and Verónica B. Rajal

Abstract Glyphosate-based herbicides (GBHs) are used in agriculture either for cropping glyphosate-resistant species or to control weeds in various crops, from herbaceous plants like tomatoes to trees such as vines and even forest plantations. Their extensive use exposes the land surface and water bodies to the herbicide, posing a risk to non-target organisms worldwide. GBHs are broken down in the environment by the whole soil or water microbiome. There is incomplete understanding of different bacterial groups' roles in this process. Although not every single species can be isolated, its functional profile or metabolism counts. A species can be removed from the ensemble without a major negative impact on the overall process as long as other microorganisms perform that same function. We currently have some insight into what single bacteria do when degrading glyphosate. In fact, the classic approach for bioremediation consists of isolating and studying the removal potential of single type of microorganism. Using this approach, researchers have identified the aminomethylphosphonic acid (AMPA) and sarcosine pathway as a primary route of glyphosate breakdown. However, there remains a need for a glyphosate removal strategy that mimics natural microbiomes' action to avoid glyphosate pseudo persistence by accumulation in the environment.

Keywords Pseudo-persistent · Synthetic community · Hormesis · Microbiome · Resilience · Sustainability

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5.1 Introduction: Glyphosate

In the mid-20th century, there was a shift in agricultural practices that allowed an increase in food production. Known as the Green Revolution, crop yields increased because of the combination of new developments in technology for mechanization, generation of higher-yielding plants, and synthesis of novel agrochemicals (Pellegrini and Fernández 2018; John and Babu 2021). Although there were undeniable positive impacts on food security and land use reduction, the environmental cost of higher energy consumption and contamination associated with agrochemicals production was significant (Pellegrini and Fernández 2018; John and Babu 2021).

Among the novel compounds to improve crop yield, a herbicide introduced in the seventies, commonly known as glyphosate (N-(phosphonomethyl)glycine), revolutionized the market by allowing higher profits from cropping glyphosate-resistant (GR) plants (Duke and Powles 2008; Benbrook 2016). This synthetic compound, a glycine analogue, interferes with the shikimic acid pathway (present in plants and some microorganisms) by inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase, preventing the production of amino acids critical for protein synthesis and growth. Hence, glyphosate kills organisms without resistance (Fig. 5.1). To date, there have been 11 herbicide modes of action described, and glyphosate is the only compound within its group. Glyphosate-based herbicides

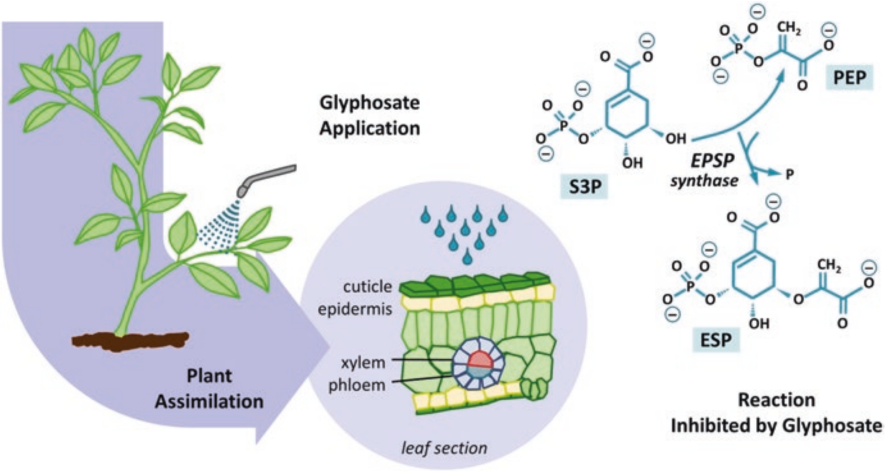

Fig. 5.1 Glyphosate's mode of action. (1) Contact and absorption: after application, glyphosate readily penetrates the cuticle; (2) Translocation: cell to cell migration begins towards the phloem which transports it throughout the plant; and (3) Site of action: glyphosate reaches the plant's growing tissues; (4) Mechanism of action: inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS) that catalyzes the reaction between shikimate-3-phosphate (S3P) and phospho-enolpyruvate (PEP) to produce 5-enolpyruvilshikimate-3-phosphate (ESP), which after dephosphorylation becomes a precursor of the amino acids phenylalanine, tyrosine, and tryptophan

(GBHs) act as broad-spectrum systemic post-emergence herbicides, i.e., after emergence and growth. Once in contact with the herbicide, a plant absorbs it through its green organs (stems and leaves) to later translocate it to regions of active growth, where it accumulates hindering plant development (Duke and Powles 2008) (Fig. 5.1).

However, since its introduction, the use of glyphosate has diversified. Because of its herbicidal power and alleged low toxicity, its use expanded beyond agriculture (Duke 2018). Indeed, it was used in different countries to keep weeds away from roadsides (Huang et al. 2005) and railways (Amaro-Blanco et al. 2019; Kudsk and Mathiassen 2020), to maintain clean schoolyards or sidewalks (Markets and Markets 2017), to clean water bodies (Robichaud and Rooney 2021), and even to fight illegal drug production by spraying coca plantations in the middle of the Colombian jungle (Camacho and Mejía 2017; Idrovo and Rodríguez-Villamizar 2018).

5.2 Current Use and Concerns

During its early years, glyphosate was used moderately compared to other herbicides. However, the introduction of genetically engineered (GR) crops in 1996 was the starting point of a worldwide explosion in the use and mass production of GBHs (Benbrook 2016; Duke 2018). Two major factors drove glyphosate's use increase; first the generation of GR staple crops such as soybean (*Glycine max*), corn (*Zea mays*), and cotton (*Gossypium hirsutum* L.), and later in the year 2000, the loss of patent protection which enabled industries all over the world to manufacture technical grade glyphosate or other GBHs (Benbrook 2016). Since its introduction, solely in agriculture, glyphosate application worldwide rose from about 51 million kg to approximately 747 million kg in two decades (Benbrook 2016). Moreover, a recent forecast for the glyphosate market estimated an annualized average revenue growth rate of 6.32% between 2016 and 2022, projecting that by 2022 it will reach USD 9.91 billion (Markets and Markets 2017).

Regarding the environmental fate of glyphosate used in agriculture, there are two possible outcomes for the sprayed plants. Regular plants (without glyphosate resistance) will die, and their biomass along with the residual herbicide will accumulate in the soil surface until its degradation. However, GR species will incorporate the glyphosate, translocating it to different tissues, and finally exuding part of the herbicide by the roots and storing the remaining part in the fruits or grains of oilseed plants. However, when the GR plant dies, it will also leave its glyphosate-containing biomass to degrade in the soil surface, just like non-GR plants. The storing of glyphosate in plant biomass expands its life in the environment (Mamy et al. 2016). In soil, the herbicide favors quality degradation by changing chemical, physical, and biological properties, affecting adversely the soil's microbiota (Romano-Armada et al. 2017), which is often in charge of keeping the balance between the soil's biotic and abiotic components to sustain its quality and health (Martinez et al. 2018).

Glyphosate residues in the soil bind tightly to inorganic particles, preventing the herbicide from moving into ground water, but not from being transported by runoff. Contrary to previous conclusions that the herbicide was immobilized by adsorption to the sediment in water bodies, recent studies show the potential of glyphosate toxicity in wetlands via biofilm concentration. The herbicide concentrates in biofilms and finds its way up in the trophic chain (Beecraft and Rooney 2021). Moreover, low doses of GBHs in the water stimulate the growth of harmful algae (Dabney and Patiño 2018), adding to the detrimental effect of the herbicide in water ecosystems.

5.3 Ecosystem Effects

Although GBHs are designed to facilitate agriculture, they can indirectly affect the crops negatively by altering the microbial soil dynamics in charge of recycling nutrients and controlling phytopathogens, and by chelating metals preventing the proper nutrient uptake by the plants (Martinez et al. 2018). The selection pressure caused by years of GBH's application upon the rhizosphere microbiome is believed to be involved in the emergence of the so-called superweeds (i.e., plants with natural resistance to multiple herbicides) via microbial acquired resistance and horizontal gene transfer (Cuhra 2018). Glyphosate is not the sole culprit for this phenomenon, accounting for 42 resistant weed species worldwide; it only poses a medium risk of herbicide resistance compared to other herbicides (Moss et al. 2019). However, it plays an important role because of its unique mode of action, and it is part of the problem along with other herbicides used in unsustainable agricultural practices around the world (Davies et al. 2019; Moss et al. 2019).

When considering yield and revenue, it is easy to forget that weeds are living organisms as well, and they are part of the ecosystem. Therefore, as a part of the agroecosystem, weeds also provide environmental services by harboring decomposers, predators, and pollinators. The practice of farming herbicide-resistant crops, in addition to the abuse of glyphosate application to control weeds, has a relevant impact on biodiversity in two major direct ways by changing the plant and microbial composition of either soil or water bodies. Thus, the trophic nets are altered at two critical levels: producers and decomposers, disrupting proper nutrient cycling and energy transfer along with other systemic functions such as pollination (Schütte et al. 2017). To mention a notable example of the impact of weed control on biodiversity at a global scale, the use of glyphosate to grow herbicide-resistant crops in the United States is believed to be one of the culprits for reduction of the monarch butterfly (*Danaus plexippus*) population. The primary hypothesis is that the extended use of glyphosate decimated the population of milkweeds (*Asclepias syriaca*) in the reproduction areas of the butterfly, reducing the food availability for its larvae with a consequent life cycle perturbation (Belsky and Joshi 2018).

5.4 Glyphosate's Paradox

Due to the accumulation of glyphosate in the environment, many non-target organisms are constantly exposed to it (Primost et al. 2017). Different reports showed the toxic effects of glyphosate along a range of animals, from lower invertebrates to higher vertebrates (Gill et al. 2018). Although the shikimic acid pathway is absent in mammals, several adverse effects such as genotoxicity, cytotoxicity, and endocrine disruption have also been reported in humans (Gill et al. 2018). The innocuous status of glyphosate has been challenged over the last two decades. Concerned researchers showed alarming data that led to a change in categories for glyphosate from safe to probably carcinogenic for humans in 2015 by the International Agency for Research on Cancer (IARC) (Cressey 2015; Sergi 2019). However, since then, other studies and literature revisions dissent with IARC's conclusion stating that the data does not support glyphosate's carcinogenic and genotoxic risk to humans (Acquavella et al. 2016; Brusick et al. 2016; Williams et al. 2016).

Although the controversy surrounding glyphosate's safety (Peterson Myers et al. 2016; Duke 2020), and the use of alternative herbicides when possible (Buerge et al. 2020), there is a tendency to sustain its use because of its high herbicidal effectiveness compared to other compounds and its unique mode of action (Fig. 5.1). Within the technological package of many cash crops, other herbicides such as atrazine, paraquat, and metolachlor (regarded as endocrine disruptor, associated with Parkinson's disease and classified as Category III by the US EPA, respectively) present higher risks for human health and the environment regarding toxicity and ecosystem organization perturbation (Klingelhöfer et al. 2021). Scientists who believe that the benefits of using glyphosate instead of other herbicides outweigh its harmful potential are searching for alternatives to reduce negative environmental impacts and human health deterioration due to glyphosate overuse and accumulation. Therefore, as expected, the countries currently leading glyphosate-related research (USA, Brazil, Canada, China, and Argentina) are those with the highest values of herbicide use (Klingelhöfer et al. 2021).

5.5 Glyphosate Removal Efforts

Glyphosate is virtually everywhere (Lupi et al. 2015); the compound's high stability and the current rate of application in agriculture turn it into a pseudo-persistent pollutant. Thus, there is a threat of environmental degradation because of its accumulation due to a combination of overuse and slow degradation once in the environment (Primost et al. 2017). In this regard, several physical and chemical methods of degradation have been explored (Fig. 5.2), most of which consist of adsorption and advanced oxidation processes (Feng et al. 2020). However, these alternatives are not practical when facing the need to remediate large soil extensions or water volumes. In these cases, biologically mediated remediation deems to be the best option.

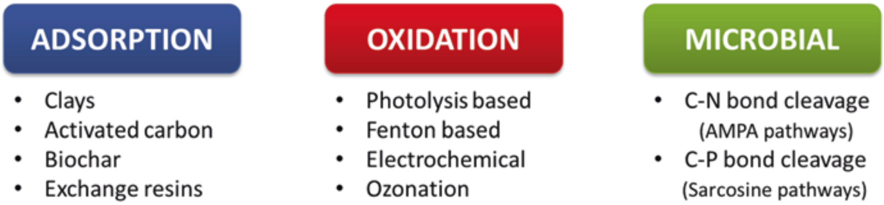

Fig. 5.2 Physical, chemical, and biological alternatives for glyphosate removal

Microbial-mediated degradation of pesticides is an environmentally friendly and cost effective alternative. Nevertheless, this technique requires long residence time, even at favorable environmental conditions, for the biological treatment to achieve high mineralization rates (Feng et al. 2020). Also, in the case of glyphosate, special attention must be paid to the production of intermediate metabolites such as aminomethylphosphonic acid (AMPA) with higher environmental persistence and destructive potential (Primost et al. 2017). In the soil system, the amount of AMPA (in combination with the soil microbial biomass) serves as a good predictor of soil degradation (Romano-Armada et al. 2019).

To date, as proposed by Zhan et al. (2018), the AMPA and the sarcosine pathway are the two major microbial metabolic pathways described for glyphosate breakdown. The pathway yielding AMPA and glyoxylate involves cleavage of the C–N bond via catalysis of glyphosate oxidoreductase (Bhatt et al. 2021), then the intermediate metabolite AMPA can be excreted in the environment or further degraded through the action of C-P lyase. The sarcosine pathway, involves direct cleavage of the glyphosate C–P bond by the enzymatic complex C-P lyase, producing phosphate and sarcosine, which are later used in microbial metabolism (Fig. 5.3). In both pathways, the intervention of C-P lyase is key to mineralize glyphosate, removing the AMPA metabolite from the environment (Bhatt et al. 2021).

Until the late 1980s, the sarcosine pathway was thought to be exclusive to Gram negative microorganisms (Wackett et al. 1987) because of the absence of evidence showing C-P lyase expression in Gram positive bacteria. However, Gram positive strains *Arthrobacter* sp. GLP-1, *Arthrobacter* sp. GLP-1/Nit-1, and *Streptomycetes* sp. StC can degrade glyphosate by means of the sarcosine pathway (Pipke et al. 1987; Pipke and Amrhein 1988b; Obojska et al. 1999). Moreover, *Bacillus cereus* CB4 presents both AMPA and sarcosine pathways as degradation mechanisms (Fan et al. 2012). Nevertheless, within the Fungi kingdom, thus far only *Purpureocillium lilacinum* and *Penicillium* 4A21 are thought to be able of using the sarcosine pathway (Spinelli et al. 2021; Correa et al. 2023) (Table 5.1).

Regardless of the glyphosate degrading pathway present used by the microorganisms described in the literature, most microbial isolates can use glyphosate as a phosphorus source. Conversely, not many are able to use the compound as a carbon and nitrogen source. In fact, only four strains have been described that are capable of using the compound as a carbon source: *Achromobacter* sp. LW9, *Agrobacterium radiobacter* SW9, *Comamonas odontotermitis* P2, and *Ochrobactrum intermedium*

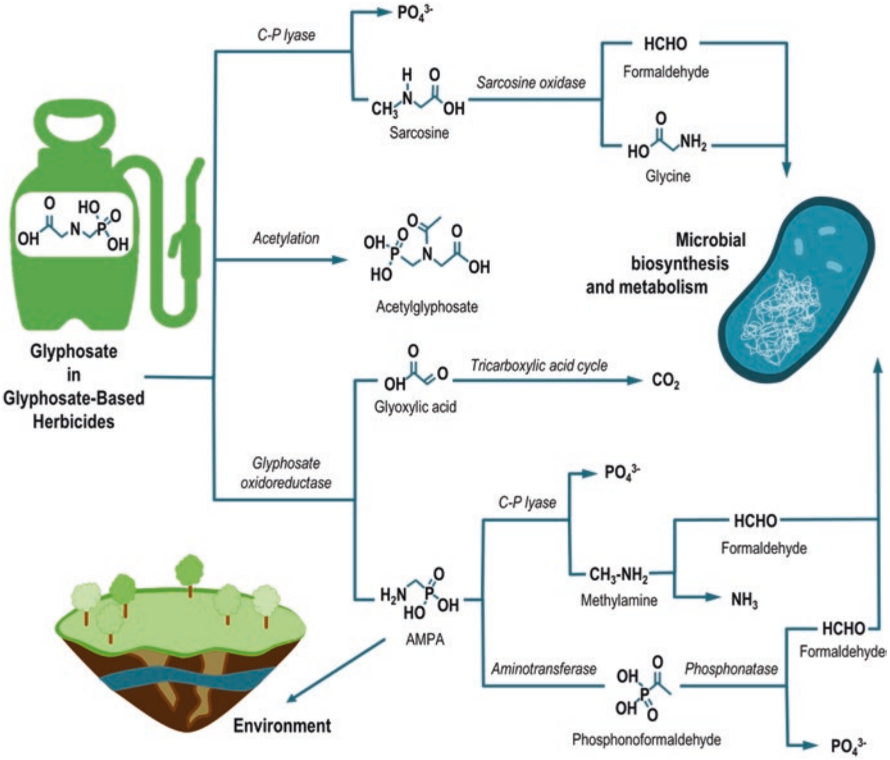

Fig. 5.3 Degradation pathways of glyphosate in bacteria (Feng et al. 2020)

Sq20; three others are able of using it as nitrogen source: *Arthrobacter* sp. GLP-1/Nit-1, *Streptomycete* sp. StC, and *Penicillium chrysogenum* (Table 5.1).

5.6 Current Approach for Bioremediation

The alternatives described for bioremediation have focused on microbial isolation for their use in glyphosate removal (Elarabi et al. 2020; Masotti et al. 2021). Oftentimes, the sources of isolation are contaminated soils or soils from fields with a long history of herbicide application (Dick and Quinn 1995; Fan et al. 2012; Sviridov et al. 2012; Ermakova et al. 2017; Firdous et al. 2018; Xu et al. 2019; Pérez Rodríguez et al. 2019; Firdous et al. 2020). However, promising microorganisms come from sources as diverse as sewage sludge (Balthazor and Hallas 1986; Wackett et al. 1987; Jacob et al. 1988; Mcauliffe et al. 1990; Obojska et al. 1999), rhizosphere (Kryuchkova et al. 2014), and even samples of everyday domestic appliances such as the water from a central heating system (Obojska et al. 2002) (Table 5.1).

Table 5.1 Microbial isolates with the potential for glyphosate bioremediation

Gram negative bacteria				
Strain	Source	Breakdown pathway	Glyphosate as a nutrient source	References
Achromobacter sp. LW9	Activated sludge from a glyphosate containing waste stream	AMPA	Sole source of C in phosphate presence	Mcauliffe et al. (1990)
Achromobacter sp. MPK 7A	Glyphosate-polluted soil	Sarcosine	Sole source of P	Ermakova et al. (2017)
Achromobacter sp. MPS 12A	Methylphosphonic acid-polluted soil	Sarcosine	Sole source of P	Sviridov et al. (2012)
Agrobacterium radiobacter	Sludge from water treatment plant	Sarcosine	Sole source of P	Wackett et al. (1987)
Agrobacterium radiobacter SW9	Activated sludge from a waste stream	AMPA	Sole source of C in phosphate presence	Mcauliffe et al. (1990)
Alcaligenes sp. GL	Contamination during glyphosate resistance assay in cyanobacterium *Anacystis nidulans* culture	Sarcosine	Sole source of P	Lerbs et al. (1990)
Comamonas odontotermitis P2	Glyphosate-polluted soil	AMPA + Sarcosine	Sole source of C Sole source of P	Firdous et al. (2020)
Enterobacter cloacae K7	Plant rhizoplane	Sarcosine	Sole source of P	Kryuchkova et al. (2014)
Flavobacterium sp. GD1	Activated sludge from industrial plant	AMPA	Sole source of P	Balthazor and Hallas (1986)
Ochrobactrum anthropi GPK3	Glyphosate-polluted soil	AMPA + Sarcosine	Sole source of P	Sviridov et al. (2012)
Ochrobactrum intermedium Sq20	Glyphosate-polluted soil	Sarcosine	Sole source of C	Firdous et al. (2018)
Ochrobactrum sp. GDOS	Soil	AMPA	Sole source of P	Hadi et al. (2013)
Providencia rettgeri GDB 1	Glyphosate-polluted soil	AMPA	-	Xu et al. (2019)
Pseudomonas pseudomallei 22	Soil	AMPA	Sole source of P	Penaloza-Vazquez et al. (1995)
Pseudomonas sp. 4ASW	Glyphosate-polluted soil	Sarcosine	Sole source of P	Dick and Quinn (1995)
Pseudomonas sp. GLC11	Mutant of *Pseudomonas* sp. PAO1	Sarcosine	Sole source of P	Selvapandiyan and Bhatnagar (1994)
Pseudomonas sp. LBr	Activated sludge from a glyphosate containing waste stream	AMPA + Sarcosine	Sole source of P	Jacob et al. (1988)
Pseudomonas sp. PG2982	*Pseudomonas aeruginosa* ATCC 9027	Sarcosine	Sole source of P	Kishore and Jacob (1987)
Pseudomonas sp. SG-1	Sample from aerobic digester	AMPA	Sole source of P	Talbot et al. (1984)
Rhizobiaceae meliloti 1021	*Rhizobiaceae meliloti* mutant (transposon induced)	Sarcosine	Sole source of P	Liu et al. (1991)

Gram positive bacteria

Strain	Source	Breakdown pathway	Glyphosate as a nutrient source	References
Arthrobacter atrocyaneus ATCC 13752	German cell cultures collection and ceparium	AMPA	Sole source of P	Pipke and Amrhein (1988a, b)
Arthrobacter sp. GLP-1	Contamination in *Klebsiella pneumoniae* culture	Sarcosine	Sole source of P	Pipke et al. (1987)
Arthrobacter sp. GLP-1/Nit-1	Mutant of *Arthrobacter* sp. GLP-1	Sarcosine	Sole source of P Sole source of N	Pipke and Amrhein (1988a, b)
Bacillus aryabhattai FACU3	Soil sample from agro-industrial zone	AMPA	-	Elarabi et al. (2020)
Bacillus cereus CB4	Glyphosate-polluted soil	AMPA + Sarcosine	Sole source of P	Fan et al. (2012)
Geobacillus caldoxylosilyticus T20	Central heating system water	AMPA	Sole source of P	Obojska et al. (2002)
Lysinibacillus sphaericus	Mainly soil (mixture of five strains)	Sarcosine	-	Pérez Rodríguez et al. (2019)
Streptomycete sp. StC	Raw sludge from wastewater treatment plant	Sarcosine	Sole source of P Sole source of N	Obojska et al. (1999)

Fungi

Strain	Source	Breakdown pathway	Glyphosate as a nutrient source	References
Aspergillus niger	Soil	AMPA	Sole source of P	Krzyśko-Lupicka et al. (1997)
Aspergillus oryzae A-F02	Aeration tank in a pesticide factory	AMPA	Sole source of P	Fu et al. (2017)
Mucor IIIR	Arable soil	AMPA	Sole source of P	Krzyśko-Łupicka and Orlik (1997)
Penicillium 4A21	Amazon forest soil with added glyphosate	AMPA + Sarcosine	Sole source of P	Correa et al. (2023)
Penicillium IIR	Arable soil	AMPA	Sole source of P	Krzyśko-Łupicka and Orlik (1997)
Penicillium chrysogenum	Soil	AMPA	Sole source of N	Klimek et al. (2001)
Penicillium notatum	Spontaneous growth on the synthetic herbicide 9-di-*n*-butyl-9-hydroxyfluorenyl-9-phosphonate	AMPA	Sole source of P	Bujacz et al. (1995)
Purpureocillium lilacinum	Agricultural environment	Sarcosine	Sole source of P	Spinelli et al. (2021)
Scopulariopsis sp.	Soil	AMPA	Sole source of P	Krzyśko-Lupicka et al. (1997)
Trichoderma harzianum	Soil	AMPA	Sole source of P	Krzyśko-Lupicka et al. (1997)

Glyphosate microbial remediation studies commonly involve using it as a nutrient source, either of carbon, nitrogen, or phosphorus (Table 5.1). Bacteria use diverse mechanisms to break down the compound, consequently removing it from the environment. Degradation of the herbicide is the main researched strategy, i.e., there are no studies that show microbial bioremediation by inner cell accumulation (if possible) or EPS immobilization of the compound. Moreover, within pesticides degradation strategies, microorganisms are commonly assayed as single strains or forming consortia.

Bacteria present a higher degradation efficiency for glyphosate when applied in consortia, which have a higher diversity of catabolic pathways for biodegradation, rather than as cultures of single organisms (Góngora-Echeverría et al. 2020). Hence, bioremediation of many toxicants through microbial consortia proved to be more efficient than using pure cultures (Pileggi et al. 2020). For example, this strategy enhanced the removal of contaminants such as lindane and Cr (VI) from liquid and soil systems (Aparicio et al. 2018; Raimondo et al. 2020). Unfortunately, field evaluations of bioremediation potential are scarce (Pérez Rodríguez et al. 2019), reaching oftentimes a maximum assay scale of controlled bioremediation of environmental samples within the laboratory (Fu et al. 2016; Cheloufi et al. 2017), turning the isolated bacteria into good prospects for a bioreactor but with little impact at the field level.

5.7 Setting the Basis for the Future in Bioremediation

Understanding the role of specific enzymes and functional genes of single microorganisms involved in glyphosate breakdown is critical to overcoming scale setbacks (Pérez Rodríguez et al. 2019; Bhatt et al. 2021; Masotti et al. 2021). This information gives insights for proper land management to favor the microbial activity by generating optimal soil environmental conditions such as pH, aeration, humidity, and carbon to nitrogen ratio. Current studies about environmental degradation explore microbial community molecular metadata via next-generation sequencing (NGS) and high-throughput DNA sequencing (Miseq), to give insight about diversity and abundance as health and quality biomarkers. In the study of soil degradation due to Lanzhou lily (*Lilium davidii* var. unicolor) monoculture in China, specific shifts in the microbial structure were identified as positively and negatively related to lily's culture, concluding that the phylum *Proteobacteria* and the genus *Sphingomonas* could be considered as good indicators of sustainable soil management (Shi et al. 2021).

However, studies of glyphosate's impact on the soil microbiota have not given consistent results (Roslycky 1982). Depending on the study, the experimental outcomes of the impact of glyphosate's application on the soil microbial community gave conflicting results, showing negative effects (Kremer and Means 2009; Zobiole et al. 2011; Tofiño Rivera et al. 2020), inconclusive or unknown knock-on effects (Lane et al. 2012; Mandl et al. 2018), no effect at all (Kepler et al. 2020), or even potential positive effects (Locke et al. 2008). These results serve as good reminders that the soil system is complex and dynamic, and its behavior depends on a wide set of environmental, social, and economic variables. Several years of specific pesticides application or tilling leave a legacy that shapes the microbiome of a soil, leading, for example, to completely different microbiomes in adjacent plots.

5.8 Changing Lanes Towards Future Strategies

Although some studies stated that the response of a soil microbiome towards glyphosate application can be applicable to other soils (Busse et al. 2000), the available literature proves otherwise. For example, the prokaryote and fungal soil community sequencing of a 2-year long field study on corn and soybean cropped in a range of different sites showed no significant differences in composition between soils from plots with and without GBH's application (Kepler et al. 2020). Conversely, the high-throughput sequencing of the bacterial and fungal microbiome of vineyard soils with different under-vine weed control managements showed dramatic differences in the microbial community composition of soils treated with glyphosate compared to other management practices (Chou et al. 2018). Nevertheless, a recent study proved the potential of a synthetic microbial community tailored to mimic the root microbiome of *Arabidopsis*¸ which after slight composition modifications was able to induce plant growth promotion under the application of low doses of glyphosate (Ramirez-Villacis and Finkel 2020).

Understanding the soil microbiome behavior when faced with glyphosate is paramount in weed management science (Gornish et al. 2020) for many reasons. First, to avoid inducing glyphosate resistance by horizontal gene transfer from bacteria to plants (Cuhra 2018). Second, to avoid inducing emergence of phytopathogens which require the input of other pesticides (Kremer and Means 2009; Zobiole et al.

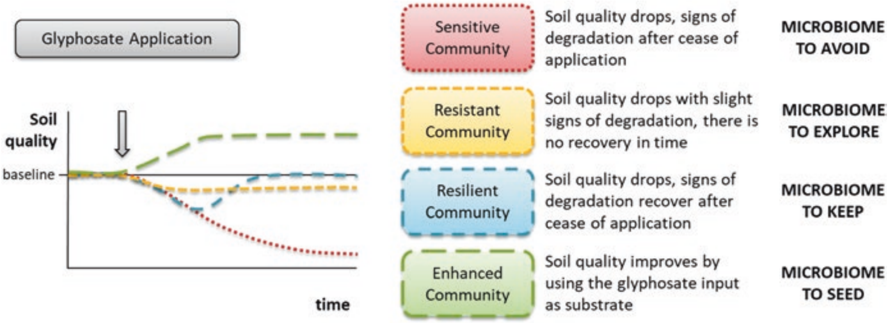

Fig. 5.4 Hypothetical behavior of different types of soil and root microbiomes after the first input of glyphosate followed by continuous and systematic application. Understanding the microbial community strengths and weaknesses is essential for the future search for bacterial ensembles which prove resilient to glyphosate's application negative effect

2011). And finally, to apply agricultural practices that favor optimal soil environmental conditions for microbial communities with the potential to improve plant growth (Ramirez-Villacis and Finkel 2020) and soil quality after glyphosate application.

Currently, it is possible to determine changes in the microbial community's composition and functions following a perturbation event. Hence, through the interpretation of such responses, the likelihood of identifying the strengths and weaknesses of the microbial community faced with glyphosate application is higher. Targeting resilient microbiomes opens up the opportunity for two strategies of in situ glyphosate degradation: taking them as a template for synthetic communities' creation, or to enrich and use them to inoculate the soil. Both alternatives could speed up the process for successful bioremediation at the field level (Fig. 5.4).

5.9 Conclusion

Future studies should be performed to weigh the impact of glyphosate application on the soil microbial community's functional structure and metabolism. There is a need to change the current approach on bioremediation, which seeks solutions through a reduced number of microorganisms, to explore the possibilities given by omics methodologies combined with ecological analysis of the soil microbiome.

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Chapter 6
Role of Enzymes in Biodegradatison of Pesticides: General Aspects and Recent Advances

Rupa Rani, Vipin Kumar, and Pratishtha Gupta

Abstract Environmental pollution is one of the prominent problems of the twenty-first century. Since the introduction of pesticides for the killing of pests leads to an increase in crop productivity, indiscriminate use of pesticides for pest and vector control causes soil and water pollution due to environmental persistence, toxicity and accumulation. Several physicochemical strategies have been employed for the degradation of pesticides from polluted soil and water, but these techniques are costly and produce toxic products. Consequently, there is a need for effective and safe techniques for pesticides bioremediation. This chapter presents an overview of pesticides with various physicochemical and biological strategies for efficient pesticides bioremediation. This chapter also deals with several bacteria and fungi that have been employed in the biodegradation of pesticide residues. Biodegradation ability is based on enzymes which include oxidoreductase (GOX), monooxygenase (Esd, Ese, Cytochrome P450), dioxygenases (TOD), carboxylesterases (E3), phosphotriesterases (OpdA, OPH, PTE), haloalkane dehalogenases (AtzA, LinB and TrzN), haloalkane dehydrochlorinases (LinA), diisopropylfluorophosphatase (DFPase), paraoxonase (PON1), SsoPox, organophosphate acid anhydrolase (OPAA).

Keywords Pesticides · Biological methods · Bioremediation · Enzymes

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Table 6.1 Pesticides, their characteristics and examples

Pesticides	Characteristics	Examples
Acaricides	Kill mites feeding on animals and plants	Chlorenthol, chlorfenson, bifenazate, cyhexatin, dicofol, dinoseb
Fungicides	Kill fungi (such as moulds, blights, rusts, and mildews)	Azoxystrobin, Bordeaux mixture, captan, dinocap, pentachlorophenol (PCP), sulphur, thiram
Herbicides/ weedicides	Kill weeds and other plants	Dinoseb, atrazine, isoproturon, maleic hydrazide, simazine, 2,4D, 2,4,5-T, Dicamba
Insecticides	Kill insects and arthropods	Aldrin, aldicarb, carbamyl, DDT, endosulfan, HCH, lindane, malathion
Molluscicides	Kill snails and slugs	carbonyl, metaldehyde, methicarb, PCP, phorate
Microbial pesticides	Kill microorganism pests	Bordeaux mixture, cupric hydroxide, streptomycin, tetracycline
Nematicides	Kill nematodes that feed on plant roots	Aldicarb, methyl isocyanate, methyl bromide
Rodenticides	Control rodents including mice	Aluminium phosphide, methyl bromide, sodium fluoroacetate, zinc phosphide, warfarin

Source: Duke (2018)

6.1 Introduction

During the green revolution, to meet the need of food production for increasing human population, fertilizers and pesticides were used to increase crop productivity and prevent pest attacks (Verma et al. 2014). Pesticides are various groups of inorganic and organic chemicals such as insecticides, herbicides, fungicides, rodenticides, nematicides used to control or kill pests such as insects, herbs, weeds, rodents, nematode, and microorganisms (Table 6.1). An increase in the consumption of pesticides, with the introduction of aldrin, benzene hexachloride (BHC), dieldrin, dichlorodiphenyltrichloroethane (DDT), endrin, and 2,4-dichlorophenoxyacetic acid (2,4D) was mainly began after World War II (Ortiz et al. 2013). However, indiscriminate and unregulated use of pesticides has increased its residues in air, water, soil, and food chain causing negative effects to human health, birds, wildlife, domestic animals, fish (Sharma et al. 2016).

In addition to this, pesticides can be categorized according to their chemical composition, which comprises four main groups, namely organochlorines, organophosphorus, carbamates and pyrethrin and pyrethroids (Fig. 6.1) with examples (Table 6.2).

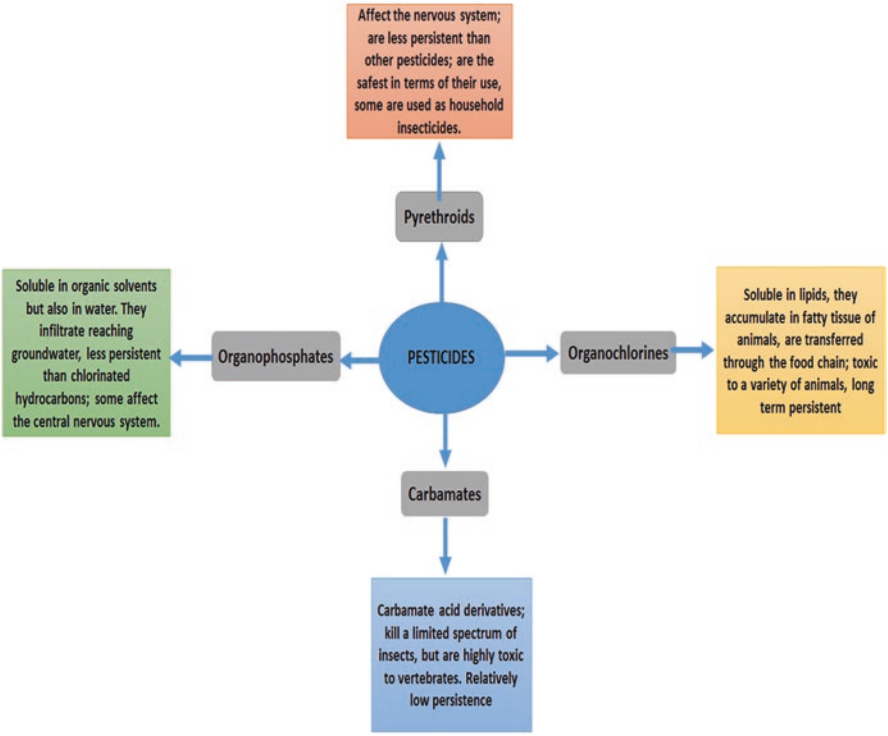

Fig. 6.1 Type of pesticides based on the chemical composition

Table 6.2 Types of pesticides and their examples

Types of pesticides	Examples
Organochlorines	Endosulfan, DDT, aldrin, chlordane, dicofol, dieldrin, endrin, fipronil, lindane, heptachlor, hexachlorocyclohexane
Organophosphorus	Azinphos-methyl, acephate, bromophos, chlorpyrifos, coumaphos, diazinon, dimethoate, dichlorvos, disulfoton, dioxathion, ectophos, fenitrothion, fenitrooxon, glyphosate, fonofos, leptophos, mathamidophos, malathion, parathion, profenofos, phenthoate, phosmet, phorate, phosphothion, trichlorfon
Carbamates	Aldicarb, carbofuran, carbaryl, cartap, carbosulfan
Pyrethroids	Chlorfenvinphos, cypermethrin, deltamethrin, flumethrin, fenvalerate, ivermectin, permethrin

Source: Huang et al. (2018)

6.2 Organochlorine Pesticides

Organochlorine pesticides or chlorinated hydrocarbons are organic compounds consisting of five or more covalently bonded chlorine atoms, mainly used in agriculture for controlling pests, vector control and in public health. These are non-polar, lipophilic, and persistent. Therefore, unregulated and indiscriminate application of organochlorine pesticides leads to a long-term residual effect in the environment which results in environmental pollution and accumulation in mammals. Aldrin, chlordane, dieldrin, DDT, endosulfan, and lindane are the most common examples of organochlorine pesticides (Ahmad and Ahmad 2014).

6.3 Organophosphorus Pesticides

Organophosphorus pesticides are a broad spectrum of pesticides as they control a wide range of pests. These can be heterocyclic, cyclic, and aliphatic with phosphorus present in the centre. These pesticides are less toxic as compared to organochlorine pesticides. They have multiple functions such as it can be used as stomach and contact poisons as well as fumigants resulting in nerve poisons. They showed toxicity to vertebrates and invertebrates by binding to acetylcholinesterase or cholinesterases leading to interruption of nerve impulses. Common examples of organophosphorus pesticides are parathion, malathion, diazinon and glyphosate (Ortiz-Hernández et al. 2013).

6.4 Carbamates

Carbamates can be used as a contact poison, stomach poison and fumigant poison. It is similar to organophosphates in the mode of action, such as by interrupting nerve signals transmission leads to poisoning which causes the death of pest. However, their origin is different, as carbamates are obtained from carbamic acid, whereas organophosphates are derived from phosphoric acid. It can also be used as a contact poison, stomach poison and fumigant poison. Carbamates cause less environmental pollution due to their similar molecular structure to that of natural organic substances resulting in easy degradation. Some of the widely used insecticides are bendiocarb, carbaryl, carbofuran, dioxacarb, fenoxycarb, fenobucarb, isoprocarb, methomyl and propoxur (Kaur et al. 2019).

6.5 Pyrethroids

Synthetic pyrethroid can be synthesized by copying the structure of natural pyrethrins and used against household pests. As compared to natural pyrethrins, synthetic pyrethroid pesticides are non-persistent with longer residual effects. These pesticides are low toxic to mammals and birds while more toxic to insects and fish. These pesticides are less toxic as compared to organophosphates and carbamates. Allethrin, cyfluthrin, cypermethrin, deltamethrin, and permethrin are the most used synthetic pyrethroid pesticides (Ortiz-Hernández et al. 2013).

6.6 Different Approaches for Pesticide Remediation

Several methods such as physicochemical and biological play major roles in the remediation of contaminated sites as well as decreasing the residual levels to safe and acceptable levels resulting in minimizing the toxic effects of pesticides on the human health and environment.

6.6.1 Physicochemical Methods

Physicochemical treatments, such as the Fenton process, heterogeneous photocatalysis (HPC), plasma oxidation and ozonation, thermal desorption (at low temperature) and incineration (Table 6.3) have been applied for the removal of contaminants.

6.6.2 Biological Methods

Several biological systems, mainly bacteria and fungi are used in the degradation of pesticides from contaminated sites. Because of the adaption of several metabolic pathways, wide distribution and diversity, microorganisms can be vitally used for the remediation of pesticides. The degradation efficacy relies on optimization of environmental conditions, for instance, pH of the soil, temperature, moisture contents as well as microbial community (Chishti et al. 2013; Javaid et al. 2016). Various microorganisms that have the potential to degrade pesticides are listed in Table 6.4.

Table 6.3 Characteristics and limitations of different physicochemical methods

Physicochemical methods	Characteristics	Limitations
Fenton process	Production of reactive hydroxyl radicals ($^{\cdot}OH$) by oxidation of Fe^{2+} ions in the presence of hydrogen (H_2O_2), permanganate (MnO^{4-}), persulfate ($S_2O_8^{2-}$), and ozone (O_3) (Baldissarelli et al. 2019)	Reduces soil pH, which makes it harmful for soil microorganisms resulting in hindering the cultivation of crops (Cheng et al. 2016)
Heterogeneous photocatalysis (HPC)	Use of TiO_2, ZnO, ZnS as photosensitizers in photo induced processes. Semiconductors stimulate the displacement of electrons through ultraviolet irradiation from the valence to the conduction band, resulting in the production of hydroxyl radicals used in the degradation of pollutants (Santos et al. 2015)	It depends on the particle size, structure, morphology, surface, and adsorption. Recovering semiconductors to be reused is laborious and challenging (Castro et al. 2016)

(continued)

Table 6.3 (continued)

Physicochemical methods	Characteristics	Limitations
Plasma oxidation and ozonation	Produce electrons with a high electric charge. Provide energy for reactive molecules, for instance, hydrogen peroxide, hydroxyl, ozone, oxygen and forming free radicals (Aggelopoulos et al. 2015; Cheng et al. 2016)	Need high energy for generating oxidizing compounds (Brillas et al. 2003)
Thermal desorption (at low temperature)	The heating of contaminated media in the gas stream at a temperature between 300 and 1000°F leads to the volatilization of organic compounds. The products formed are passed through a burner (contaminants are destroyed) or condenser (converts the gas phase into a liquid phase) or they are encapsulated by carbon adsorption beds (immobilize, but do not destroy the contaminants) (Parte et al. 2017)	Need highly specialized facility and cost-effective (Parte et al. 2017)
Incineration	The heating (at a temperature between 1000 and 1800 °F) of contaminated media leads to volatilization of organic compounds and partial oxidation. Further, the destruction of organic compounds at 1600 and 2200 °F temperature, which leads to the formation of ash which will be further disposed of in a landfill, if it meets safety regulations (Parte et al. 2017)	Need highly specialized facility and cost-effective (Parte et al. 2017)

Table 6.4 Pesticide degradation by microorganisms

Pesticides
Organophos

(continued)

Table 6.4 (continued)

Pesticides	Types	Bacteria	References
Organochlorine	Endosulfan	*Pseudomonas* sp. TAH	Zaffar et al. (2018)
		Pseudomonas mendocina ZAM1	Mir et al. (2017)
		Stenotrophomonas maltophilia OG2	Ozdal et al. (2017)
		Pseudomonas sp. RPT 52	Gupta et al. (2016)
		Klebsiella sp. M3	Singh and Singh (2014)
		Alcaligenes faecalis strain JBW4	Kong et al. (2014)
		Bacillus subtilis	Kumar et al. (2014)
		Agrobacterium tumefaciens	Thangadurai and Suresh (2014)
		Alcaligenes faecalis JBW4	Kong et al. (2013)
		Pseudomonas, Bacillus	Harikumar et al. (2013)
		Pseudomonas fluorescens	Giri and Rai (2012)
		Achromobacter xylosoxidans C8B	Singh and Singh (2011)
		Azotobacter sp.	Castillo et al. (2011)
		Pseudomonas sp. IITR01	Bajaj et al. (2010)
		Pseudomonas aeruginosa	Kalyani et al. (2009)
		Bordetella sp. B9	Goswami and Singh (2009)
		Achromobacter xylosoxidans CS5	Li et al. (2009)
		Ochrobacterum sp., *Burkholderia* sp., *Arthrobacter* sp.	Kumar et al. (2008)
		Pseudomonas aeruginosa.	Arshad et al. (2008)
		Pseudomonas aeruginosa, Pseudomonas spinosa, Burkholderia cepacia	Hussain et al. (2007)
		Rhodococcus erythropolis, Stenotrophomonas maltophilia	Kumar et al. (2007)
		Bacillus sp.	Shivaramaiah and Kennedy (2006)
		Staphylococcus sp., *Bacillus circulans I, Bacillus circulans II*	Kumar and Philip (2006)
		Pseudomonas sp.	Lee et al. (2006)
		Klebsiella oxytoca	Kwon et al. (2005)
	Aldrin	*Pseudomonas fluorescens*	Erick et al. (2006)
	Dieldrin	*Bacillus* sp., *Arthrobacter* sp.	Jagnow and Haider (1972)
	Endrin	*Micrococcus* 204, *Arthrobacter* sp. 278, *Pseudomonas* sp. 27, *Bacillus* sp. 4	Patil et al. (1970)
	DDT	*Azoarcus*	Ortiz et al. (2013)
		Eubacterium limosum	Yim et al. (2008)
		Ralstonia eutropha strain A5	Hay and Focht (2000)

(continued)

Pesticides	Types	Bacteria	References
	Methyl parathion	*Cyanobacteria*	Ibrahim et al. (2014)
		Pseudomonas sp. strain WBC-3	Wang et al. (2014)
		Stenotrophomonas maltophilia M1	Mohamed (2009)
		Pseudomonas sp. A3	Zhongli et al. (2002)
		Pseudomonas sp. WBC	Yali et al. (2002)
		Plesiomonas sp M6	Zhongli et al. (2001)
		Plesiomonas sp. strain M6	Cui et al. (2001)
	Glyphosate	*Pseudomonas aeruginosa* and *Bacillus megaterium*	Al-Arfaj et al. (2013)
		Agrobacterium radiobacter P230	Horne et al. (2002b)
		Geobacillus caldoxylosilyticus T20	Obojska et al. (2002)
		Pseudomonas monteilii	Horne et al. (2002a)
		Nocardiodes simplex NRRL B24074	Mulbry (2000)
	Monocrotophos	*Pseudomonas stutzeri* MTCC 2300	Barathidasan and Reetha (2013)
		Paracoccus sp. M1	Jia et al. (2007)
		Pseudomonas aeruginosa F10B and *Clavibacter michiganensis* SBL11	Singh and Singh (2003)
		Pseudomonas mendocina	Bhadbhade et al. (2002a)
		Pseudomonas spp., *Bacillus megaterium., Arthrobacter* spp., *Arthrobacter atrocyaneus*	Bhadbhade et al. (2002b)
	Fenitrothion	*Burkholderia* sp. NF100	Hayatsu et al. (2000)
Carbamates	Methomyl	*Stenotrophomonas maltophilia* M1	Mohamed (2009)

In recent years, the use of fungi as an effective tool for the biodegradation process has increased due to relatively easy cultivation and possession of a great enzymatic metabolism (Camacho-Morales and Sánchez 2016). Several studies that reported pesticides degradation by fungi are listed in Table 6.5.

6.7 Several Enzymes Involved in Pesticide Degradation

Enzymes play an essential role in the bioremediation of individual pesticides. The use of enzymes to degrade or transform pesticides is an emerging technology as it is more effective than physicochemical techniques. Enzymes are involved in the pesticide degradation via evolved metabolic resistance and several intrinsic detoxification mechanisms in the target organism, whereas in the environment through biodegradation by water and soil microorganisms. Pesticide metabolism involves (i) transformation of the parent compound to a more water-soluble and a less toxic product via hydrolysis, reduction, or oxidation, (ii) conjugation of pesticide

Table 6.5 Pesticide degradation by fungi

Pesticides	Compound	Fungi	References
Organochlorine	Endosulfan	*Aspergillus niger*	Bhalerao and Puranik (2007)
		Penicillium sp.	Romero-Aguilar et al. (2014)
		Trametes versicolor, Pleurotus ostreatus, Gloeophyllum trabeum	Ulčnik et al. (2013)
		Mortierella sp.	Kataoka et al. (2010a)
		Trametes hirsuta	Kamei et al. (2011)
		Botryosphaeria laricina JAS6., *Aspergillus tamarii* JAS9	Silambarasan and Abraham (2013)
	Dieldrin	*Cordyceps brongniartii* ATCC66779, *Cordyceps militaris* KS-92	Xiao and Kondo (2013)
		Phlebiabrevispora Nakasone TMIC33929(strain YK543)	Kamei et al. (2010)
		Mucor racemosus strain DDF	Kataoka et al. (2010b)
	Endrin	*Trichoderma viride*	Patil et al. (1970)
	DDT	*Trichoderma viride*	Patil et al. (1970)
	Heptachlor	*Phlebia* sp.	Xiao et al. (2011)
Organophosphorus	Chlorpyrifos	*Cellulomonas fimi, Phanerochaete chrysosporium*	Barathidasan et al. (2014)
		Trichoderma harzianum, Rhizopus nodosus	Harish et al. (2013)
		Acremonium sp. GFRC-1	Kulshrestha and Kumari (2011)
		Verticillium sp. DSP	Fang et al. (2008)
		Trichosporon sp.	Xu et al. (2007)
		Hypholama fascicularae, Coriolus versicolor	Bending et al. (2002)
	Glyphosate	*Alternaria alternata*	Lipok et al. (2003)
		Penicillium chrysogenum	Klimek et al. (2001)
	Monocrotophos (MCP)	*Aspergillus niger* MCP1	Jain et al. (2012)

metabolites to an amino acid or sugar resulting in a decrease in toxicity as well as increase in water solubility, (iii) conversion of pesticide metabolites into non-toxic secondary conjugates. Bacteria and fungi involved extracellular or intracellular enzymes which are involved in pesticide metabolism (Ortiz-Hernández et al. 2013). Enzymes involved in bioremediation were mainly oxidoreductases, monooxygenase, dioxygenases, carboxylesterases, phosphotriesterases, haloalkane dehalogenases, haloalkane dehydrochlorinases, diisopropylfluorophosphatase, Paraoxonase (PON1), organophosphate acid anhydrolase (OPAA), carboxylesterases (Table 6.6). Several enzymes that have been applied for the degradation of pesticides from polluted environments are present in Table 6.7.

Table 6.6 Enzymes and their characteristics

Enzymes	Characteristics
Oxidoreductase (GOX)	Oxidoreductases are a group of an enzyme with broad substrate specificity that catalyses oxidation and reduction reaction by the transfer of electrons from an electron donor (reductant) to an acceptor (oxidant). Glyphosate oxidase (GOX) is a flavoprotein amine oxidase that is involved in herbicide glyphosate bioremediation that catalyses the oxidation of herbicide and releases the keto acid glyoxylate by producing aminomethyl phosphonate (AMPA).
Monooxygenase (Esd and Ese, Cytochrome P450)	Monooxygenases catalyse the transfer of O^2 (one atom) to an organic compound, which leads to an increase in reactivity and water solubility of xenobiotic compounds during degradation. Esd and Ese belong to the two-component flavin diffusible monooxygenase family (TC-FDM), which play an important role in the degradation of endosulfan and its toxic metabolite endosulphate. Cytochrome P450 uses oxygen to oxidize or hydroxylate substrates in an enantiospecific manner. It also contains a catalytic Fe^{2+}-containing porphyrin group which binds to carbon monoxide at 450 nm. Cytochrome CYP1A1 also termed aryl hydrocarbon hydroxylase is an example of cytochrome P450, and has the ability to bioremediation of herbicides such as chlortoluron, atrazine, and norflurazon. Cytochrome CYP76B1 is another example of cytochrome P450, which catalyses the oxidative dealkylation of phenylurea herbicides such as linuron, isoproturon, and chlortoluron.
Dioxygenases (TOD)	Dioxygenases are a broad group of enzymes that act similar to monocyclic aromatics, monooxygenase aliphatic olefins and other miscellaneous substrates. Toluene dioxygenase (TOD) is an example of dioxygenase for a range of compounds such as monocyclic aromatics, fused aromatics, linked aromatics and aliphatic olefins.
Carboxylesterases (E3)	Esterase 3 (E3) is an α/β hydrolase fold carboxylesterase, which is involved in detoxification-mediated resistance to organophosphorus and pyrethroid insecticides. It operates through a catalytic triad, including aspartate (E351), serine (S218) and histidine (H471).

(continued)

Table 6.6 (continued)

Enzymes	Characteristics
Phosphotriesterase (OPH, OpdA, PTE)	Phosphotriesterase catalyses the hydrolysis of organophosphorus triesters, belongs to the amidohydrolase metalloenzyme family. Organophosphate hydrolase (OpdA), the enzyme is an $(\alpha/\beta)_8$ barrel structure used as a commercial product to degrade residues of the organophosphorus present in wastes and solid. After poisoning with highly toxic organophosphate pesticides, the addition of OpdA improved survival in rats and monkeys.
Haloalkane dehalogenases (LinB, AtzA and TrzN)	Haloalkane dehalogenases belong to the α/β−hydrolase fold family. LinB, AtzA and TrzN are the examples of haloalkane dehalogenases. LinB plays a crucial role in the degradation of β-HCH and δ-HCH. AtzA and TrzN hydrolyses halide–carbon bonds. In the atrazine catabolic pathway, AtzA is the first enzyme encoded by atzA-atzF from the transmissible pADP1 plasmid. Iron-dependent AtzA was involved in the dechlorination of atrazine and related chloro-s-triazine herbicides. Zinc-dependent TrzN was involved in the dechlorination of amides, S-alkyl groups, O-alkyl groups and halides.
Haloalkane dehydrochlorinases (LinA)	LinA catalyses the dehydrochlorination of the insecticide γ-HCH which can be further catabolised by the other enzymes of the lin operon.
Diisopropylfluorophosphatase (DFPase)	DFPase is a six-bladed ß-propeller structure having two Ca^{2+} ions, which play a vital role in the catalysis and provide structural integrity. Administration of pegylated DFPase in rats reduces the rate of lethality with a subcutaneous $3xLD_{50}$ dose of soman (G-type nerve agents).
Paraoxonase (PON1)	Six-bladed propeller structure that uses Ca^{2+} ions within its active site. It also exhibited anti-oxidative, anti-inflammatory, anti-atherogenic, anti-diabetic, antimicrobial, properties along with paraoxon and organophosphorus detoxifying properties.
SsoPox	SsoPox is an $(\alpha/\beta)_8$ barrel folded structure in which the active site is present at the C-terminal section of the structure. It showed activities at up to 100 °C in the presence of denaturing agents such as detergents.
Organophosphate Acid Anhydrolase (OPAA)	OPAAs are dipeptidases that cleave dipeptide bonds in which the C-terminal residue is proline. OPAA has undergone a series of mutations to increase its catalytic activity and substrate specificity.

Source: Scott et al. (2008); Verma et al. (2014); Bhandari et al. (2021), Bhandari et al. (2021); Verma et al. (2014), Scott et al. (2008)

Table 6.7 Summary of pesticide degrading enzymes of various microbial strains

Enzyme	Originating species	Cofactor requirements	Documented target pesticide(s)	References
PTE	*Brevundimonas diminuta*	Zn	Diethyl-VX, Dimethyl-VX	Bigely et al. (2019)
DFPase	*Loligo vulgaris*	Ca^{2+}	Diisopropyl fluorophosphate, sarin, cyclosarin	Melzer et al. (2012), Zhang et al. (2018)
PON1	Human liver	Ca^{2+}	Paraoxon	Purg et al. (2017)
OPAA	*Alteromonas* sp.	Mn^{2+}	Paraoxon	Xiao et al. (2017)
Ssopox	*Sulfolobus solfataricus*	Co^{2+}, Fe^{3+}	Paraoxon	Elias et al. (2008)
Glyphosate oxidase (Gox)	*Agrobacterium* strain T10, *Pseudomonas* sp LBr	Flavin (FAD)	Glyphosate	Scott et al., (2008)
Esd	*Mycobacterium* sp.	Flavin and NADH	Endosulfan and Endosulphate	Scott et al. (2008)
Ese	*Arthrobacter* sp	Flavin (FMN)	Endosulfan and Endosulphate	Scott et al. (2008)
Cyp1A1/1A2	Mammalian (Rat)	Heme and NADH	Atrazine, chlortoluron and norflurazon	Scott et al. (2008)
Cyp76B1	*Helianthus tuberosus*	Heme and NADH	Chlortoluron, linuron and isoproturon	Scott et al. (2008)
cytochrome P450	*Pseudomonas putida*	Heme and NADH	Pentachlorobenzene and Hexachlorobenzene	Scott et al. (2008)
TOD	*Pseudomonas putida*	Fe^{2+} and NADH	Trifluralin herbicides	Scott et al. (2008)
E3	*Lucilia cuprina*	None	Phosphotriester insecticides and synthetic pyrethroids	Scott et al. (2008)
OPH	*Agrobacterium radiobacter*	Fe^{2+} and Zn^{2+}	Insecticides phosphotriester	Scott et al. (2008)
OpdA	*Pseudomonas diminuta; Flavobacterium*	Fe^{2+} and Zn^{2+}	Methyl parathion, parathion, malathion, coumaphos	Scott et al. (2008)
PdeA	*Delftia acidovorans*	None	Organophosphorus compounds	Scott et al. (2008)
LinA	*Sphingomonas sp., Sphingobium sp.*	None	Hexachlorocyclohexane (γ-isomer)	Scott et al. (2008)
LinB	*Sphingomonas sp., Sphingobium sp.*	None	Hexachlorocyclohexane (β− and δ−isomers)	Scott et al. (2008)

(continued)

Table 6.7 (continued)

Enzyme	Originating species	Cofactor requirements	Documented target pesticide(s)	References
AtzA	*Pseudomonas* sp. ADP	Fe^{2+}	Chloro-s-triazine herbicides	Scott et al. (2008)
TfdA	*Ralstonia eutropha*	Fe^{2+} and α-ketoglutarate	pyridyloxyacetate herbicides and 2,4-dichlorophenoxyacetic acid	Scott et al. (2008)
TrzN	*Nocardioides* sp.	Zn^{2+}	Chloro-s-triazine herbicides	Scott et al. (2008)
DMO	*Pseudomonas maltophilia*	NADH and a Fe-S centre	Dicamba	Scott et al. (2008)
Organophosphate Hydrolase (OpdA)	*Agrobacterium radiobacter*	Binuclear Fe^{2+}-Zn^{2+}	Methyl paraoxon	Horne et al. (2002b)

6.8 Conclusion

In addition to controlling or killing pests, pesticides can move off-site resulting in contamination of water, soil and the ecosystem resulting in damage to non-target organisms. The bioremediation process for the detoxification and/or removal of pesticide residues from polluted soil is the best option available in integrated agricultural management practices, due to its eco-friendly, cost-effective and efficacious nature. Various microorganisms (bacteria and fungi) are used in the removal of pesticides from contaminated sites. Bacterial degradation involves specific genes and enzymes for the breakdown of functional groups present in the pesticides. In conclusion, although significant research has been done on the enzymes associated with the biodegradation of pesticides, further research in relevant environmental conditions is needed to confirm the ability of bacteria and fungi for large-scale decontamination. In addition, significant degradation of pollutants will be enhanced using genetically engineered microorganisms that will produce many recombinant enzymes using eco-friendly technology is still unexplored.

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Chapter 7
The Environmental Implication and Microbial Remediation of Pesticide Pollution: A Critical Assessment of the Concept, Strategies, and Future Perspective

Barkha Kamal, Rekha Goswami, and Abhilasha Mishra

Abstract The environment is polluted with organic contaminants from many sources such as the transportation, chemical industry, and pesticide application in agricultural regions. Pesticides are used in over 500 distinct formulations in the environment today, with agriculture accounting for the majority of pesticide use. Organic (carbon-based) compounds that comprise manufactured molecules have been classified as persistent organic pollutants. These contaminants stay in soils for a long period, where they enter into the food chain directly or seep down to underground water. Their potential as carcinogens, as well as their prevalence in the water, soil, and air, raised concerns about their remediation. Bioremediation is a process which utilizes microbes or microbial enzymes to treat polluted places in order to restore them to their previous state. Microbes either consume the toxins or assimilate all toxic substances from the environment, making the area virtually contaminant-free. Organic molecules are generally eaten up, whereas heavy metals and pesticides are digested within the system. In this chapter, various microbes and recent advance tools for enhanced efficiency of pesticides bioremediation have been discussed in detail.

Keywords Bioremediation · Microbes · Enzymes · Pesticide · Pollution

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7.1 Introduction to Persistent Agrochemical/Pesticides

Persistent Organic Pollutants (POPs) are harmful substances which emerged due to anthropogenic activities. POPs impart negative consequences on habitats, wildlife, and people. The environment is polluted with organic contaminants by direct input, transit, and precipitation processes from many sources such as the transportation, chemical industry and other organics, chlorination treatment, and pesticide application in agricultural regions (Kordel et al. 1997; Widenfalk 2002). Many concern pollutants are toxic and recognized that they are harmful to human-being. Unfortunately, these chemicals are persistent in environment in many circumstances (Berdowski et al. 1997). These pollutants can infect drinking water wells once they have entered into the groundwater and cause health problems. Long-range atmospheric transmission is also a possibility for these compounds. The tendency of these compounds to accumulate in animal fat tissue is one of the main concerns. Because of the increasing quantities of hazardous substances within higher trophic level species, such as mammals, indirect accumulation or biomagnifications may create health concerns over time (Kaufman 1983; Moerner et al. 2002). Other compounds are waste products produced by human and natural activities, with human activity accounting for the majority of discharges (furans and dioxins). POPs include highly dangerous industrial chemicals, i.e., PCBs (Polychlorinated biphenyls), pesticides, i.e., DDT (Dichlorodiphenyltrichloroethane), and unintentional by-products such as furans and dioxins, among other substances due to commercial operations and burning. POPs are among the most harmful pollutants discharged into the environment by humans, according to extensive scientific studies. Persistent and refractory organic chemicals, for example, chlorinated aromatics, heterocyclics, and nitroaromatics have contaminated groundwater, soil, and sediments. Even after decades later, the exact regions where chemicals were spilled or released tend to retain the highest quantities of these contaminants (Kleka et al. 2001; Buccini 2004). Over time, actions were taken to reduce and eliminate the manufacture, usage, and discharge of these compounds (Moerner et al. 2002). Stockholm Convention on POPs states that POPs have hazardous properties, bioaccumulate, nondegradable, and are transferred across international borders by water, air, and migratory species, accumulating in aquatic and terrestrial ecosystems far from their point of release. These agreements create stringent worldwide standards for initial POPs lists. This Convention on POPs emphasizes on lowering and eradicating twelve POPs (dubbed the "Dirty Dozen") from the environment. Eight pesticides (DDT, aldrin, dieldrin, chlordane endrin, heptachlor, toxaphene, and mirex); two chemicals (hexachlorobenzene and polychlorinated biphenyls); and two undesired by-products (furans and dioxins) are among the twelve substances as mentioned in (Fig.7.1) (Kleka et al. 2001; Gorman and Tynan 2001). Both instruments also allow for the addition of additional compounds to these lists. They establish the following safeguards: Restrictions or prohibition on the manufacturing and use of purposefully created POPs, diminution on their import and export, arrangements for the safe

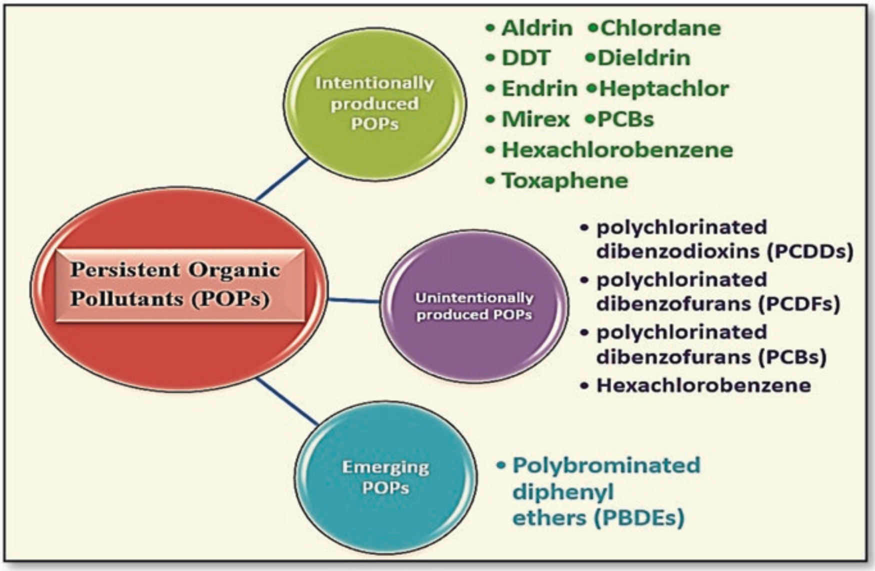

Fig. 7.1 Different types of persistent organic pollutants (POPs)

handling of reserved stock, provisions for the reduction of emissions of unintended produced POPs such as furans and dioxins.

The European Community is dedicated to ensuring that these two environmental agreements are implemented effectively. Together with the other 15 Member States, it signed both international instruments on POPs. The Protocol was ratified on April 30, 2004, while the Stockholm Convention was approved on November 16, 2004. The World Bank is also working on a new programme called Persistent Organic Pollutants (POPs), which intends to cooperate and to protect environment and human health around the world against POPs (Buccini 2004). In addition, the scientific community is working on this issue as a result of the deregulation of various substances, such as pesticides have been evolved for utilized in landfarming and non-agricultural purposes.

Contamination caused by soil despite the fact that most nations have banned the use of chlorinated pesticides, these chemicals are nevertheless widely used around the world. Former production locations and obsolete pesticide supplies both have significant quantities. This problem is particularly severe in former communist bloc countries in Eastern Europe and Asia. Pesticides were overproduced and distributed centrally, resulting in massive volumes of toxic chemicals being accumulated. Stocks that have been poorly secured and contain a substantial amount of chlorinated chemicals are now give rise to a severe threat to the humans and the environment (Vijgen 2005). Recent studies have shown that methanogenic granular sludge has a potential to eliminate chlorinated pesticides—HCH, methoxychlor, and DDT from the soil if used as inoculum. Use of a surfactant was suggested as a way to solve these flaws. Surfactant effects on bioremediation of chlorinated pesticide- pollutants soil have been reported (You et al. 1996; Walters and Aitkin 2001; Quintero et al. 2005).

7.2 Prevalence and Fate of Pesticides in the Environment

Initial considerations on pesticide performance in the environment pesticides have been used for a long time: Sulphur was utilized as a fumigant by the Chinese about 1000 BC Seed of *Strychnos nuxvomica* (strychnine) which is also known as *Nux vomica*, was used to kill rats, and tobacco leaves water extracts were used on herbs to remove insects in the 17th century.

In the nineteenth century, pesticides derived from plants involve rotenone from roots of *Derris elliptica* and pyrethrum from *Chrysanthemum blooms*. The weed killer arsenic trioxide was utilized; the Colorado beetle was controlled with copper arsenite (Paris Green); and the Bordeaux mixture (copper sulphate, water, and lime) was used to combat vine downy mildew. 10% Sulphuric acid was utilized to remove dicotyledonous weeds without hurting monocotyledonous crop cultivated plants having waxy coats on their leaves in the twentieth century. Pesticide residues were discovered in certain treated vegetables and fruits in the 1920s, causing public outrage. Development of insecticide and use of farmers in cultivation and public health rose rapidly after WWII. Pesticides are widely used for bug control to prevent the spread of diseases like malaria, river blindness, and typhus. Pesticides were used in amount of 140 tonnes in 1940.

Synthetic organic pesticide manufacture and use skyrocketed during the mid-1940s. The US Environmental Protection Agency had registered around 23,400 pesticide products by 1991 (Singhvi et al. 1994). Pesticides were utilized in 600,000 tonnes in 1997, with the agriculture business accounting for 77%, commercial, industrial, and government entities for 12%, and private households accounting for the remaining 11% (Moerner et al. 2002; Fishel 2005). Pesticides are used in over 500 distinct formulations in the environment today, with agriculture accounting for the majority of pesticide use. Pre-harvest crop losses would average approximately 40% worldwide without adequate pest management, according to study as shown in (Fig. 7.2).

Post-harvest pest control efforts must also be mandatory, as they pose a risk to the environment without efficient pesticide control (Kennedy 1998). Pesticides are applied to crops in the amount of four million tonnes per year around the world for pest management, however only 1% of the entire pesticides applied exactly reach the target pests (Pimentel et al. 1993; Zhang et al. 2004).

Their potential as carcinogens, as well as their prevalence in the water, soil, and air, raised concerns about their continued use in cultivation. Under these circumstances, the harmful impact of chemicals use on public health and the environment has gotten a lot of attention (Gavrilescu and Nicu 2005). One of the areas where pesticides are thought to pose a threat is the environment. Pesticides constitute an

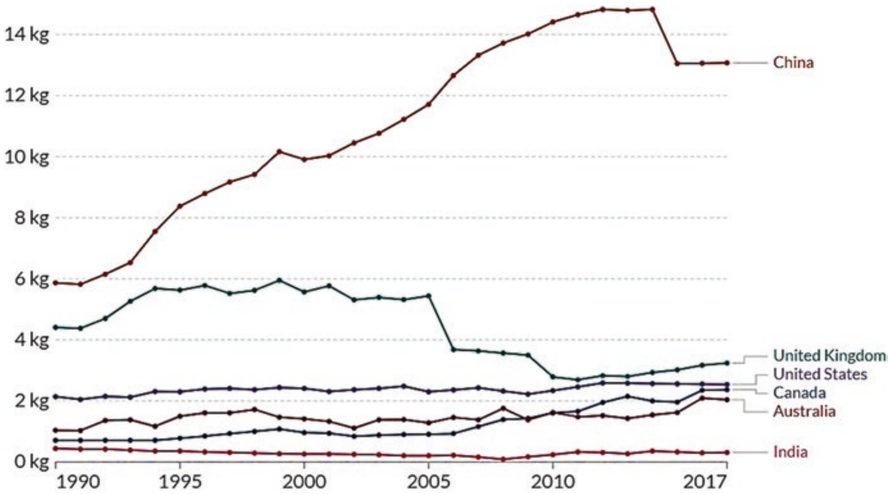

Fig. 7.2 Average pesticide use per hectare cropland from 1990 to 2017 (Max Roser 2019)

environmental risk, and a variety of tools are now available to mitigate this risk, including restrictions on chemical usage and the imposition of fees (Singhvi et al. 1994; Basrur 2002).

Many factors influence the possibility for pesticides to contaminate surface water or groundwater, including pesticide properties, soil qualities, crop management practices, and hydraulic loads on the soil. Pesticides come in a variety of sizes and shapes. This is what enables them to target certain creatures, such as weeds or insects. Chemical structure also plays a role in determining how a pesticide moves through the surroundings. A few pesticides are water soluble; some pesticides are having ability to volatilize from a liquid to a gaseous state and hence can spread in the air very easily. Other aspects to consider while examining the chemical architect and ability to decompose or transform in the surrounding environment, as well as how much it will take for the change to occur. A few pesticides become nontoxic to both their target organisms and the rest of the atmosphere during metamorphosis. Other insecticides breakdown into harmful compounds than the original. Various processes for the fate of pesticides in the environment are shown in (Fig. 7.3).

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Pesticides degrade at varied rates depending on their chemical structure in the environment. For example, soil organisms can destroy one pesticide in existence while another takes many years to disintegrate (Nash and Woolson 1967; Kerle

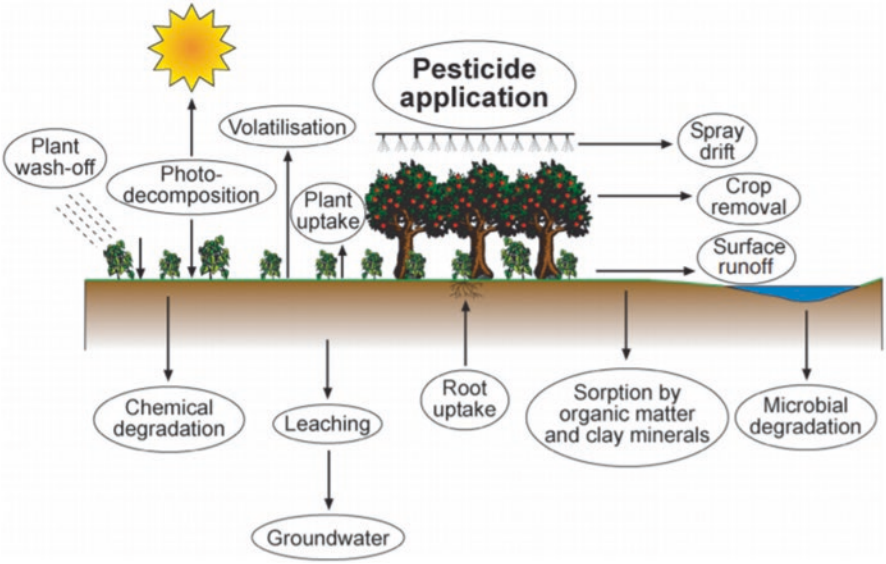

Fig. 7.3 Various processes for the fate of pesticides in the environment. (Reproduced with permission from Sarmah et al. 2004)

et al. 1996). A pesticide's structure changes when it is degraded or transformed, and this changes how it goes in the environment.

7.3 Environmental Implications of Pesticides and Overview of Mitigation Strategies

Bioremediation is a procedure in which microbes or microbial enzymes treat polluted places in order to restore them to their previous state. Bioremediation methods are classed as either ex situ or in situ. Pesticides are naturally degraded under environmental conditions to either water or CO_2 or less active by-product is known as in situ bioremediation. It is a low-maintenance, low-cost, eco-friendly benign, and long-term solution for contaminated soil clean up. Ex situ bioremediation necessitates excavating contaminated soils and transporting them to another location for treatment, which can be costly. Generally, in situ bioremediation methods are preferred over ex situ bioremediation methods to regenerate contaminated soils due to the huge extent of agricultural land. There are three major classes of bioremediation methods: (1) bioattenuation, which is based on the natural process of degradation; (2) The addition of nutrients, water, and electron donors or acceptors to artificially enhance pesticide decomposition is called biostimulation; (Hussain et al. 2009); and (3) The microorganisms use that have the ability to break down substances (Goswami et al. 2018). A bioremediation technology's use is influenced by the quantity, and type and toxicity of the polluting chemical species present.

7.3.1 Bioattenuation, Biostimulation, and Bioaugmentation: An Efficient Strategies of Bioremediation

7.3.1.1 Bioattenuation

This is a natural biodegradation process that does not require human involvement. The process of bioremediation is determined by microorganisms' metabolic ability to clean or change the pesticide molecule, which is contingent on bioavailability and accessibility. Biodegradation by microorganisms in agro and, to a lesser amount, contact with soil matrices is mostly responsible for the processes involved. This method is frequently referred to as the "do-nothing" approach, however it necessitates continuous monitoring of the contamination in the soil. Natural attenuation takes time depending on-site circumstances and the type of pollutant (Rifai et al. 1995).

7.3.1.2 Biostimulation

By providing the right circumstances for microorganisms in a soil, biodegradation can be accelerated. Moisture, temperature, redox conditions, organic matter, pH, and nutrients all affect chemical diffusion and microbial activity in the soil, and hence the efficacy of bioremediation (Hussain et al. 2009). In the biostimulation process, the correct nutritional ratio of carbon, nitrogen, and phosphorous is critical (Wolicka et al. 2009). Land farming and composting are biostimulation activities and they include carbon sources and nutrients, as well as humidity management (Tyagi et al. 2011; Goswami et al. 2018).

7.3.1.3 Bioaugmentation

In present scenario, the remediation sector and the scientific community have focused on bioremediation systems that use bioaugmentation processes. Changed microorganisms are commonly used in bioaugmentation to speed up the detoxifying and degradation process in contaminated environments. It is possible to employ changed microorganisms that are isolated from environment or that have been genetically transformed in the lab (Tyagi et al. 2011). As a result of their weaker competitiveness and adaptability, bioaugmentation strategies for bioremediation are more prone to failure than native microorganisms in contaminated soils. As an alternative, immobilization of microbial enzymes or degraders on the variety of carriers provides them more stability and resistant to environmental fluctuations. It is

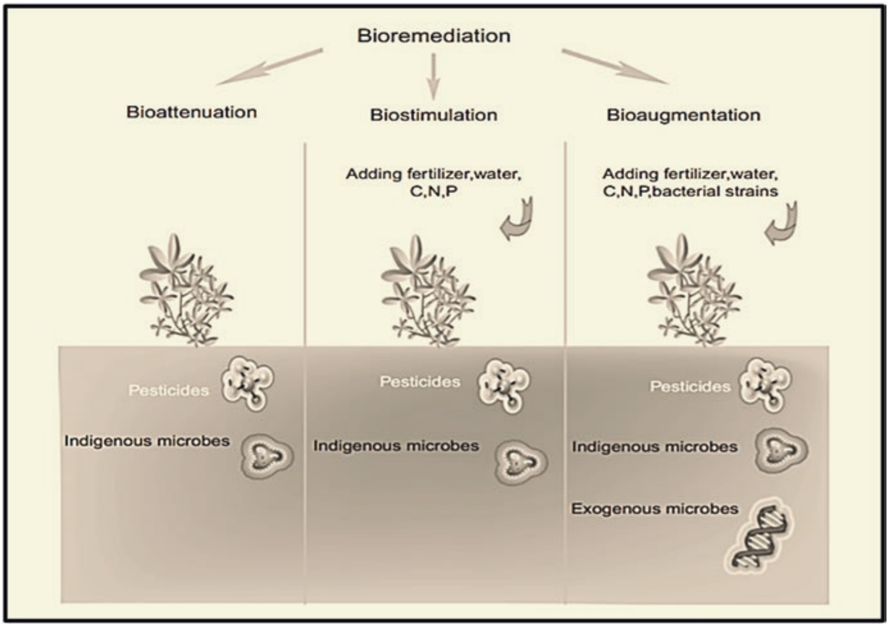

Fig. 7.4 Bioattenuation, Biostimulation, and Bioaugmentation processes (Reproduced with permission from Ying 2018)

therefore possible to restore pesticide-contaminated sites using bioremediation, but it is still in its early phases of development. Bioremediation is limited to biodegradable chemicals since not all toxins in disturbed soils are substrates for microbial absorption. (Goswami et al. 2018). Schematic representation of Bioattenuation, Biostimulation, and Bioaugmentation processes is shown in (Fig. 7.4).

7.4 Bioremediation as a Sustainable Alternative of Pesticide Degradation

Various agro bioremediation technologies have been devised and deployed, variety from in situ surface practices through engineered soil pile and land-farming approaches to the usage of entirely soil slurry reactor systems for excavated soil treatment. The main aim of the numerous processes is to produce the required environment for the proper biological organisms to develop and degrade contaminants. Bioremediation has now been utilized to successfully repair hydrocarbon-contaminated locations. The following are some of the benefits of bioremediation techniques:

- They are usually the most cost-effective remedial options (Grommen and Verstraete 2002).

- The practices are adjustable to changing circumstances of environment, and bacteria that can breakdown novel synthetic chemical compounds emerge over time (Mandelbaum et al. 1995).
- The methods are thought to be eco-friendly, but incineration and other processes that require more energy and equipment are thought to be more polluting.
- The methods can be employed on-site, and in many cases, in situ, among dilute or extensively scattered pollutants (Iwamoto and Nasu 2001).

On the downside, bioremediation has failed to decrease pollutant levels to established concentration criteria on numerous occasions, and the methods/practices are frequently criticized as being excessively sluggish. Consumers have been hesitant to employ technology of bioremediation because of its historical background of failures as a result of the promotion of "quick-fix" technologies (Portier 2012). There could be a various reason for the failures and slow bioremediation rates, the most important of which is that the current environmental circumstances are unsuitable for the growth promotion. Furthermore, the kinetics of biodegradation and microbial growth, including when impurity levels decrease and the rates of subsequent breakdown, are similar. The surrounding of the pollutants (water solubility, structure, biodegradability, bioavailability, substrate/metabolite concentration, toxicity, and co-metabolism potential), the properties of the nature and soil (hetero or homogeneous environment; oxygen content, nutrients, and water; presence or absence of toxins) are the main factors that influence the contaminant degradation rate. In this systems, fewer microbial interventions are more time-consuming. When non-homogeneous process of environment, the cost of sampling and analysis rises dramatically, and it may become the project's most expensive component. Increased use of microbial technology can result in faster processes, more process dependability, and lower end-points (Ward et al. 2003). Natural attenuation procedures can take anywhere from five to twenty-five years, in situ subsurface processes 0.5–3 years, composting/soil pile processes 1–18 months, slurry phase and land-farming systems 1–12 months, and acceleration methods 15 days (Ward and Singh 2004).

Per day average pollutant degradation rates in natural absorption processes to enhance slurry phase systems can range from 5 to 10,000 ppm. To determine the suitability of bioremediation as a clean up strategy, some authors have suggested strategy and questions to examine concerning the nature of contaminants, such as (a) What consequence does the contamination period have on the clean of easily degradable chemicals, while persistent chemicals may still necessitate remediation? (b) How effective are recognized systems by microbes and/or the local population by microbes at degrading contaminants? (c) What variables are limiting population expansion, pollutant degradation, and the ability to meet clean-up standards? For remediation of chlorinated solvents, natural attenuation and electron donor administration were options, while biostimulation was evaluated for the action of phenols and chlorinated solvents (Hughes et al. 2000). For treating polycyclic aromatic hydrocarbons (PAHs), bioventing using low-rate airflow to provide sufficient oxygen for sustainable microbial activity along with prevention of contaminant volatilization was a possibility. For nitroaromatics, phenols, and PAHs, agro treatment or composting was used, and bioslurry techniques were used for all of the above compounds. All treatment strategies, with the exception of electron donor administration, were promising approaches to monoaromatic hydrocarbon bioremediation.

The perceived benefits of bioremediation processes develop commercial interest and alternative research in bioremediation technologies in the early 1990s, prompting investors, technologists, and entrepreneurs to establish a large number of bioremediation companies with the mission of developing and implementing bioremediation technologies. To put it mildly, many businesses suffered at best, and just a few have managed to stay true to their initial aims. Given the abundance of soil remediation potential, we are still waiting for a robust bioremediation-based manufacturing sector to emerge. Bioremediation is the way of reducing or eliminating hazardous pollutants by employing living organisms (typically bacteria, cyanobacteria, fungus, actinomycetes, and plants). These creatures could be found in nature or grown in a lab. These organisms either consume the toxins or assimilate all toxic substances from the environment, making the area virtually contaminant-free. Organic molecules are generally eaten up, whereas heavy metals and pesticides are digested within the system. Bioremediation takes advantage of this method by encouraging the development and/or rapid multiplication of organisms capable of degrading specific pollutants and converting them to harmless by-products. Significantly, bioremediation used with a variety of standard physio- chemical treatments to improve their efficacy.

7.4.1 Microbial Degradation

Microbial breakdown occurs when pesticides are used as nutrient by microbes like fungi and bacteria. Approximately, ten thousand fungal colonies were used in the bioremediation of pesticides from wastewater and soil (Dindal 1990; Melling 1993). Microbial metabolic potential use to remove soil contaminants is a safe and cost-effective alternative to existing physicochemical methods (Vidali 2001). Microbes (natural attenuation) can be employed to detoxify toxins in the environment (Siddique et al. 2003). Scientific papers have indicated the use of in situ bioremediation with naturally existing microorganisms (Swannell et al. 1996; Bhupathiraju et al. 2002; Moretti 2005). Under soil conditions that encourage microbial growth, microbial breakdown can be quick and comprehensive. Warm temperatures, a balanced pH, appropriate soil moisture, aeration (oxygen), and fertility are among these factors. Microbial deterioration is also influenced by the amount of adsorption. Because adsorbent pesticides are less accessible to some microbes, they degrade more slowly.

7.4.2 Chemical Degradation

Pesticide breakdown by chemical mechanisms that do not include a living organism is known as chemical degradation. The rate and type of chemical reactions are influenced by pesticide adsorption in the soil, soil temperature, moisture, and soil pH levels. Many pesticides, particularly organophosphate insecticides, are sensitive to hydrolysis in high pH (alkaline) soils.

7.4.3 Photodegradation

Photodegradation is the degradation of pesticides in presence of sunlight. Foliage has a broad range of stability when exposed to sunlight and pesticides sprayed on the soil surface. Pesticide exposure to sunlight can be reduced through mechanical soil integration during or after application, as well as irrigation or rainfall.

7.4.4 Phytoremediation

Growing plants on contaminated locations allows contaminating components to penetrate via the roots of the plants and reached in different parts such as leaves, stems, roots, etc. this process is known as phytoremediation. The key character of phytoremediation is that it is less damaging to the environment, has a higher level of public acceptance, and does not require excavation or heavy traffic (Matsumoto et al. 2009). For their growth and development, plants have a tendency to aggregate necessary heavy metals such as Fe, Zn, Mn, Mg, Mo, Cu, Ni, etc. and pesticides from water and soil. Plants have been proven to have valuable enzymatic degrading processes. Pesticides can be degraded by plants, which have been demonstrated to have helpful enzymatic pathways (Hance 1973). Plant development is relied on various environmental parameters such as availability of nutrients, pH, type of soil, water, and so on, therefore using plants alone in remediation has limitations. Long-term treatments or use in conjunction with other rapid remedial efforts may thus yield the greatest benefits from phytoremediation. Plants absorb a wide variety of compounds that are carried through the air on leaves surface, despite these limits. In United States and Europe in situ phytoremediation has become very popular (Meharg and Cairney 2000; Gaur and Adholeya 2004). Phytoremediation is limited because soil contamination should not go beyond a particular depth where the plant's roots come into touch with the pollutants. Because of the restricted growth rate of a selected species of plants and restriction to the area surrounded by roots, decontaminating a place often takes longer. To completely recover a site, it may be essential to go through numerous cycles of culture and harvest. Finally, once vegetation has been poisoned, it must be properly disposed of Mulligan et al. (2001).

7.4.5 Fungal Bioremediation

Fungi play an important and significant role in the application of bioremediation. Fungi are one of the few microbes that release a wide range of extracellular enzymes (Baarschers and Heitland 1986; Bumpus et al. 1993; Twigg and Socha 2001). The white-rot fungus *Pleurotus pulmonarius* and *Phanerochaete chrysosporium* have changed very resistant pesticides into hydroxylated and N-dealkylated metabolites. *Phanerochaete chrysosporium* is developed as a prototype system for bioremediation among fungal systems. Biodegradation relies heavily on oxidative enzymes. White-rot fungus are filamentous organisms that outperform bacteria in terms of the variety of chemicals they can oxidize (Masaphy et al. 1993; Barr and Aust 1994; Mougin et al. 1994; Van et al. 1999). Members of the Zygomycetes, such as arbuscular mycorrhizal fungi and mucoraceous fungus are certainly other fungi that can be employed in bioremediation. Other bioremediation alternatives include aquatic fungi and anaerobic fungi. *Saccharomyces cerevisiae, S. carlbergensis, Candida tropicalis,* and *Candida utilis,* among other fungi employed in bioremediation, are significant in removing undesirable chemicals from industrial effluents (Stephen 2001).

7.4.6 Mechanisms of Bioremediation

Bioremediation works by reducing, degrading, detoxifying, mineralizing, or transforming more hazardous pollutants into less toxic pollutants. Agrochemicals, insecticides, chlorinated compounds, xenobiotic compounds, nuclear waste, hydrocarbons, greenhouse gases, etc. are examples of pollutant types. To remove harmful waste from a polluted atmosphere, cleaning techniques are used. Through the all-encompassing and action of microorganisms, bioremediation is utilized in the degradation, immobilization, eradication, and detoxification of different wastes of chemicals from the surrounding.

Microorganisms used in bioremediation, as well as the processes and mechanisms involved in both dead and living biomass (Verma and Jaiswal 2016). Biosorption and bioaccumulation are two different types of bioremediations. Biosorption is a fast and adjustable passive adsorption mechanism (Ahalya et al. 2003). Metals are retained by physicochemical interactions, viz. complexation, adsorption, crystallization, ion exchange, precipitation, etc. among the functional groups and the metal on the cell surface (Gadd and White 1993). pH, temperature, ionic strength, particle size, amount of biomass, and the availability of other ions in the solution can all affect metal biosorption (Volesky 2004). As it is independent on cell metabolism, living organism biomass can be used for biosorption.

Bioaccumulation encompasses both intracellular and extracellular mechanisms, with passive absorption playing a minor and ill-defined role. Biosorption has a low selectivity because the binding occurs solely through physical interaction. A microorganism's cell wall contains a variety of macromolecules, including as proteins and polysaccharides that contain a various functional group, such as imidazole, carboxyl, ester sulphate, sulfhydryl, phenol, thioether, carbonyl, amide, hydroxyl, and amino groups. The cell wall composition of microorganisms can be influenced by their cultivation method, which can be used to improve their adsorption capability (Gadd and White 1993). Bacteria can eliminate metals from wastewater by using functional groups present in their cell walls, such as carboxyl, aldehydes, and ketones groups, resulting in less chemical sludge (Qu et al. 2014). Algae like red, brown, and green are also employed as biosorbents. Ion exchange can be performed by some functional components found in microorganism like uronic acid with sulfate and carboxyl groups, galactans, xylans, and alginic acid. The value of utilizing phycobiont as biosorbents is that, unlike other microorganisms, i.e., fungi, and bacteria, they rarely create hazardous chemicals (Das et al. 2008). Adsorption is also done with fungi and yeasts. Fungi have the advantage of being widely diverse in size, ranging from mushrooms to minute molds. They are simple to grow and produce a lot of biomasses. Glycoproteins and polysaccharides which include phosphate, amine, sulfate imidazole, hydroxyl and sulfhydryl groups are abundant in the fungi cell wall (Varma et al. 2011; Huang et al. 2014) (Tables 7.1–7.3).

The majority of metals are non-biodegradable; therefore, they have a tendency to accumulate in microorganisms (Fukunaga and Anderson 2011). Cumulation of metal is affected by a various element, including the degree of temperature, exposure, salinity, and metal content, making it hard to collect specific information on how it happens in bioremediation (Varma et al. 2011). The metal concentration regulates the accumulation process, which is complex and varies depending on the metabolic pathway (Fukunaga and Anderson 2011).

7.4.7 Factors Affecting Microbial Bioremediation

In bioremediation process, it involves microbes, fungus, algae, and plants degrading, eliminating, altering, immobilizing, or detoxifying various physical and chemicals contaminants from the nature. Microorganisms' enzymatic metabolic pathways aid in the progression of biochemical events that aid in pollution breakdown. Only when microorganisms come into contact with substances that assist them in generating energy and nourishment to multiply cells to act on pollution. The composition of chemicals and contaminants concentrations and physicochemical properties of the environment all influence the efficiency of bioremediation (Fantroussi and Agathos 2005).

The key contributors include the microbial population's ability to degrade pollutants, contaminants' accessibility inhabitants of microbes, and surrounding conditions such as soil variety, temperature, soil pH, nutrients availability, and oxygen.

Table 7.1 Microbes used in pesticide bioremediation

S. No.	Microbe used	Name of pesticide	Result/effectiveness	References
1	*Delftia lacustris* IITISM30 and *Klebsiella aerogenes* IITISM42	Endosulfan	Bacterial isolates promoted endosulfan phytoremediation in soil	Rani et al. (2019)
2	Microbial consortia (*Pseudomonas fulva* and *Brevibacterium frigoritolerans, Bacillus* aerophilus)	Phorate	Phorate is metabolized between 97.65 and 98.31% at 100, 200, and 300 mg kg^{-1}. Metabolites were discovered to be sulfone > sulfoxide	Jariyal et al. (2018)
3	*Ochrobactrum sp.* strain HZM	Quinalphos	Hydrolyzed quinalphos to produce 2hydroxyquinoxaline and diethyl phosphate, which is used as carbon sources	Talwar et al. (2014)
4	*Klebsiella sp*	Chlorpyrifos	The *Klebsiella* sp isolate was able to degrade toxic chlorpyrifos into nontoxic products, increasing soil microorganism growth and dehydrogenase activity	Jariyal et al. (2018)
5	*Pseudomonas putida* X3 strain (Genetically engineered)	Methyl parathion and cadmium	Methyl parathion was removed completely within 40 h, but the existence of cadmium in the initial stage of remediation quiet delayed MP degradation	Zhang et al. (2016)
6	*Rhizobium* isolates (SR G, SR I, SR 01)	Glyphosate and Monocrotophos	SR G was found to be the most efficient in removing monocrotophos (monocomplex) from the supernatant of glyphosate, followed by SR I and SR 01	Kumar et al. (2017)
7	*Bacillus cereus*	ß Cypermethrin	*B. cereus* synthesized Pyrethroid hydrolase having ability to metabolize ß Cypermethrin	Narayanan et al. (2020)
8.	*Pseudomonas nitroreducens*	DT 50 for 2,4-D, diazinon and carbofuran	*Ochrobactrum* sp. pure strain showed ability to degrade atrazine and glyphosate	Virgilio et al. (2020)

7.4.7.1 Biotic or Biological Factors

Biotic factors aid in the breakdown of organic components by microbes with limited antagonistic interactions, carbon sources, between microbes, and protozoa–bacteriophage interactions. The pace of pollutant degradation is often influenced by the quantity of catalyst available either in the biochemical reaction or the concentration of the pollutant. Enzyme activity, mutation, interaction, (competition, predation, and succession) gene transfer, population size, increased production of biomass, and composition are among the most important biological aspects (Boopathy 2000; Madhavi and Mohini 2012).

Table 7.2 Enzymes used for the bioremediation of pesticides

Enzyme used	Pesticide	Organism used	References
Oxidoreductases (Gox)	Glyphosate	*Pseudomonas* species and strain of LBr *Agrobacterium* T10	Bhatt et al. (2021)
Monooxygenase enzymes:			
ESd	Endosulphan and Endosulphato	Species of *Mycobacterium* genus	Sutherland et al. (2002)
Ese	DDDT, Endosulphan, Aldrin, Malathion, and Endosulphato	*Arthrobacter* sp.	Kumar and Sachan (2021)
Cyp1A1/1^{a}2	Isoproturon, Atrazine, and Norflurazon	Rats	Ortiz et al. (2013)
Cyp76B1	Isoproturon, Linuron, and Chlortoluron	*Helianthus tuberosus*	Didierjean et al. (2002)
P450	Hexachlorobenzene and Pentachlorobenzene	*Pseudomonas putida*	Jones et al. (2001)
Dioxygenases (TOD)	Herbicides Trifluralin	*Pseudomonas putida*	Gunjal (2021)
E3	Synthetic pyrethroids and insecticides phosphotriester	*Lucilia cuprina*	Campbell et al. (1998)
Phosphotriesterase enzymes:			
OPH/OpdA	*Flavobacterium* sp., *Agrobacterium radiobacter,* and *Pseudomonas diminuta*	phosphotriester	Scott et al. (2008)
Haloalkane Dehalogenases:			
LinB	Hexachlorocyclohexane (β and δ isomers)	*Sphingobium* sp.	Ito et al. (2007)
AtzA	Herbicides chloro-s-trazina	*Pseudomonas* sp. ADP	Ortiz et al. (2013)
TrzN	Herbicides chloro-s-trazina	*Nocardioides* sp.	
LinA	Hexachlorocyclohexane	*Sphingobium* sp. *Shingomonas* sp.	Ito et al. (2007)
TfdA	2,4 -dichlorophenoxyacetic acid and pyridyl-oxyacetic	*Ralstonia eutropha*	Kumar and Sachan (2021)
DMO	Dicamba	*Pseudomonas maltophilia*	Yao et al. (2015)

Abiotic or environmental factors: Pollutants in the environment interact with the metabolic activity and physicochemical properties of the microbes targeted throughout the procedure. The environmental factors influence the success of the microbe–pollutant interaction. conditions. pH, temperature, moisture, water solubility, soil structure, nutrients, oxygen content, site conditions and redox potential, resource deficiency and presence of pollutants, chemical architecture, concentration, type, toxicity, and solubility are all factors that influence microbial activity and growth (Madhavi and Mohini 2012; Adams et al. 2015).

Table 7.3 Various matrixes used for pesticides degradation by cell immobilization

S. No.	Matrix used	Pesticides	Microorganism used in immobilization	Removal rate	References
1.	Calcium-alginate immobilized cell systems	Coumaphos, an organophosphate insecticide	*Escherichia coli*	80%	Mansee et al. (2005)
2.	Alginate Beads and tezontle	Organophosphate (OP) pesticides Methyl parathion (MPt) and tetrachlorvinphos (TCh)	Bacterial consortium	MPt78% TCh 49%	Yanez et al. (2009)
3.	A ceramic material, granular sepiolite	Propachlor (2-chloro-N-isopropylacetanilide)	*Pseudomonas* strain	98%	Martin et al. (2000)
4.	Green bean coffee	DDT	*morganii. P. Pseudomonas* aeruginosa, *P. putida, Stenotrophomonas maltophilia, F. oryzihabitans, Flavimonas oryzihabitans*, and *Morganella aeruginosa*	68%	Barragan et al. (2007)
5.	Ca-alginate beads	Diuron herbicide	Species of *Delftia acidovorans* WDL34 and *Arthrobacter*	65%	Bazot and Lebeau (2009)

In most aquatic and terrestrial environments, contaminant biodegradation can occur in a pH range of 6.5–8.5, which is usually ideal for degradation. The type and number of soluble elements that are reachable as in the osmotic pressure and pH osmotic pressure of aquatic and terrestrial systems, all influence contaminant metabolism (Cases and De Lorenzo 2005).

7.4.8 Limitations of Bioremediation

Bioremediation technology has a number of drawbacks. The nature of the organisms is a fundamental constraint. Biological pollution remediation is not a good deed. Rather, it is a plan for ensuring one's own existence. When it comes to bioremediation, the majority of organisms work in environments that meet their demands. To stimulate the organisms to decompose or absorb the pollution at a reasonable rate, some form of environmental modification is required. The organism must often be exposed to less amounts of the contaminant over an extended time period. This causes the body to develop the metabolic pathways necessary for the pollutant to be digested. It is required to provide fertiliser or oxygen to the substance holding the contaminant when utilizing microorganisms. When done in situ, this can be harmful to other creatures. When simple chemicals and metals are taken up, the organisms are likely to be exposed to dangerous quantities of these contaminants. The petroleum companies are engaged in a legal battle with the Environmental Protection Agency over the increased costs of adhering to clean air act standards. When undertaking in situ remediation, this is a concern. Under laboratory conditions, bioremediation has been shown to be effective. It also works for a variety of field conditions, according to short-term studies. Bioremediation's popularity is boosted by the perception that it is more "green" than other remediation procedures. Despite the huge risks, companies and individuals are investing in biotechnology futures. As a result, companies of bioremediation and biotechnology have a bright future ahead of them, regardless of their long-term efficacy.

Bioremediation is only possible with biodegradable chemicals. This approach is prone to total and quick deterioration. In the environment, biodegradation products more persistent or harmful as the parent chemical (Sharma 2020).

7.5 Recent Advance Tools Used For Enhanced Efficiency Of Pesticides Bioremediation

Due to unequal use of pesticides to control pest and vectors, it is highly needed to come with some techniques or tools to decrease its effects on environment because the pesticides residues show high toxicity, persistent and recalcitrance behaviour. Removal of pesticides and its residues by means of bioremediation seems to be very effective technology because it is having low cost, highly efficient in removing the toxic content and eco-friendly in nature. During the process of bioremediation, microbial community plays a vital role and converts most of the toxic compounds into the nontoxic compounds (Nawaz et al. 2011). In the process of bioremediation, microbes are considered as one of the best tools for the detoxification process. Many other tools are also involved in the bioremediation process to enhance its efficiency towards the removal of pesticides (Demnerová et al. 2005). Some of the effective strategy and tools in reference to pesticides bioremediation are discussed further.

7.5.1 Enzyme Technology

Generally, the degradation of pesticides through the enzymatic action is highly active during in situ mechanism and also by targeting specific type of enzymes with necessary physiological traits. Intrinsic detoxification process, metabolic resistance, biodegradation via soil and water microorganisms are various methods used for the degradation of pesticides through enzyme technology. The chemical structure of the pesticides used in agricultural sectors possesses diverse biochemistry which requires broad range of catalytic mechanism as well as extensive variety of the enzymes classes (Scott et al. 2008).

For the pesticides removal, bioremediation is used at a very high extent in which the rate of degradation totally depends upon the microorganism potentials although this process worked very slowly, results in decrease of the feasibility during bioremediation process (Ghosh et al. 2017). To cope up with this limitation, microbial enzymes are extracted from the whole organism to use in the rectification of the pesticides (Thatoi et al. 2014). Basically, enzymes are known as complex biological macromolecules which enhance the activity rate and act as catalyst in the biochemical reaction during the degradation of the various pesticides used to control pests. Enzyme has ability to enhance the reaction rate by depressing the molecules activation energy (Kalogerakis et al. 2017). Enzymes have ability to increase the reaction rate by declining the activation energy of the molecules. For the pesticides bioremediation some specific enzymatic systems were highly used such as glutathione S transferases, hydrolases, and mixed function oxidase system (Li et al. 2007). Classes of various enzymes used in the bioremediation of the pesticides such as:-

7.5.1.1 Oxidoreductases

This group contains clusters of enzymes which specially enhance the catalytic rate during the transfer of the electron from oxidation to reduction state of the molecules. Additionally, it requires cofactors which act as electron acceptor, electron donors, or for both cases. This group of the enzymes further divided into the 22 subclasses. Some of the enzymes used in the bioremediation process of the pesticides describe given below:

Oxygenase

Aromatic compounds or the pesticides degrade aerobically in the presence of oxygenase enzymes by means of cleaving the aromatic compound ring by the addition of one or more oxygen molecules in it. On the basis of number of oxygen atoms used during the process, this enzyme was categorized into two subgroups, i.e., monooxygenase and dioxygenase. Various numbers of herbicides, fungicides, and pesticides are degraded by oxygenase enzymes (Sivaperumal and Kamala 2017).

The bioremediation process when catalyse by using one oxygen atom then monooxygenase enzyme works whereas when two oxygen atom works it is called dioxygenases, with the help of these enzymes the reaction rate as well as solubility get increased. Previous study showed that dehalogenation, denitrification, dehalogenation, and hydroxylation are some mechanisms occurs during the degradation process of pesticides (Arora et al. 2010). As discussed formerly cofactor plays a vital role during the process of cleaving the aromatic compounds containing pesticides, on basis of this it is further sub-classified into two groups, i.e., flavin dependent and P450. The NAD (P) H. Esd (endosulfan diol), Ese (endosulfan ether), and heme-containing enzyme are the substrates able to reduce flavin and P450 monooxygenases enzyme, respectively (Galán et al. 2000). ESe and Esd are also have capability of detoxifying the persistent insecticides which contains endosulfan and its metabolite endosulfate (Sutherland et al. 2004). Previous studies showed that there were some monooxygenase enzymes which do not required any cofactors for the reaction activity such as tetracenomycin F1 monooxygenase and quinol monooxygenases isolated from Streptomyces genus and *E.coli* bacteria, respectively (Arora et al. 2010). Various herbicides such as chlortoluron, atrazine, linuron are degraded by another type of P450 oxidoreductase enzyme, i.e., cytochrome CYP1A1, which have tendency to catalyse the degradation rate during the breakdown of the compounds. Mostly enzymes which fall under the class of P450 oxidoreductase contain iron porphyrin group (Yamada et al. 2002; Didierjean et al. 2002; Kawahigashi et al. 2005).

Oxidase enzymes are also come under the class of oxidoreductases in which basically molecular form of oxygen plays a role as electron acceptor. In pesticides bioremediation one of the enzymes, i.e., glyphosate oxidase, denoted as GOX is used for remediating the glyphosate herbicide. Basically, GOX is flavoprotein amine oxidase-based enzyme which is extracted from the bacterial strain of Pseudomonas species. Glyphosate is a type of herbicides which affects the weeds in large scale by aiming the enzyme, i.e., 5-enolpyruvylshikimate 3-phosphate synthases (EPSPS) during shikimic acid pathway. During the remediation process, GOX splits glyphosate into aminomethylphosphonate (AMPA) and releases the keto acid glyoxylate (Scott et al. 2008).

7.5.1.2 Hydrolases

This group of enzymes required no cofactor for the initiation of the degradation during bioremediation process. This group of enzymes have potential to hydrolyse various biochemical classes belonging to esters, peptide, ureas, thioesters, etc. During the bioremediation process, this enzyme group does not undergo any kind of cofactors which makes its very compatible and ideal for the removal of pesticides under enzyme technology. Different types of enzymes used for the remediation of pesticides, such as: -

Phosphotriesterases (PTEs)

PTEs are one of the best pesticides degrading enzymes. Generally, these enzymes have potential to detoxify and hydrolyse the harmful organophosphate pesticides by decreasing its ability to deactivate Acetylcholinesterase (AchE) (Singh and Walker 2006; Porzio et al. 2007; Theriot and Grunden 2011; Shen et al. 2010; Holásková et al. 2012). *Pseudomonas diminuta* bacterial strain was very primarily used for the isolation PTEs enzyme which poses high catalytic behaviour for the organophosphate pesticides.

Esterases

These enzymes basically hydrolyse the group which contain carboxylic esters, amides, and phosphate esters (Bansal 2012). Various kinds of insecticides such as carbamates, pyrethroids, and organophosphates are hydrolysed by enzyme named carboxylesterases due to the presence of ester bond. This class of enzymes are further classified into esterases A in which Cys residue present at active centre and esterases B in which Ser residue present at active centre (Bhatt et al. 2021)

7.5.2 Genetic Engineering

In general, genetic engineering is the technique where the recombinant DNA (rDNA) play vital role and used to change the genetic structure of the specified organism. This technique includes disruption, amplification, and modification of the specific genes that encode the enzyme in the metabolic pathways, minimize pathways process, increase redox reaction rates, enable heterologous genes to provide novel traits (Abraham et al. 2002; Shimizu 2002). During degradation process of the pesticides various genetic methods have been grown and help in enzyme optimization (Shimizu 2002; Cases and De Lorenzo 2005). For the first time organophosphate pesticides detoxification was done by genetically modified microorganism and genes which encoded hydrolases have been cloned and articulated in *Pseudomonas pseudoalcaligens, E. coli, Streptomyces species, pichia species* (Fu et al. 2004; Ningfeng et al. 2004; Yu et al. 2009; Shen et al. 2010; Wang et al. 2012). Many enzymes have specific gene for its activity and coding such as methyl parathion hydrolase coded by the mpd gene and organophosphorus hydrolase coded by opd gene (Zhang et al. 2005; Yan et al. 2007).

7.5.3 Gene Editing Tool

This technique basically used to modify as well as to manipulate the DNA structure with the use of molecular scissor engineered nucleases enzymes with great potential (Butt et al. 2018). These tools help in enhancing the bioremediation process by eliminating the pesticides, convert the toxic pesticides into the simpler compounds (Basu et al. 2018; Hussain et al. 2018). Gene editing tools such as ZFN, CRISPR-Cas, and TALEN are highly used for pesticides bioremediation. (Singh et al. 2018; Waryah et al. 2018; Wong 2018).

ZFN stands for Zinc Finger Nucleases. It showed potential to behave as DNA binding domain because of the presence of eukaryotic transcription factors. ZFNs have nucleotide cleavage domain which is specifically eliminated from the *flavobacterium okeanokoites.* CRISPR-Cas is one of the most effective and productive

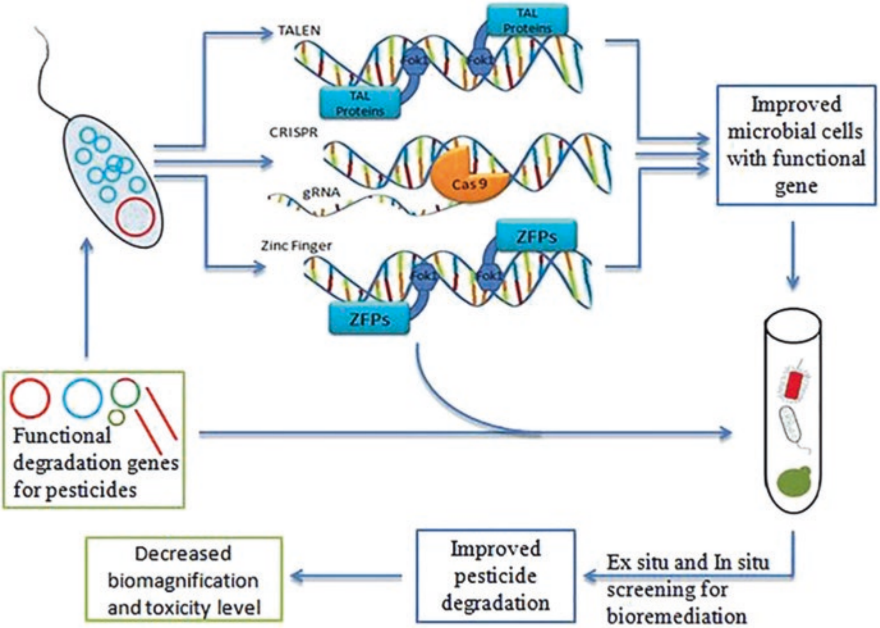

Fig. 7.5 Gene editing tools for bioremediation (reproduced from Jaiswal et al. 2019 available under CC BY 4.0)

tools for gene editing during the degradation of pesticides (McMahon et al. 2018; Yadav et al. 2018).

CRISPR-Cas tools divided into three types I, II, III (Behler et al. 2018). TALENS stands for Transcription activator like effector nucleases. This one is very advanced gene editing and modification tool. TALENs are originated from the Xanthomonas bacterial species.

Comparatively, CRISPR-Cas tool is found to be very simple, easy to use, as compared to other two (Ju et al. 2018). CRISPR-Cas tools mainly access the gene interaction, genetic and phenotypic relation with the gene knock out system (Vander Sluis et al. 2018). On the other hand, TALENs and ZFNs show positive approach for mutagenesis due to random binding to DNA sequence (Stein et al. 2018) shown in Fig.7.5.

7.5.4 *Cell Immobilization*

Researchers adopted cell immobilization methods to retain catalytic behaviour for a longer duration (Martin et al. 2000; Richins et al. 2000; Chen and Georgiou 2002). As compared to other conventional methods of pesticides bioremediation using whole cell immobilization showed significant results. Previous studies showed that due to cellular and genetic structure modification by the immobilization process which results in showing higher efficiency towards degradation of the pesticides, it was also observed that immobilized cell is very less vulnerable to get contaminated by toxic compounds and shows high tolerance to the disturbances occurring during the reaction process, which makes it is a good candidate for the pesticides bioremediation process (Ha et al. 2008).

Cell immobilization process mainly done by two processes:

A. Based on physical retention
B. Based on chemicals bonds

In cell immobilization method for pesticides bioremediation various kinds of substrate are used such as clays, glass, ceramics, and silicates (inorganic substrate); cellulose, starch, dextran, agarose, chitin, alginate, keratin (organic substrate) (Ahmad and Sardar 2015). For the selection of appropriate substrate materials some characteristics are to be ensured like sterilization ease, physical behaviour of the substrate, reusable and must be cost-effective in nature. Various xenobiotic pesticides degradations were done through cell immobilization techniques by using polymeric gels as a substrate (Uemoto and Saiki 2000).

For the pesticides removal some scientist used volcanic rock known as tezontle, which is highly porous in structure results in providing large surface areas for the contact, sterilized and can be reused. In this study biofilm formation by cell immobilization was done by means of the bacterial development into the micro pores present in the volcanic rocks (Yanez et al. 2009).

Researchers used recombinant *E.coli* through cell immobilization to decontaminate the wastewater containing insecticides compounds (Qiao and Yan 2000). Experimental observations revealed that the rate of degradation depends upon the type of ester bonds present. Pesticides compounds which contain carboxyl ester bonds were degraded very rapidly as compared to other ester bond containing compounds (Huang et al. 2001).

7.6 Conclusions and Future Prospects

Persistent Organic Pollutants (POPs) are harmful substances which emerged due to anthropogenic activities. POPs impart negative consequences on habitats, wildlife, and people. Over time, actions were taken to reduce and eliminate the manufacture, usage, and discharge of these compounds. Many factors influence the possibility for pesticides to contaminate surface water or groundwater, including pesticide properties, soil qualities, crop management practices, and hydraulic loads on the soil. Degradation of pesticides through the enzymatic action is highly active during in situ mechanism and also by targeting specific type of enzymes with necessary physiological traits. Various enzymes used in the bioremediation of the pesticides such as oxidoreductases, hydrolases, phosphotriesterases (PTEs), esterases. Bioremediation technology has a number of drawbacks also. Surrounding conditions such as soil variety, temperature, soil pH, nutrients availability, and oxygen affect the microbial degradation of pesticides. During degradation process of the pesticides various genetic methods have been grown and help in enzyme optimization. Gene editing tools basically used to modify as well as to manipulate the DNA structure with the use of molecular scissor engineered nucleases enzymes with great potential. Although microbial bioremediation is very effective to eliminate pesticide residues from the environment but still it requires popularization and some modifications for more practical applications.

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Part II

Latest Tools and Techniques of Pesticides Bioremediation

Chapter 8
Pesticide Bioremediation: OMICs Technologies for Understanding the Processes

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Abstract The use of pesticides in agriculture worldwide significantly offers crop protection from pests, enhances crop yields, and guarantees the quality of the agricultural products during storage, which generates economic benefits for farmers. Due to this, millions of tons of pesticides are released into crop fields each year. However, only a small proportion of the total amount of pesticides employed reaches the biological target. The rest is spread into the environment, causing soil, water, and air contamination events. The presence of pesticide wastes in the environment is related to adverse effects on biodiversity and human health. Bioremediation is an effective strategy for the treatment of pesticide-contaminated sites. However, the establishment of efficient pesticide bioremediation approaches requires considering important aspects of microbial metabolism and physiology as well as deep knowledge of the metabolic pathway, enzymes, and cellular processes implicated in microbial-mediated pesticide biodegradation. Recently, OMIC studies focused on pesticide biodegradation and bioremediation have generated significant information on the genes and proteins related to the pesticide degradation processes, the metabolites derived by microbial-mediated pesticide degradation, and the strategies

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employed by the microorganisms to counteract the stress caused by pesticide exposure. In the present chapter, the application of OMIC studies related to pesticide biodegradation and bioremediation is fully reviewed to describe the relevance of the global analysis through OMIC approaches to generate scientific information that lets us achieve a better understanding of the pesticide bioremediation processes.

Keywords Pesticide · Degradation · Transcriptomics · Proteomics · Metabolomics

8.1 Introduction

World population growth has resulted in the demand for goods and services, especially food. For food production, it is necessary to guarantee the productivity of crops, so the pesticides application has resulted in a necessary practice to protect crops from pests and diseases. In modern agriculture, the use of pesticides helps to reduce crop losses and preserve the quality of farm products (Giri et al. 2021). Pesticides also have important uses for the control of different pests in homes, gardens, and public facilities (Chandran et al. 2019). Pesticides are synthetic or natural compounds employed for the control of harmful fungi, insects, rodents that threaten plants, animals, and the human health (Verma et al. 2014; Spina et al. 2018; Mir et al. 2020). Over the past few decades, an enormous increase in the use of pesticides has been observed worldwide (Singh et al. 2020a). According to the FAO (2021), the annual global pesticide utilization is approximately 4.2 million tons, of which 52% is used in Asia, 32.3% in the Americas, 11.7% in Europe, 2% in Africa, and 1.7% in Oceania.

As a consequence of pesticides use, these chemicals are dispersed in extended areas causing severe pollution and environmental threats derived from their persistence and toxicity. In addition, pesticide waste has been contaminating soil, water, and air, and they can also be found in clandestine deposits or as obsolete or expired products. A pesticide is recognized as obsolete when it has exceeded its expiration date, when its use has been prohibited, when it has lost its biological effectiveness, or when its owners no longer desire it. Its compounds also include waste generated through pesticide manufacture or formulation, among others. The FAO (2021) has carried out work with regard to the existence of obsolete pesticides in different parts of the world, and they report data taken during the last two decades. Thus, the FAO reports a total stock of 291,000 tons of obsolete pesticides, of which 83% are in European countries, 9.4% in Africa, and 3.9% in Latin America, while the remaining stocks are in countries of Asia and the Near East.

Due to pesticide waste dispersion, contaminated sites, and the existence of obsolete pesticides, it is clear that they represent a risk for the environment and health. Therefore, the development of strategies for adequate pesticide waste treatment is crucial. Interestingly, due to economic, environmental, and social acceptance aspects, pesticide biodegradation is one of the most viable options. Due to their extraordinary metabolic diversity and genetic plasticity, microorganisms show an outstanding capacity to degrade different pollutants, including pesticides (Rodríguez et al. 2020).

Initial pesticides biodegradation research aimed to isolate and characterize cultivable microorganisms, mainly bacteria, capable of degrading and transforming pesticides into less toxic molecules and propose them for polluted sites bioremediation strategies. In natural environments, there is a great diversity of microorganisms; however, only a small proportion of such microorganisms can be isolated and successfully cultivated in laboratory conditions. To access the biodiversity of the non-cultivable microorganisms new research tools were developed (Rodríguez et al. 2020), based on the search and identification of enzymes related to the pesticide degradation process, their transcriptional regulators, as well as studies of their kinetic behaviors and their structure–function relationship (Castrejón-Godínez et al. 2019).

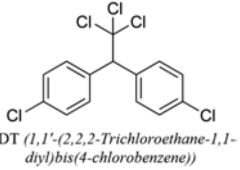
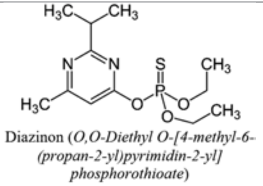
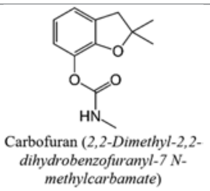
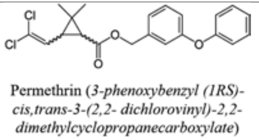
OMIC technologies constitute a valuable set of tools that permit a better understanding of the xenobiotic bioremediation processes and their adequate managing and monitoring. For example, methods for DNA sequencing have made it possible to study the genes of a single organism or multiple organisms (genomics); analyze microbial DNA taken directly from environmental samples (metagenomics); evaluate the microbial gene expression under different environmental and experimental conditions (transcriptomics); analyze the protein expression patterns (proteomics) as well as identify and characterize the low molecular weight metabolites (metabolomics) present in microorganisms. Through the application of OMIC technologies in the field of bioremediation, questions related to the metabolic mechanisms employed by microorganisms to eliminate pollutants, such as pesticides, can be answered (Castrejón-Godínez et al. 2019; Dangi et al. 2018; Rodríguez et al. 2020).

In this chapter, we highlight and discuss pesticide biodegradation by bioremediation processes, the understanding and combining the conventional bioremediation methods with advanced aspects of the OMIC technologies provide valuable information related to the metabolic and functional characteristics of microorganisms during the pesticide biodegradation processes. The use of OMIC technologies permits the evaluation of key aspects such as changes in the gene and proteins expression profiles during the pesticide biodegradation process, as well as the characterization of the metabolites derived from such process.

8.2 Pesticide Classification

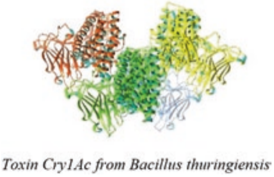
According to their main characteristics, such as toxicity, average life, use, and chemical composition, pesticides are classified in different ways. According to their chemical composition, pesticides are grouped into several families (Jayaraj et al. 2016). Table 8.1 shows examples of compounds of the most relevant pesticides families, descriptions of their uses, characteristics, chemical composition, and structures.

Table 8.1 General characteristics of some pesticides (Ortiz-Hernández et al. 2013; EPA 2018)

Pesticides family	Characteristics	Main composition	Example of chemical structure
Organochlorines	Were commonly used in the past (for example, DDT). Soluble in lipids, toxic to a variety of animals, long-term persistent.	Carbon atoms, chlorine, hydrogen, and occasionally oxygen. They are nonpolar and lipophilic.	 DDT (*1,1′-(2,2,2-Trichloroethane-1,1-diyl)bis(4-chlorobenzene)*)
Organophosphates	Are used in agriculture, homes, gardens, and on animals. Soluble in organic solvents but also in water. Affect the central nervous system. They are absorbed by plants and then transferred to leaves and stems, which are the supply of insects.	Possess central phosphorus atom in the molecule. In relation with organochlorines, these compounds are more stable and less toxic in the environment. They can be aliphatic, cyclic, and heterocyclic.	 Diazinon (*O,O-Diethyl O-[4-methyl-6-(propan-2-yl) pyrimidin-2-yl] phosphorothioate*)
Carbamates	Are widely used in homes, gardens, and agriculture. Carbamate acid derivatives. They affect the functioning of the nervous system in ways similar to the organophosphates. The effects are usually reversible in humans and kill a limited spectrum of insects.	Chemical structure based on a plant alkaloid *Physostigma venenosum.*	 Carbofuran (*2,2-Dimethyl-2,2-dihydrobenzofuranyl-7 N-methylcarbamate*)
Pyrethroids	Pyrethroids are synthetic versions of the pyrethrin, which is found in chrysanthemums. Are used mainly household insecticides and in agriculture. Are toxic to the nervous system.	Compounds similar to the synthetic pyrethrins (alkaloids obtained from petals of *Chrysanthemum cinerariaefolium*).	 Permethrin (*3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate*)

(continued)

Table 8.1 (continued)

Pesticides family	Characteristics	Main composition	Example of chemical structure
Biological	*Bacillus thuringiensis* is used and applied against forest pests and crops, particularly against butterflies. Also affect other caterpillars.	Microorganisms or their metabolic products.	 *Toxin Cry1Ac from Bacillus thuringiensis*

8.3 Microbial Biodegradation and Bioremediation of Pesticides

Because microorganisms are constantly exposed to pesticides, they have developed catabolic processes for pesticide biodegradation, so they play an essential role in their elimination from the environment. Biodegradation is a process that eliminates pollutants or reduces their toxicity or concentration to permitted levels according to environmental legislation. It involves the breakdown of pesticides by microorganisms, resulting in less complex substances, such as water, CO_2, and salts. Complete degradation of pesticides into inorganic compounds is known as mineralization. In some cases, the degradation produces less toxic and simpler compounds, which leads to partial biodegradation (Villaverde et al. 2017; Ortiz-Hernández et al. 2018).

Studies on microbial pesticides degradation are helpful for the development of bioremediation strategies. Biodegradation and bioremediation are closely related processes and are based on the metabolism of pesticides by microorganisms. The main difference between both processes is that biodegradation is a natural process that occurs in polluted sites, and bioremediation is a biological technology (Singh 2008).

The term bioremediation encompasses the use of different biological systems like bacteria, yeast, fungi, algae, protozoa, among others, to eliminate pollutants from the environment (soil, water, air) through degradation and, removal, or the conversion of toxicants pollutants into non-toxicants, resulting in a reduction in the environmental concentration to permissible levels (Dua and Joshi 2020; Mir et al. 2020; Singh et al. 2020b). Bacteria are the most used biological system in bioremediation because they are easily cultivable in simple low-cost culture media and show higher growth rates in comparison to other microorganisms. Moreover, bacteria can be genetically modified, which give them an extra feature that increases their potential in xenobiotic degradation (Ortiz-Hernández et al. 2011, 2013). Bioremediation is an innovative technology that employs the metabolic and physiological potentialities of microorganisms to degrade compounds through the action of enzymes that modify contaminants to less harmful products (Villaverde et al. 2017) and remove them from polluted sites (Bhatt et al. 2021). The effectiveness of the bioremediation processes is dependent on adequate microbial growth and activity, and successful bioremediation strategies frequently require the control of environmental parameters at polluted sites to favor the microbial growth and increase the rate of degradation (Sharma 2012).

Bioremediation can be classified into two categories: In situ, where the degradation or the removal of the contaminants is carried out in the polluted place, and ex situ, which requires the mobilization of contaminated water or soil to a site under controlled conditions for its treatment. In turn, both categories are classified according to the information shown in Table 8.2.

The pesticide biodegradation processes are dependent on environmental factors and the availability of nutrients in polluted sites. High pesticide bioconversion rates require the bioavailability of the pollutant, as well as the control of environmental and nutritional factors related to the growth and metabolic activities of microorganisms. They include:

8.3.1 Microbial Population

The pesticide degradation rates in polluted sites are determining by the autochthonous microbial diversity and their capacity to degrade pesticides. The microbial population, distribution, and ecological interaction between microorganisms affects the biodegradation potential in this sites. Microorganisms show great genetic and physiological plasticity; they can adapt over time to environmental changes caused by the presence of pollutants, enhancing their ability to efficiently degrade pesticides. Bioremediation strategies require the identification characterization and selection of the microorganisms with the higher effectiveness for pesticide removal in the condition of the polluted sites (Zulfiqar and Yasmin 2020).

Several microorganisms such as bacteria, cyanobacteria, yeast, fungi, and algae are considered extracellular enzyme-producing. Among microorganisms, due to their outstanding capability to produce extracellular enzymes such as peroxidases, laccases, and oxidases, related to the lignin degradation process, the most promising for the bioremediation of persistent compounds are white-rot fungi, these enzymes have also been reported as efficient for the degradation of several organic pollutants, pesticides included. On the other hand, several pesticides degrading bacterial strains have been isolated from different environments. In these microorganisms, esterases, cytochrome P450, and glutathione *S*-transferases are the leading enzymes implicated in pesticide degradation. These enzymes can catalyze key metabolic reactions for the pesticide degradation processes, such as dehalogenation, hydrolysis, hydroxylation of benzene rings, metabolism of side chains, oxidation of amino groups (NH_2) to nitro groups (NO_2), oxygenation of carbon double bonds, reduction of nitro groups to amino groups, replacement of sulfur atoms with oxygen, and ring cleavage (Ortiz-Hernández et al. 2013; Sun et al. 2020).

Table 8.2 Bioremediation technologies

Strategies	Technology	Description	References
In situ bioremediation technologies	Natural attenuation	Is a proactive approach that focuses on the verification and monitoring of natural remediation processes also known as passive remediation.	Juwarkar et al. (2014)
	Bioventing	Involving air supply, this technology uses the organisms present in the contaminated site as well as the nutrients available to carry out the degradation process of the contaminants.	Juwarkar et al. (2014)
	Phytoremediation	Use of plants and their associated microorganisms to absorb, accumulate, metabolize, volatilize, or stabilize contaminants originated from human activities present in the environment, such as pesticides, petroleum hydrocarbons, chlorinated solvents, explosives, heavy metal, and radionuclides.	Verma and Shukla (2016); Kovacs and Szemmelveisz (2017)
	Bioaugmentation	Is the addition of organisms or enzymes to a site for eliminating contaminants, in which allochthonous or genetically modified microorganisms capable of degrading pollutants are inoculated in the contaminated site.	Ajlan (2016); Chaturvedi and Khurana (2019); Baćmaga et al. (2017); Nwankwegu and Onwosi (2017)
	Biostimulation	Is based on the addition of electron acceptors or donors, as well as nutrients to stimulate the degradation of a compound by the endogenous microbial population.	Ortiz-Hernández et al. (2018)

(continued)

Table 8.2 (continued)

Strategies	Technology	Description	References
Ex situ bioremediation technologies	Composting	A process of nutrient recycling through decomposition of biodegradable wastes by microbes. Can be used not only for the recycling of organic matter but also for the removal of chemical contaminants such as synthetic organic compounds or other xenobiotics, including pesticides.	Ortiz-Hernández et al. (2018); Chen et al. (2015a)
	Bioreactors	Is a container where chemical processes are performed by biochemically active organisms or substances derived from them. With the bioreactors, a biologically active environment is sought, maintaining the ideal environmental conditions (pH, temperature, oxygen concentration, etc.) for the organisms.	Ortiz-Hernández et al. (2018)
	Electro-bioremediation	Consists of the application of electric current directly to the soil, which increases the nutrients bioavailability and transforms the contaminants to simpler compounds.	Annamalai and Sundaram (2020)
	Biobeds	Biobeds are bioreactors developed for treating pesticide residues generated during agricultural activity, such as water from the washing of spraying equipment or any residue from the preparation of pesticide sprays (Dias et al. 2020).	Dias et al. (2020)
	Biomineralization	Biodegradation of organic substances into inorganic components.	Lacina et al. (2015)
	Biosorption	Is based on the uptake of substances by biosorbents agents, as a different sort of biomass, through physicochemical mechanisms such as adsorption or ionic exchange.	Flores-Trujillo et al. (2021)

8.3.2 *Pesticide Composition*

The pesticide biodegradation patterns are influenced by the specific physicochemical characteristics of each pesticide. Parameters such as molecular weight, structure, functional groups, and chemical elements present in the molecule greatly influence the pesticide degradation rates in the polluted sites (Zulfiqar and Yasmin 2020).

8.3.3 Environmental Parameters

The effectiveness of pesticide remediation in the environment is influenced by different parameters such as moisture, nutritional sources, pH, soil properties, and temperature. Microorganisms implicated in bioremediation strategies require optimum environmental parameters for survival, development, and adequate metabolic activities (Zulfiqar and Yasmin 2020).

Bioremediation technology has different disadvantages, one of which is the impossibility of replicating the results obtained at the laboratory level under field conditions. In addition, the use of bacterial strains of a single species is not enough to implement the process although the use of genetic engineering to obtain genetically modified organisms could be an option. Nevertheless, due to limited research on the characterization of uncultured microorganisms and the inability to replicate the environmental conditions in which they inhabit, OMIC approaches are being used to evaluate the potential of non-cultivable microbial strain for biodegradation and removal of pesticides in contaminated sites.

8.4 Pesticide Degradation Pathways

The role of microorganisms in pesticide degradation has long been recognized. They are constantly exposed to pesticide compounds and they have developed catabolic processes to degrade them through the use of different strategies and enzymatic pathways. Degradation by microorganisms is a process that breaks down xenobiotic compounds into less complex substances, water, CO_2, and salts. Several pollutants can be completely degraded under soft conditions compared with degradation mediated by physical and chemical means. Because pesticides have various chemical structures, individual degradation reactions in metabolic pathways must be versatile; this reaction can include conjugation, hydrolysis, oxidation, and reduction. These reactions are achieved through the catalytic activities of different enzymes such as cytochrome P450, dehydrogenases, ligninases, mono- and dioxygenases, among others. Bacterial genetics and molecular biology have widely contributed to identifying and characterizing the genes involved in pesticide degradation and understanding the pesticide degradation processes (Ortiz-Hernández et al. 2013). Table 8.3 shows a list of genes that encode for enzymes that catalyze reactions making the degradation of different pesticides families possible. Here, we provide examples of two types of pesticides that are degraded by bacteria containing genes specific for this purpose.

Table 8.3 Genes reported with the ability to degrade pesticides

Enzyme	Gene	Microbial species	Pesticide	Reference
Bacteria				
Organophosphorus hydrolase (OPH)	*opd*	*Pseudomonas diminuta*	Parathion	Mulbry et al. (1986)
	ophB	*Burkholderia* sp. JBA3		Kim et al. (2007)
	ophC2	*Stenotrophomonas* sp. SMSP-1	Methyl parathion	Shen et al. (2010)
	oph	*Arthrobacter* sp. B-5	Isofenphos	Ohshiro et al. (1999)
	opdE	*Enterobacter* sp.	Methyl parathion	Chino-Flores et al. (2012)
Methyl Parathion Hydrolase (MPH)	*mpd*	*Plesiomonas* sp. M6	Methyl parathion	Fu et al. (2004)
	mph	*Arthrobacter* sp. L1 (2006)	Methyl parathion	Parween et al. (2016); Ortiz-Hernández et al. (2013)
	mpdB	*Burkholderia cepacia*	Methyl parathion Paraoxon Parathion Fenitrothion	Ekkhunnatham et al. (2012)
Organophosphorus Acid Anhydrolase (OPAA)	*opa*A	*Alteromonas* sp. JD6.5	Cyclosarin (GF)	Harvey et al. (2005)
Organophosphates Degrading Agrobacterium (OPDA)	*opd*A	*Agrobacterium radiobacter* P230	Coumaphos Coroxon Diazinon Methyl parathion	Horne et al. (2002a)
Organophosphorus hydrolase (OpdB)	*opdB*	*Lactobacillus brevis* WCP902	Chlorpyrifos	Islam et al. (2010)
Aryldialkylphosphatase (ADPase)	*adp*B	*Nocardia* sp. B-1	Parathion Coumaphos	Mulbry (1992)
Hydrolysis of coroxon (HOCA)	*hoc*A	*Pseudomonas monteilii* C11	Coroxon	Horne et al. (2002b)
Phosphonate Ester Hydrolase (PEH)	*peh*A	*Burkholderia caryophylli* PG2982	Glyphosate	Dotson et al. (1996)
Phosphonatase	*phn*	*Bacillus cereus*	Phosphonate	Lee et al. (1992)
Isofenphos-Methyl Hydrolase (Imh)	*imh*	*Arthrobacter* sp. scl-2	Isofenphos-methyl Isofenphos Isocarbophos Butamifos	Li et al. (2012)
Carbofuran hydrolase	*mcd*	*Achromobacter* sp. WM11	Carbofuran	Tomasek and Karns (1989)

(continued)

Table 8.3 (continued)

Enzyme	Gene	Microbial species	Pesticide	Reference
Atrazine chlorohydrolase (AtzA) Hydroxy-atrazine ethylaminohydrolase (AtzB) *N*-isopropyl-ammelide isopropyl-amino-hydrolase (AtzC) Cyanuric acid amidohydrolase (AtzD) Biuret amidohydrolase (AtzE) Allophanate hydrolase (AtzF)	*atzABCDEF*	*Pseudomonas* sp. ADP	Atrazine	Sene et al. (2010)
Fungi				
P-OPH	P-*opd*	*Penicillium lilacinum*	Methyl parathion Parathion Paraoxon Coumaphos Demeton-S Phosmet Malathion	Liu et al. (2004)

8.4.1 Organophosphate Biodegradation Pathway

Organophosphates (OPs) are widely used as insecticide compounds in the agricultural industry to protect crops from different pests (Pinto et al. 2019; Santillan et al. 2020). Different bacteria with the capability of degrading organophosphate pesticides use them as energy, carbon, or phosphorous sources, as has been reported (Singh 2009). In such bacteria, the organophosphate pesticide biodegradation process has been related to the expression of hydrolytic enzymes, denominated as organophosphorus hydrolases (OPH) or phosphotriesterases. These enzymes are encoded in the *opd* gene, a highly conserved sequence in bacteria (El-Sayed et al. 2018). Another important organophosphate pesticide degrading enzyme is methyl parathion hydrolase (MPH), a phosphotriesterase encoded by the *mpd* gene that catalyzes the methyl parathion hydrolysis to yield *p*-nitrophenol (PNP) and dimethylthiophosphoric acid (Bara et al. 2017). Subsequently, PNP is degraded through two oxidative pathways: the Hydroquinone pathway, used mainly by Gram-negative bacteria such as *Moraxella* sp., *Pseudomonas putida* DLL-E4, and *Pseudomonas* sp. WBC-3 (Chen et al. 2016), and the Hydroxyquinol pathway in Gram-positive bacteria, *Bacillus sphaericus* JS905 and *Rhodococcus opacus* SAO101 (Zhang et al. 2012). However, some bacteria such as *Burkholderia cenocepacia* CEIB S5-2 (Ortiz-Hernández et al. 2021), *Burkholderia zhejiangensis* CEIB S4-3 (Castrejón-Godínez et al. 2019), and *Serratia* sp. strain DS001 (Pakala et al. 2007) can biodegrade PNP employing both metabolic pathways (Fig. 8.1).

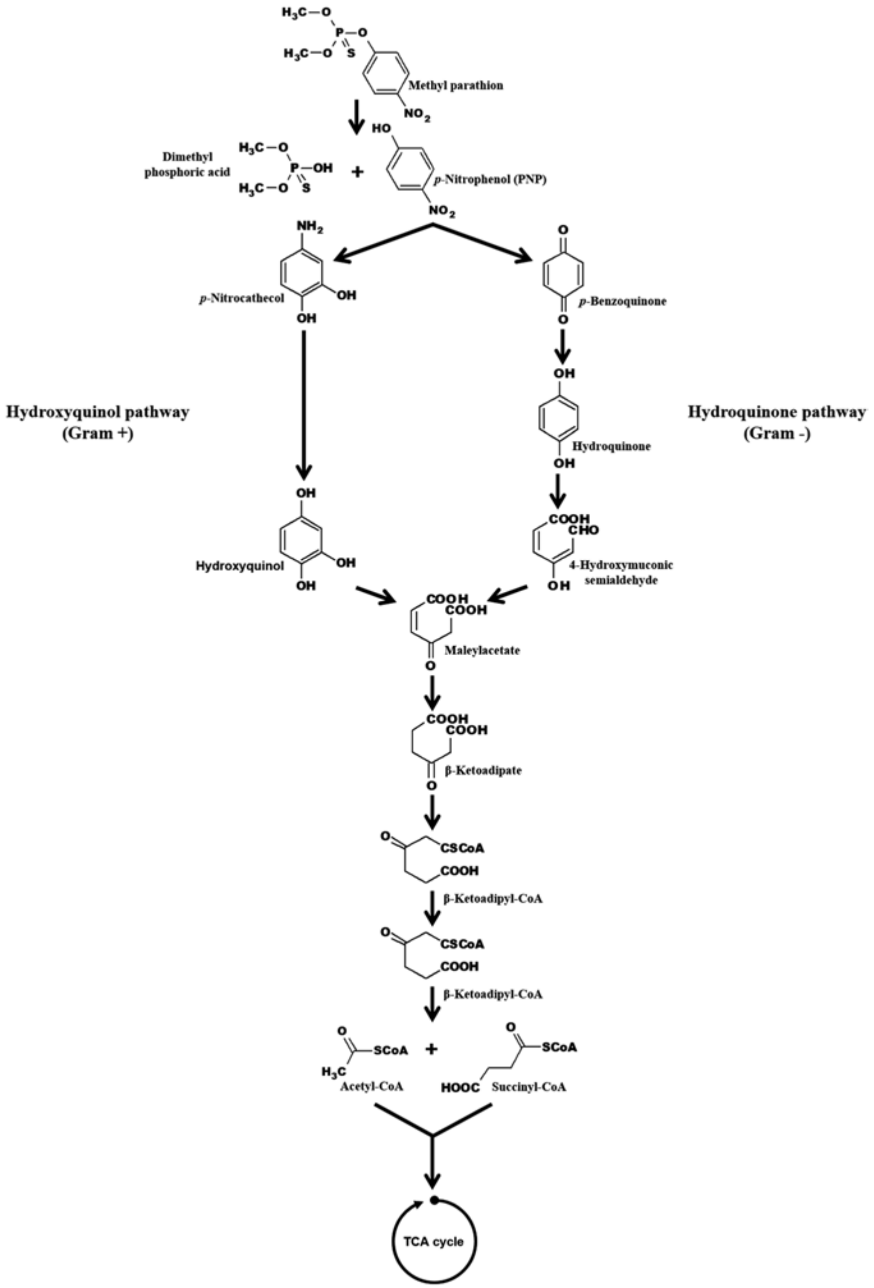


Fig. 8.1 Biodegradation Methyl parathion pathways

8.4.2 Carbaryl Degradation Pathway

Another example of a pesticide biodegradation pathway is carbaryl (1-naphthyl-*N*-methylcarbamate), an *N*-methylcarbamate class chemical insecticide broadly used in agriculture to control pests. The intensive and widespread use of carbaryl causes pollution in soil and groundwater, as well as adversely affecting plants, animals, and humans (Siampiringue et al. 2015). Different microorganisms have been reported with the capability of biodegrading carbaryl (Doddamani and Ninnekar 2001; Hamada et al. 2015; Li et al. 2019). Swetha and Phale (2005) reported the metabolic pathway for carbaryl mineralization in *Pseudomonas* sp. strains C4, C5, and C6. In carbaryl biodegradation, the first step is carbaryl hydrolysis that renders 1-naphthol and methylamine as main products. 1-naphthol is then conducted for its degradation to the intermediate metabolism via the naphthalene pathway, to produce salicylate and gentisate and finally to the TCA cycle, while methylamine is metabolized via the glyphosate pathway (Fig. 8.2). The carbaryl mineralization includes the catabolic activity of several enzymes, the first is the metabolic process carbaryl hydrolase, codified by the *mcbA* gene (Trivedi et al. 2016).

8.5 Applications of the OMICs in Pesticides Bioremediation

Bioremediation has a high potential for the effective treatment and restoration of polluted environments (Bharagava et al. 2017; Pande et al. 2020; Skinder et al. 2020). This environmental remediation approach is based on the isolation, identification, and characterization of microorganisms capable of efficiently degrading different xenobiotic compounds. These microorganisms are commonly native to polluted sites (Watanabe 2001; Singh et al. 2014). However, microorganisms characterized with great bioremediation potential can fail in the complete pollutant biodegradation in the field, or their use is not suitable for the treatment of contaminated sites with the presence of a complex mixture of pollutants (Rayu et al. 2012; Dangi et al. 2018). Due to this, for successful bioremediation implementation, it is crucial to determine the factors implicated in the regulation of growth, resistance, and metabolic capabilities employed for such microorganisms to deal with xenobiotics (Singh and Nagaraj 2006). Recently, the application of the OMIC approaches has taken on great relevance in bioremediation to bring information to solve these kinds of questions (Rawat and Rangarajan 2019). OMIC research comes from the development of technologies for genome sequencing but now, this term includes a set of research tools such as genomics (genes), transcriptomics (mRNA), proteomics (proteins), and metabolomics (small chemical compounds). The conjunction of these tools permits the integrative study of a biological system capable of pollutant biodegradation at impacted sites (Chakraborty et al. 2012). Therefore, research in pesticide bioremediation can take advantage of these novel technologies for the design of effective remediation strategies (Rana et al. 2019). Furthermore, these approaches

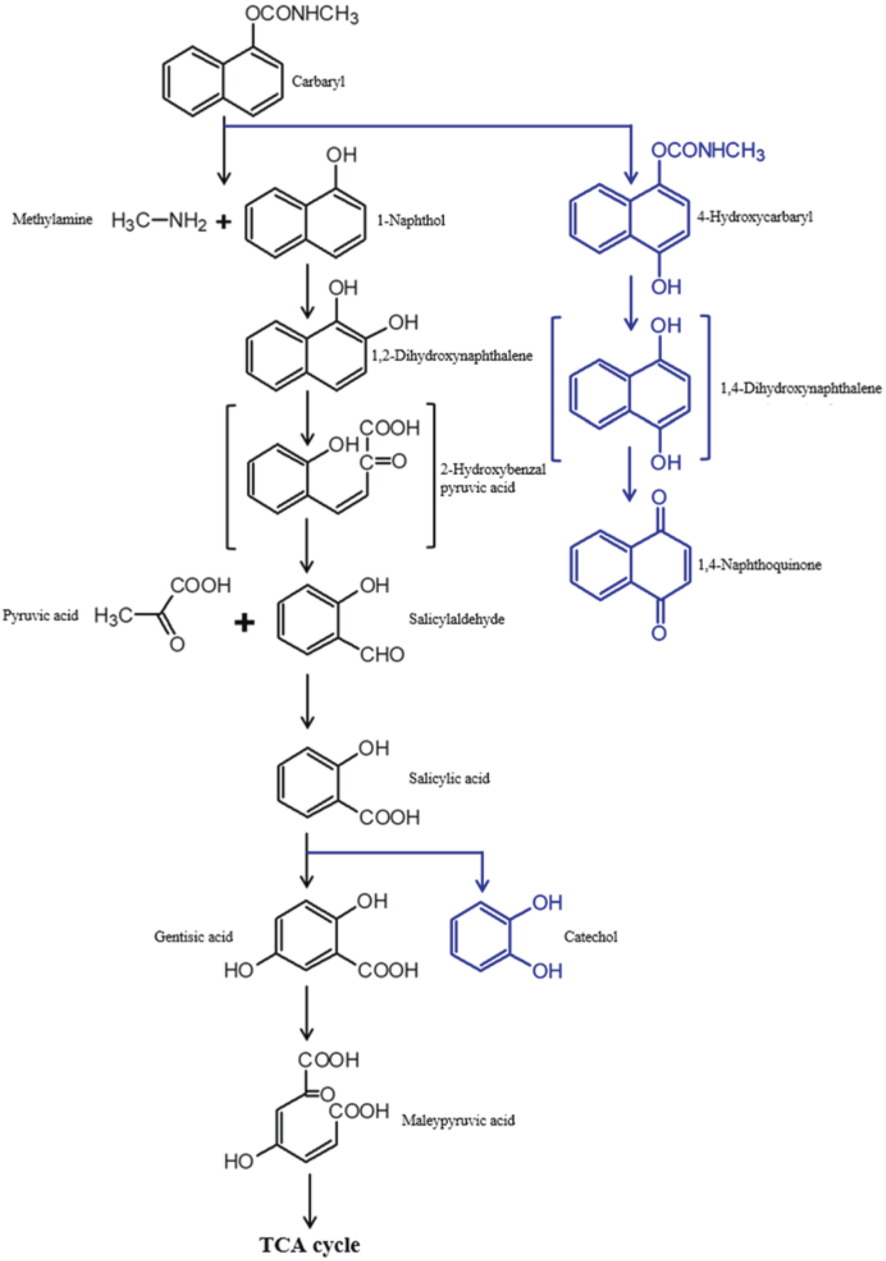


Fig. 8.2 Biodegradation pathway of carbaryl. Black structures, canonical pathway of carbaryl biodegradation by *Pseudomonas* sp. C4, C5, and C6. Blue structures correspond to metabolites identified during biodegradation of carbaryl by *Burkholderia* sp. C3

permit the integration of the information related to the pesticide biodegrading genes and enzymes and the metabolites generated through their degradation or produced in response to the pesticide exposition. Recent studies on the application of these technologies in pesticide bioremediation are described below.

8.5.1 Genomics

The pesticide degrading capabilities of several microorganisms have been reported (Abatenh et al. 2017; Endeshaw et al. 2017; Parte et al. 2017; Nayak et al. 2018; Sun et al. 2020). The bioremediation potential of most of these microorganisms has been characterized in pure cultures in the laboratory. However, the identification and characterization of the key genes, enzymes, and catabolic pathways implicated in pollutant biodegradation in such microorganisms are considered to be a time-consuming process. The determination of the genomes of pesticide degrading microorganisms can accelerate the identification of the crucial catabolic genes that mediate the biodegradation of different pesticides (Kapley and Purohit 2009; Iyer et al. 2018; Castro-Gutiérrez et al. 2020; Lee and Kalia 2020). Table 8.4 shows examples of available genomes of microorganisms capable of degrading pesticides, most of them published in the last five years (2016–2021), highlighting the increasing relevance of this research approach in pesticide bioremediation. According to the available genomic information, Gram-negative bacteria are the most studied microorganisms in pesticide biodegradation. The most relevant bacterial genera reported included *Burkholderia*, *Pseudomonas*, *Ochrobactrum*, *Sphingobium*, and *Sphingomonas*. The genome analysis permits the identification of the structural genes that coded for the main enzymes implicated in the pesticide biodegradation pathway and gene sequences implicated in regulating the response to pesticide exposition (Ortiz-Hernández et al. 2013). Different authors have proposed that the genes for pesticide biodegradation identified in genomics studies could be cloned through recombinant ADN technologies, and their coding enzymes subsequently produced in heterologous systems for application in microbial bioremediation strategies (Johri et al. 1996; Kulshreshtha 2013; Jaiswal et al. 2019; Mir et al. 2020).

The number of available genomes of microorganisms capable of biodegrading pesticides has increased in the last few years. However, there is an unbalance between the reports of pesticide degrading microbial species and the number of genomes of microorganisms with pesticide degrading capabilities deposited in databases. Moreover, most genomic studies have been carried out on a limited number of bacterial species, and the more studied pesticides belong to organochlorines and organophosphorus families. As a result, more genomic studies are necessary, especially in the genome sequencing of novel pesticide degrading bacterial and fungal species and the inclusion of a more significant number of pesticide families in the studies.

Table 8.4 Available genomes of pesticide degrading microorganism

Pesticide family	Pesticide/chemical	Microorganism	Bioproject ID	Reference
Acetanilide	Propanil	*Spirosoma sordidisoli* TY50	PRJNA514978	Zhang et al. (2019a)
Anilinopyrimidine	Cyprodinil	*Acinetobacter johnsonii* LXL_C1	PRJNA480925	Wang et al. (2019b)
Benzamidazole	Carbendazim	*Rhodococcus* sp. CX1	PRJNA636212	Long et al. (2021)
Carbamates	Carbaryl	*Pseudomonas putida* XWY-1	PRJNA224116	Zhu et al. (2019)
Neonicotinoid	Acetamiprid	*Pigmentiphaga* sp. D-2	PRJNA524485	Yang et al. (2020)
	Paichongding	*Sphingobacterium* sp. G1-14	PRJNA387067	Yin et al. (2019)
Nitrophenols	*p*-Nitrophenol	*Burkholderia* sp. SJ98	PRJNA81431	Kumar et al. (2012)
		Pseudomonas putida DLL-E4	PRJNA244741	Hu et al. (2014b)
		Rhodococcus sp. BUPNP1	PRJNA383111	Sengupta et al. (2019a)
Organochlorine	Alachlor	*Micrococcus luteus* 2385	PRJNA265206	Pathak et al. (2016)
	Endosulfan	*Pseudomonas strain* W15Feb9B	PRJNA265207	Chauhan et al. (2016)
	DDT	*Ochrobactrum* sp. DDT-2	PRJNA296453	Pan et al. (2017)
		Stenotrophomonas sp. DDT-1	PRJNA286061	Pan et al. (2016)
	Lindane	*Pseudomonas aeruginosa* MTB-1	PRJNA225944	Ohtsubo et al. (2014a)
		Pseudomonas sp. TKP	PRJNA225946	Ohtsubo et al. (2014b)
		Sphingobium japonicum UT26	PRJDA19949	Nagata et al. (2010)
		Sphingomonas sp. MM-1	PRJNA185470	Tabata et al. (2013)
		Sphingobium sp. MI1205	PRJNA196450	Tabata et al. (2016a)
		Sphingobium sp. TKS	PRJNA195946	Tabata et al. (2016b)
	Pentachlorophenol	*Sphingobium chlorophenolicum* L-1	PRJNA50015	Copley et al. (2011)
		Sphingobium fuliginis ATTC 27551	PRJNA548252	Azam et al. (2019)

Pesticide family	Pesticide/chemical	Microorganism	Bioproject ID	Reference
Organophosphorus	Chlorpyrifos	*Cupriavidus nantongensis* X1	PRJNA315593	Fang et al. (2016)
		Enterobacter cloacae MR2	PRJNA195541	Parakhia et al. (2019)
		Ochrobactrum sp. CPD-03	PRJNA478098	Nayak et al. (2020)
		Paracoccus sp. TRP	PRJNA60841	Li et al. (2011)
		Pseudomonas putida JR16	PRJNA453848	Rank et al. (2018)
		Sphingomonas paucimobilis AIMST S2	PRJNA478628	Ravintheran et al. (2019)
	Chlorpyrifos Methyl parathion Parathion Triazophos	*Pseudomonas stutzeri* strain YC-YH1	PRJNA268715	Shi et al. (2015)
	Ethyl paraoxon	*Achromobacter xylosoxidans* ADAF13	PRJNA311337	Iyer et al. (2018)
		Ochrobactrum anthropi FRAF13	PRJNA312205	Iyer and Damania (2016)
		Pseudomonas putida CBF10-2	PRJNA312605	Iyer et al. (2018)
		Pseudomonas stutzeri ODKF13	PRJNA312382	Iyer et al. (2018)
	Ethyl paraoxon	*Rhizobium radiobacter* GHKF11	PRJNA312606	Iyer et al. (2018)
		Stenotrophomonas maltophilia CBF10-1	PRJNA312840	Iyer et al. (2018)
	Fenamiphos	*Microbacterium esteraromaticum* MM1	PRJNA377799	Panneerselvan et al. (2018)
	Fenitrothion	*Burkholderia* sp. *strain* YI23	PRJNA74517	Lim et al. (2012)
	Glyphosate	*Enterobacter* sp. E20	PRJNA263377	Cao et al. (2019b)
	Methyl parathion	*Burkholderia* sp. *strain* MP-1	PRJNA238425	Liu et al. (2014)
		Burkholderia cenocepacia CEIB S5-1	PRJNA268776	Martínez-Ocampo et al. (2015)
		Burkholderia cenocepacia CEIB S5-2	PRJNA301637	Martínez-Ocampo et al. (2016)
		Burkholderia zhejiangensis CEIB S4-3	PRJNA264584	Hernández-Mendoza et al. (2014)
		Pseudomonas putida MR3	PRJNA195540	Parakhia et al. (2014)
	Phorate	*Brevibacterium frigoritolerans* GD44	PRJNA528841	Jin et al. (2020)
	Phoxim	*Bacillus amyloliquefaciens* YP6	PRJNA488691	Meng et al. (2019a)
		Brevibacterium frigoritolerans GD44	PRJNA224116	Jin et al. (2020)

(continued)

Table 8.4 (continued)

Pesticide family	Pesticide/chemical	Microorganism	Bioproject ID	Reference
Phenylureas	Linuron	*Variovorax* sp. WDL1	PRJNA394818	Albers et al. (2018a)
		Variovorax sp. WDL1	PRJNA394818	Albers et al. (2018b)
Pyrethroid	Cypermethrin	*Pseudomonas* sp. MS15a	PRJNA514341	Aguila-Torres et al. (2020)
		Pseudomonas sp. MS19	PRJNA514341	Aguila-Torres et al. (2020)
		Rhodococcus sp. MS13	PRJNA514341	Aguila-Torres et al. (2020)
		Rhodococcus sp. MS16	PRJNA514341	Aguila-Torres et al. (2020)
Triazines	Atrazine	*Arthrobacter* sp. ZXY-2	PRJNA341911	Zhao et al. (2017)
Triazols	Difenoconazole	*Sphingomonas histidinilytica* C8-2	PRJNA507494	Heo et al. (2019)

8.5.2 Metagenomics

There is a great diversity of different classes of microorganisms in natural and polluted environments, most of which are uncultivable in laboratory conditions (Tringe and Rubin 2005). It has been reported that 99% of microorganisms are uncultivable in the laboratory due to the limitations of culture (Kirk et al. 2004; Ortiz-Hernández et al. 2011; Bodor et al. 2020). In this context, the application of genomic approaches permits the discovery of novel microorganisms with potential for remediation processes, avoiding the limitations of the pure-culture based research methodologies.

Metagenomics, also known as community genomics, environmental genomics, microbial ecogenomics, or population genomics (Panigrahi et al. 2019), is another emerging approach in bioremediation (George et al. 2010; Bell et al. 2015; Techtmann and Hazen 2016). Metagenomics analysis involves isolation of microbial DNA directly from an environmental sample such as soil, water, sediments, among other elements (Hugenholtz and Tyson 2008), avoiding the need for cultivating the microorganisms (Handelsman 2004; Stefani et al. 2015; Kumar et al. 2020; Mani 2020). The environmentally isolated DNA could be directly sequenced to determine the composition of the microbial community present in polluted sites through the use of phylogenetic markers such as the genes 16S rRNA and *rec*A, or identification of gene sequences related to enzymatic activities through a sequence based screening (Paul et al. 2006; Datta et al. 2020; Sharma et al. 2020). Furthermore, DNA isolated from polluted environments could be cloned into a suitable vector and introduce the genetic information into a well-characterized organism capable of growing in laboratory conditions. Subsequently, transformed clones are selected through functional screening to identify genes that codify for enzymes of interest for bioremediation purposes (Devarapalli and Kumavath 2015). The metagenomics analysis (Fig. 8.3) has been used for the identification of microorganisms unable to grow under laboratory conditions. Therefore, it allows the evaluation of the

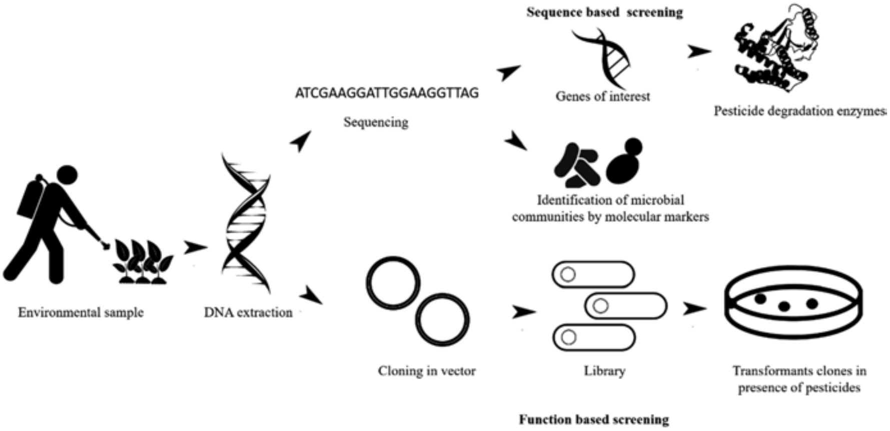


Fig. 8.3 General methodology of metagenomics

functional diversity of microorganisms present in contaminated sites, and also permits the investigation of diverse genes and metabolic pathways, unknown or poorly characterized, involved in the degradation of xenobiotics such as pesticides (Silva et al. 2013; Bashir et al. 2014; Jeffries et al. 2018; Pande et al. 2020; Sun et al. 2020).

The information about the enzymes and metabolic pathways identified is useful for the design of customized microbial strains or microbial consortia for specific applications in bioremediation (Dangi et al. 2018; Bharagava et al. 2019; Jayaraman et al. 2019). Recently, metagenomics studies have taken on relevance in the field of pesticide bioremediation. In Table 8.5, examples of the application of metagenomics in environments polluted by pesticides are shown. Through the metagenomics studies, it is possible to evaluate the microbial diversity of pesticides polluted sites (soil, water, sediments) and identify genes that encode for novel and promising enzymes implicated in pesticide biodegradation processes. Metagenomics studies in the field of pesticide bioremediation have been focused on the evaluation of microbial diversity present in pesticide polluted sites. However, studies for bioprospecting novel pesticide degrading enzymes are limited. It is important that future metagenomics studies also include the search of pesticide degrading enzymes and their biochemical characterization. As mentioned above, metagenomics is an emerging research approach in pesticide bioremediation. The number of studies is still low and, most of them are carried out in China and India. However, since there are many pesticide polluted areas around the world, the bioremediation of such pollution requires the identification and characterization of microorganisms capable of degrading pesticides, adapted to the environmental conditions of the polluted sites. The metagenomics approach could certainly help in solving this task.

8.5.3 Transcriptomics

The transcriptome is defined as the whole set of transcribed genes in an organism (Singh and Nagaraj 2006). The transcriptome analysis involves different steps, beginning with the isolation and enrichment of cellular mRNA, followed by a cDNA library synthesis. Subsequently, sequencing of complete cDNA is carried out, and the gene sequences are finally analyzed through different bioinformatic tools for functional analysis (Dangi et al. 2018).

To date, several tools for the detection of mRNAs and their expression levels are available for transcriptomic studies. The first method applied for evaluation of gene expression was low-throughput Sanger sequencing, followed by the northern blotting methodology (Alwine et al. 1977), which was performed several decades before any transcriptomics approaches were available. Subsequently, the reverse transcriptase enzyme discovery allowed the synthesis of complementary DNA by the use of mRNA as a template. The application of reverse transcriptase allowed researchers to develop new strategies for the evaluation of the transcriptional profiles in biological samples, such as hybridization (DNA microarrays), quantitative real-time PCR (qRT-PCR) and deep-sequencing technologies, such as RNA sequencing

Table 8.5 Metagenomics studies in samples from pesticide polluted environments

Pesticide family	Pesticide	Sample	Location	Microorganisms	Reference
Organophosphorus	Parathion and methyl parathion	Soil agricultural	India	Proteobacteria, Actinomycetes	Paul et al. (2006)
	Chlorpyrifos	Soil	Queensland Australia	*Candidatus Koribacter*, *Hyphomicrobium*, *Burkholderia*	Jeffries et al. (2018)
Organochlorine	Hexachlorocyclohexane (lindano), Dichlorodiphenyltrichloroethane (DDT), Dichlorodiphenyldichloroethane (DDD), and Dichlorodiphenyldichloroethylene (DDE)	Soil	South, Central and North India	*Desulfuromonas michiganensis*, *Acetonema longum, and Flavobacteriaceae*	Manickam et al. (2010)
	Hexachlorocyclohexane (lindano)	Soil HCH dumpsite	Ummari village, Lucknow, India	*Chromohalobacter*, *Marinimicrobium*, *Idiomarina*, *Salinosphaera*, *Halomonas*, *Sphingopyxis*, *Novosphingobium*, *Sphingomonas* *Pseudomonas*, *Halobacterium*, *Haloarcula*, *Halorhabdus*, *and Fusarium*	Sangwan et al. (2012)
	Dichlorodiphenyltrichloroethane (DDT) Hexachlorocyclohexane (HCH)	Freshwater and marine sediments	Hong Kong and China	*Plesiocystis*, *Anaerolinea*, *Jannaschia*, and *Mycobacterium*	Fang et al. (2014)
	Hexachlorocyclohexane (lindano)	Soil	Umari village, Lucknow, India	*Sphingobium*	Sangwan et al. (2014)

(continued)

Table 8.5 (continued)

Pesticide family	Pesticide	Sample	Location	Microorganisms	Reference
	Chlordecone	Soils, sediments, and sludge	France	Bacterial consortia and *Citrobacter*	Chaussonnerie et al. (2016)
	Hexachlorocyclohexane (lindano)	Sediment	Chinhat village in Lucknow, India	*Mycobacterium*, *Corynebacterium*, *Rhodococcus*, *Bradyrhizobium*, *Sorangium*, *Thauera*, *Methylibium*, *Candidatus*, *Anaeromyxobacter*, *Streptomyces*, and *Burkholderia*	Negi and Lal (2017)
	Dichlorodiphenyltrichloroethane (DDT), Dichlorodiphenyldichloroethane (DDD), and Dichlorodiphenyldichloroethylene (DDE) Endosulfan	Soil	India	*Proteobacteria*, *Actinobacteria*, *Firmicutes*, *Acidobacteria, and Bacteroidetes*	Regar et al. (2019)
Pesticide mixture		Activated sludge	Shandong, China	*Thauera*, *Stenotrophomonas*, *Mycobacterium*, *Hyphomicrobium*, *Allochromatium*	Fang et al. (2018)
Triazine	Atrazine (ATZ)	Freshwater and marine sediments	Hong Kong and China	*Plesiocystis*, *Anaerolinea*, *Jannaschia*, and *Mycobacterium*	Fang et al. (2014)
		Soil	India	*Achromobacter*, *Xanthomonas*, *Stenotrophomonas*, and *Cupriavidus*	Bhardwaj et al. (2020)

Pesticide family	Pesticide	Sample	Location	Microorganisms	Reference
Pesticide mixture	Trifloxystrobin + Tebuconazole, Zeta-cypermethrin, Metsulfuron-methyl, Bentazone salt, Saflufenacil, Penoxsulam, and Pyrazosulfuron-ethyl	Soil, water and sediment	Brazil	*Bacillus* sp., *Shingobacterium* sp., *Sphingobium* sp., *Megasphaera* sp., *Ralstonia* sp., *Sphingopyxis* sp.	Serbent et al. (2021)
Neonicotinoid	Thiamethoxam	Farmland soils	Beijing and Heilongjiang, China	*Rhodococcus*, *Azohydromonas*, *Ramlibacter*, *Variovorax*, *Mycobacterium*, *others*	Wu et al. (2020)

(RNA-seq). These latest techniques are currently the most used since 2008, particularly the Solexa and Illumina technologies, which provide high coverage and excellent resolution of the transcriptome's dynamic nature (Kukurba and Montgomery 2015; Lowe et al. 2017; Chandran et al. 2020).

Environmental pollutants such as pesticides induce the regulation of the gene expression in microorganisms for adaptation and resistance to adverse effects generated by pesticide exposure. This process is related to the degradation and mineralization of pesticides, and it involves cellular physical and chemical signals (Cao et al. 2019a). Cell receptors detect these signals in bacteria and fungi to facilitate pesticide passage through the membrane. The pesticide presence induces modification in the gene expression patterns, a process known as transcriptional regulation.

Transcriptomic analysis has enabled the analysis of gene expression changes in microorganisms in response (degradation or tolerance) to pesticides. In Table 8.6, transcriptomics studies focused on evaluating microorganism response to pesticide exposure are shown. These studies have been carried out in several bacterial and fungi strains. According to the studies, the use of *Escherichia coli* stands out as a model for evaluating the adverse effect of pesticide exposition at the transcriptome level. On the other hand, transcriptomic studies in pesticide degrading bacterial strains, such as the Gram-negative *Burkholderia thailandensis*, *B. zhejiangensis*, *Klebsiella jilinsis*, *K. pneumoniae*, *Pseudomonas aeruginosa*, and *P. putida*, as well as the Gram-positive *Rhodococcus erythropolis*, allowed the identification of the genetic mechanism employed by such bacteria to sense, degrade, and resist pesticides. The response to pesticide exposition in fungi such as the yeast *Saccharomyces cerevisiae* or the filamentous fungi *Aspergillus nidulans*, *Penicillium digitatum*, *P. italicum*, *Trichoderma asperellum*, and *T. atroviride* has been evaluated through transcriptomic approaches.

As a result of the transcriptional analysis in microorganisms, it is possible to identify the genes that encode to key enzymes implicated in the pesticide biodegradation processes and the molecular strategies that they employ to counteract the adverse effects of pesticide exposure, all of which is important information for the establishment of successful bioremediation strategies. However, the transcriptomic studies related to pesticide biodegradation in bacteria and fungi strains are still very few, evidencing the need to increase the research in the transcriptomics field and the number of microorganisms and pesticides molecules studied through this approach.

8.5.4 Proteomics

In organisms, the phenotypic characteristics are defined by the expression and the functionalities of different proteins (Singh 2006; Chandran et al. 2020). Around three decades ago, Marc Wilkins first introduced the term proteome to depict the set of proteins expressed by a given organism (Williams and Hochstrasser 1997; Mishra 2010). Subsequently, the concept of proteome evolved to describe all proteins expressed in a biological sample, their isoforms and modifications, the interactions

Table 8.6 Transcriptomic studies in pesticide exposure and biodegradation

Pesticide family	Pesticide	Microorganism	Reference
Bacteria			
Avermectin	Benzene	Microbial consortia	Luo et al. (2014)
	Benzoate	Microbial consortia	Luo et al. (2014)
Azoic fungicide	Carbendazim	*Rhodococcus* sp. CX-1	Long et al. (2021)
Bipyridyls	Paraquat	*Escherichia coli* O157:H7	Allen and Griffiths (2012)
		Klebsiella pneumoniae CG43	Huang et al. (2013)
		Mycobacterium tuberculosis	Namouchi et al. (2016)
Nitrophenol	*p*-Nitrophenol (PNP)	*Escherichia coli*	Chakka et al. (2015)
		Pseudomonas putida DLL-E4	Chen et al. (2016)
Organochlorine	2,4 D	Microbial communities	Dennis et al. (2003)
	Chlorimuron-ethyl	*Rhodococcus erythropolis* D310-1	Cheng et al. (2018)
	Pentachlorophenol	*Pseudomonas aeruginosa*	Muller et al. (2007)
Organophosphorus	Chlorpyrifos	*Escherichia coli* (DE3)	Aswathi et al. (2020)
	Glyphosate	*Burkholderia thailandensis*	Kang et al. (2011)
		Escherichia coli	Li et al. (2015)
		Escherichia coli K12	Lu et al. (2013)
		Enterobacter sp. NRS1	Fei et al. (2013)
	Methyl parathion	*Burkholderia zhejiangensis* CEIB S4-3	Castrejón-Godínez et al. (2019)
	Phoxin	*Bacillus amyloliquefaciens* YP6	Meng et al. (2019b)
Ortho-phenylphenate	*Ortho*-phenylphenol	*Sphingomonas haloaromaticamans* P3	Perruchon et al. (2017)
		Pseudomonas aeruginosa	Nde et al. (2008)
		Staphylococcus aureus	Jang et al. (2008)
Phenyl urea	Linuron	Microbial consortia	Albers et al. (2018b)
Sulfonylurea herbicide	Chlorimuron-ethyl	*Klebsiella jilinsis* 2N3	Zhang et al. (2019b)
Fungi			
Anilinopyrimidines	Pyrimethanil	*Saccharomyces cerevisiae*	Gil et al. (2018)

(continued)

Table 8.6 (continued)

Pesticide family	Pesticide	Microorganism	Reference
Azole fungicides	Prochloraz	*Penicillium digitatum*	Liu et al. (2015)
		Penicillium italicum	Zhang et al. (2020a)
Carbamates	Carbofuran	*Saccharomyces cerevisiae*	Gil et al. (2018)
Chloroacetanilides	Alachlor	*Saccharomyces cerevisiae*	Gil et al. (2011)
	S-metolachlor	*Saccharomyces cerevisiae*	Gil et al. (2018)
Phenylamide	Diuron	*Saccharomyces cerevisiae*	Gil et al. (2018)
Organochlorine	MCPA	*Saccharomyces cerevisiae*	Gil et al. (2018)
	Prochloraz	*Penicillium digitatum*	Liu et al. (2015)
Organophosphorus	Dichlorvos	*Trichoderma atroviride* T23	Zhang et al. (2015)
		Trichoderma asperellum TJ01	Wu et al. (2018)
	Glyphosate based herbicides	*Aspergillus nidulans*	Mesnage et al. (2020)

2,4 D 2,4-dichlorophenoxyacetic acid; *MCPA* 2-methyl-4-chlorophenoxyacetic acid

between them, their structural information, and their higher-order complexes (Tyers and Mann 2003). For large-scale protein analysis, proteomics research has integrated innovations and technologies such as two-dimensional gel electrophoresis (2D-GE), protein arrays, label-free quantification mass spectrometry, isobaric tags for relative and absolute quantitation (iTRAQ) mass spectrometry, X-ray crystallography, and nuclear magnetic resonance (NMR), for identifying differential expression and providing three-dimensional structure of proteins (Aslam et al. 2017; Sui et al. 2018). In the field of environmental sciences, proteomics has taken on relevance in the identification of catalytic proteins implicated in the biodegradation metabolic pathways of different pollutants, including heavy metals, hydrocarbons, and pesticides, in bioremediation approaches, as well as in the evaluation of the microbial resistance and response to the adverse effects derived from xenobiotics exposition (Tang et al. 2010; Seo et al. 2013; Vandera et al. 2015; Festa et al. 2017; Liu et al. 2017; Wei et al. 2017; Rawat and Rangarajan 2019). In the last few years, several proteomics studies related to pesticide bioremediation have been published (Table 8.7). These reports describe the application of proteomics in the elucidation of the degradation pathways for several pesticides belonging to different chemical families, with organophosphorus, organochlorines, and carbamates as the most relevant, as well as the protein-based response to the presence of these pesticides. Most proteomic studies have been carried out in bacteria. However, yeast such as *Saccharomyces cerevisiae* and filamentous fungi, such as *Trichoderma atroviride*, have also been reported. The application of proteomics approaches in the pesticide bioremediation research is becoming increasingly relevant. Most proteomic studies have been carried out in vitro; however, in situ application of proteomics approaches for monitoring the microbial activities at the polluted sites still has technical and methodological drawbacks to address for successful implementation.

Table 8.7 Proteomics studies in degradation of the pesticides

Pesticide family	Pesticide	Microorganisms	Reference
Organophosphorus	Dichlorvos	*Trichoderma atroviride*	Tang et al. (2010)
	Methyl parathion	*Fischerella* sp.	Tiwari et al. (2018)
	Chlorpyrifos	*Achromobacter* sp. C1	Briceño et al. (2020)
	Triazophos, methamidophos	*Enterobacter* sp. Z1	Zhang et al. (2020b)
	Chlorpyrifos	*Pseudomonas nitroreducens* AR-3	Aswathi et al. (2021)
Organochloride	Hexachlorobenzene	*Dehalococcoides mccartyi* CBDB1	Schiffmann et al. (2014)
	1,2,3,4,5,6-Hexachlorocyclohexane (HCH)	*Streptomyces* sp. M7	Sineli et al. (2018)
	Pentachlorophenol (PCP)	*Rhizopus oryzae* ENHE	Ruiz-Lara et al. (2020)
Carbamate	Aminocarb, bendiocarb, bufencarb, carbaryl, carbofuran, methiocarb, mexacarbate, pirimicarb, propoxur, xylylcarb	*Burkholderia* sp. C3	Seo et al. (2013)
	Carbofuran	*Enterobacter* sp. Z1	Zhang et al. (2020b)
Chloroacetanilide	Alachlor	*Paecilomyces marquandii*	Szewczyk et al. (2015)
	Butachlor	*Pseudomonas putida* ER1	Wagner et al. (2017)
Conazole	Tetraconazole	*Saccharomyces cerevisiae*	Sieiro-Sampedro et al. (2020)
		Saccharomyces cerevisiae T73	Briz-Cid et al. (2020)
Dicarboximide	Iprodione (IPR)	*Pseudomonas* sp. C9	Briceño et al. (2020)
Neonicotinoid	Acetamiprid	*Ensifer adhaerens* CGMCC 6315	Sun et al. (2018)
Nitrophenols	*p*-Nitrophenol	*Escherichia coli*	Chakka et al. (2015)
		Rhodococcus sp.	Sengupta et al. (2019b)
Organotin	Triphenyltin	*Escherichia coli* pET32a-CYP450	Yi et al. (2017)
Ortho-phenylphenate	*Ortho*-phenylphenol	*Sphingomonas haloaromaticamans* P3	Perruchon et al. (2017)

(continued)

Table 8.7 (continued)

Pesticide family	Pesticide	Microorganisms	Reference
Pyrethroid	Cypermethrin	*Bacillus thuringiensis* strain SG4	Pankaj et al. (2016)
	Deltamethrin	*Bacillus thuringiensis*	Guo et al. (2020)
Quinoline carboxylic acid	Quinclorac	*Burkholderia cepacia* WZ1	Negi et al. (2016)
Substituted ureas	Linuron	*Variovorax* sp. WDL1	Breugelmans et al. (2010)
Sulfonylurea herbicide	Pyrazosulfuron-ethyl	*Rhodopseudomonas palustris* PSB-S	Luo et al. (2018)
Triketone	Mesotrione	*Bacillus megaterium*	Bardot et al. (2015)
Triazine	Desethylatrazine (DEA) and desisopropylatrazine (DIA)	*Pleurotus ostreatus* INCQS 40310	Lopes et al. (2020)

8.5.5 Metabolomics

Metabolomics is a research field focused on the global analyses of the thousands of low-mass primary and secondary metabolites present in an organism (Rochfort 2005; Hernandez-Soriano and Jimenez-Lopez 2014; Muthubharathi et al. 2021). In metabolism, small molecules are intermediate or end products from the enzymatic reactions. The presence or absence, as well as concentration levels of these metabolites, reflex the metabolic state of an organism under a given condition (Alonso et al. 2015; Van Emon 2016). Different technologies, such as including gas chromatography, mass spectrometry, and nuclear magnetic resonance, have been employed for metabolite identification and quantification (Moco et al. 2007; Viant and Sommer 2013). The information generated from these experimental technologies is analyzed with the help of different bioinformatic tools (Blaženović et al. 2018). In environmental sciences, metabolomic studies have been directed to evaluate the presence, absence, or concentration changes in different small chemical compounds, mainly those associated with the organism xenobiotic exposure. The concentration levels of these small chemicals could give information about the cellular metabolic state in response to changes in the environmental conditions caused by pollutants (Aliferis and Chrysayi-Tokousbalides 2011).

Pesticide exposure may cause several adverse effects on microorganisms. Different kinds of small metabolites are produced as a cellular response to this exposure, while others reduce their cellular concentrations (Villas-Bôas and Bruheim 2007). The identification of such metabolites may lead to understanding the metabolic response of these microorganisms, and the mechanisms employed to fight with the stress generated by the exposure to these toxic chemicals. Furthermore, the identification of the metabolites derived from the pesticide biodegradation through metabolomics generates information with multiple applications, such as the elucidation of the metabolic pathways implicated in the pesticide degradation processes, ecotoxicological studies focused on environmental biomonitoring through the identification of exposure biomarkers, the safety of agricultural products, and the discovery of novel pesticides, with reduced toxicity on non-target organisms, or more effective in the control of the resistant pest (Lin et al. 2006; Kikuchi et al. 2018; Kovacevic and Simpson 2020). In Table 8.8 recent metabolomics studies related to pesticide bioremediation are listed. These studies address the identification of novel pesticide degradation derived metabolites and the microbial response from toxic effects generated by pesticide in microorganisms, such as fungi and bacteria, important knowledge for the improvement of bioremediation strategies. In the near future, the application of the findings of metabolomics studies could help to develop efficient pesticide polluted sites bioremediation processes.

8.6 Future Prospects

Intensive agricultural practices for human and animal consumption have caused a negative impact on the environment. The constant release of different pesticides is related to severe pollution in soil, water, and air, threatening flora, fauna, and human health. Hence it is necessary to apply reliable and cost-effective strategies to remediate pesticide polluted sites. One of the more promising proposed strategies involves the use of the catalytic capacities of different microorganisms to biodegrade or remove pesticides from the environment. Several of the high-potential bioremediation microorganisms have been isolated from impacted sites and cultured in the laboratory for their study and characterization. However, much of the microorganisms distributed in polluted sites are uncultivable due to the failure to replicate the necessary physicochemical and nutritional conditions for proper growth in the laboratory.

In recent years, OMIC technologies have been demonstrated as useful tools in the field of pesticide bioremediation research. The information generated through OMIC approaches has allowed (1) the genomic characterization of the pesticide degrading microorganisms (genomics), (2) the identification of microbial community structure present in polluted sites and the identification of novel enzymes with potential application in bioremediation strategies (metagenomics), (3) the evaluation of transcriptional changes in microorganisms exposed to pesticides (transcriptomics), (4) the identification and characterization of diverse enzymes related to pesticide biodegradation as well as the evaluation of the microbial response to pesticide exposure (proteomics), and (5) finally, the detection, identification, and quantification of metabolic by-products derived from pesticide biodegradation, and changes in primary and secondary metabolism derived from toxic effects of pesticides (metabolomics). Overall, the information generated through OMIC and MultiOMIC studies gives a better understanding on the microbial pesticide degradation processes. In the future, OMIC approaches will become more relevant in pesticide bioremediation research.

Table 8.8 Metabolomics studies in pesticide biodegradation and pesticide exposure microbial response

Pesticide family	Pesticide	Microorganism	Reference
Bacteria			
Hydroxy-anilide	Fenhexamid	*Lactobacillus casei* Shirota	Lénárt et al. (2013)
N-methylcarbamates	Carbaryl	*Burkholderia* sp. C3	Seo et al. (2013)
Organophosphorus	Chlorpyrifos	*Sphingobacterium* sp. C1B	Verma et al. (2020)
	Glyphosate	*Actinobacteria*	Grube et al. (2019)
		Pseudomonas sp.	Grube et al. (2019)
		Serratia sp.	Grube et al. (2019)
	Phorate	*Lactobacillus plantarum* P9	Li et al. (2018)
	Phoxim	*Bacillus amyloliquefaciens* YP6	Meng et al. (2019a)
		Enterobacter cloacae	Zhang et al. (2017)
	Profenofos	*Rahnella* sp. PFF2	Verma and Chatterjee (2021)
Phenoxy herbicides	2,4-D	*Escherichia coli* BL21	Bhat et al. (2015a)
		Rhizobium leguminosarum bv. *viciae* 3841	Bhat et al. (2015b)
Pyrethroid	Cyfluthrin	*Lysinibacillus sphaericus FLQ-11-1*	Hu et al. (2014a)
		Photobacterium ganghwense strain 6046	Wang et al. (2019a)
	Cyhalothrin	*Bacillus thuringiensis* ZS-19	Chen et al. (2015b)
	Cypermethrin	*Brevibacillus parabrevis* BCP-09	Tang et al. (2018)
Quinoline carboxylic acid	Quinclorac	*Burkholderia cepacia* WZ1	Lü et al. (2003)
Sulfonylurea	Nicosulfuron	*Pseudomonas* sp. LAM1902	Li et al. (2020)
Fungi			
Anilides	Alachlor	*Paecilomyces marquandii* IM 6003	Szewczyk et al. (2015)

(continued)

Table 8.8 (continued)

Pesticide family	Pesticide	Microorganism	Reference
Azole fungicides	Difenoconazole	*Botrytis cinerea*	Han et al. (2020)
	Epoxiconazole	*Botrytis cinerea*	Han et al. (2020)
	Fenarimol	*Botrytis cinerea*	Han et al. (2020)
	Fluquinconazole	*Botrytis cinerea*	Han et al. (2020)
	Flusilazole	*Saccharomyces cerevisiae* YCF1	Karamanou and Aliferis (2020)
	Tebuconazole	*Botrytis cinerea*	Han et al. (2020)
	Hexaconazole	*Botrytis cinerea*	Han et al. (2020)
Chloropyridinyl neonicotinoids	Acetamiprid	*Fusarium* sp. CS-3	Shi et al. (2018)
Organochlorine	β-hexachlorocyclohexane	*Penicillium griseofulvum*	Ceci et al. (2015)
	DDT	*Rhizopus arrhizus* FBL 578	Russo et al. (2019)
		Trichoderma hamatum FBL 587	Russo et al. (2019)
Organophosphorus	Dichlorvos	*Trichoderma asperellum* TJ01	Wu et al. (2020)
Phenylpyrazoles	Fipronil	*Trametes versicolor* ATCC 42530	Wolfand et al. (2016)
Phenoxy herbicides	2,4-D	*Trichoderma harzianum* IM 0961	Mironenka et al. (2020)
		Umbelopsis isabellina	Bernat et al. (2018)
Sulfonylurea	Nicosulfuron	*Penicillium oxalicum* YC-WM1	Feng et al. (2017)
Triazine	Ametryn	*Metarhizium brunneum*	Szewczyk et al. (2018)
	Atrazine	*Metarhizium robertsii* IM 6519	Szewczyk et al. (2020)
	Carbendazim	*Fusarium graminearum*	Sevastos et al. (2018)

2,4-D 2,4-dichlorophenoxyacetic acid, *DDT* dichlorodiphenyltrichloroethane

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Chapter 9
Bioremediation of Pesticides Using Microbial Consortium: Challenges and Future Perspectives

Gaye Ezgi Yılmaz, Ilgım Göktürk, Volkan Safran, Fatma Yılmaz, and Adil Denizli

Abstract The widespread use of pesticides causes serious environmental and health problems. Pesticide use not only degrades soil quality but also enters the aquatic environment, so decontamination of pesticide-contaminated areas is a very complex process. The conventional methods used to remove polluting chemicals from the environment are not sufficient for the removal of pesticides. New technologies such as environmentally friendly, economical, and versatile bioremediation methods are required that take advantage of the ability of microorganisms to remove pollution from the environment. The use of microbial consortia has very important advantages in the bioremediation of pollution caused by pesticides. In this chapter, recent applications of microbial consortia used in pesticide bioremediation are discussed.

Keywords Bioremediation · Microbial consortium · Microbial degradation · Pesticide

9.1 Introduction

Pesticides are widely used in agriculture to increase crop yield and improve the quality of agricultural products. The abuse of pesticides has resulted in serious food and environmental contamination around the world. In addition, worrisome problems for human health emerged as a result. Therefore, policies for pesticide use

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have been established by governments to ensure the correct management of pesticides and various maximum residue levels have been set in food and agricultural products. Although these measures have shown certain effects, pesticides continue to be a challenging problem that threatens human health and life (Liu et al. 2019). Intensive and unconscious use of pesticides can cause contamination of soil, sediments, and water systems, and as a result, they can accumulate in the food chain and grow biologically. Several international organizations regulate pesticides, such as the Environmental Protection Agency (EPA), the United States Department of Agriculture, the Stockholm Convention, the United States Food and Drug Administration, and the United Nations Environment Program (Nehra et al. 2021). The widespread use of pesticides causes serious environmental and health problems. In addition, intensive pesticide use negatively affects biodiversity. Pesticide use not only degrades soil quality but also enters the aquatic environment, so decontamination of pesticide-contaminated areas is a very complex process. The old methods used to remove polluting chemicals from the environment are not sufficient for the removal of pesticides. New technologies such as environmentally friendly, economical and versatile bioremediation methods are required that take advantage of the ability of microorganisms to remove pollution from the environment (Uqab et al. 2016).

In the natural environment, microbes exist in multiple species. Mixed microbial cultures have received little attention due to the lack of information about their interactions with each other. In natural environments, microbes can have unique metabolic properties. Synthetic microbial consortia can perform desired functions in naturally contaminated sites. Physical and chemical pesticide remediation is mostly not recommended due to its negative effects such as application difficulties, high cost, and unsustainability in terms of poor environmental safety. The use of potential and potent microorganisms and their biocatalytic enzymes derived from the environment for the pesticide biodegradation and their hazardous metabolites is effective and environmentally friendly. Microorganisms and their enzymatic powers can act as effective biological weapons to combat toxic agrochemicals. Potential bioremediation of chemical pesticides can be achieved with a mixed microbial consortium (Sarker et al. 2021).

Biodegradation of complex hydrocarbon often requires more than one species to be involved in the degradation process. This is especially true for pollutants composed of many different compounds, and full mineralization to CO_2 and H_2O is desirable. Mixed population communities with large enzymatic capacities are required, as individual microorganisms can only metabolize a limited range of hydrocarbon substrates (Ghazali et al. 2004). The vast majority of microorganisms, 99%, are found in microbial consortia in the open environment. Microbial consortia have more flexible and adaptive abilities to complex environmental stresses when compared to pure cultures. The development of climate-adapted mixed cultures is the most appropriate strategy to allow the emergence of ecologically stable consortia for biodegradation. Recently, there has been an increasing number of studies investigating the role of microbial consortia and non-culturable microbes in the biodegradation of pollutants. Studies have shown that the consortium is more suitable for the biodegradation of pollutants in an unstable environment, as synergistic interactions between different bacterial strains allow them to fully mineralize the pollutant (Xu et al. 2020). A wide variety of microorganisms with pesticide degrading activity have been found. It has been proven that microorganisms such as *Flavobacterium oryzihabitans*, *Arthrobacter aurescens*, and *Acinetobacter* sp. are effective in the degradation of atrazine. Similarly, *Sphingomonas paucimobilis* microorganism was found to be effective for carbofuran degradation. Besides, different types of microorganisms such as *Serratia marcescens, Stenotrophomonas* sp., *Leuconostoc mesenteroides*, *Artrobacter* sp., *Mycobacterium* sp. were found to be effective for diazinon degradation (Góngora-Echeverría et al. 2020). As can be seen from these examples, the use of microbial consortia has very important advantages in the bioremediation of pollution caused by pesticides. In this chapter, recent applications of microbial consortia used in pesticide bioremediation are discussed.

9.2 History of Pesticides

Pesticides are important chemicals used to prevent or control plant pests, various diseases, and pathogenic factors in plants to reduce or eliminate crop losses and improve crop quality. The most important advantages of pesticides are that they provide economic benefits such as reducing cost-production factors as well as increasing product yield and quality. In addition to these, although pesticides have many advantages, the intensive and uncontrolled use of pesticides causes negative effects on the environment and the health of living things (Khan et al. 2015). Since ancient times, people have tried to find and apply effective methods in order to improve their products and protect them against various pests. An example of this is that ancient peoples cultivated poisonous and nutritious plants in the same place to remove pests from nutritive plants, taking advantage of the protective effect of poisonous plants. In addition to this example, elemental sulfur was also used during this period. These practices can be counted as the first methods applied to destroy pests. This was followed by the Ebers papyrus, one of the oldest documents on pesticide use, which describes the preparations made to repel insects from plants. Primitive sulfides are used for the same purposes in traditional Chinese medicine. Likewise, Homer's work "Odysseus" is an example of the use of substances to destroy insects. In the 1500s, the first stages of using mercury and arsenic, called "para-pesticides," appeared. The use of these substances started in World War II and continued until the 1940s and later, the date of the beginning of the synthetic pesticide era. One of the most important events in the history of pesticides was Paul Muller's discovery of the first modern pesticide, dichloro-diphenyl-trichloroethane (DDT), in 1939. This discovery earned him the Nobel Prize in medicine for not only reducing the damage done by pesticides in agriculture, but also reducing health problems such as malaria or typhus, but the use of DDT did not last long. Due to the benefits of pesticides as well as their negative effects on the environment and health, according to new European Union regulations, manufacturers are required to minimize pesticide production in order to reduce the number of serious diseases in the world (Abubakar et al. 2020).

Most substances used in daily life today are registered as pesticides if they are marketed to reduce pests. Disinfecting agents are an example of this definition. Products marketed using pathogen control properties must be registered with the EPA as pesticides. Boric acid is generally used as a bleaching agent and was registered as a pesticide used in insect control. Vitamin D3 (cholecalciferol), an essential nutrient, is also a proprietary pesticide. Since high doses of vitamin D3 kill rats and mice, products containing vitamin D3 should be registered with the EPA as rodenticides. With the spread of chemical synthesis in the early to mid-twentieth century, there was a shift towards the production and use of pesticides that are less toxic to crop plants and have high specificity towards target organisms. However, since the beginning of the 1970s, the idea of developing pesticides that degrade rapidly, are non-accumulating, and are not toxic to living organisms has come to the fore even more since the beginning of the 1970s, due to the continuing problems associated with the accumulation of many pesticides in the environment and the food chain (Reeves et al. 2019).

9.3 Classification and Effects of Pesticides

Pesticides can be classified as destroying, repellent, and mitigating agents. Pesticides are well soluble in water, have a heat resistant and polar structure, so it is very difficult to reduce the lethal nature of pesticides due to these properties. Of all pesticide types, insecticides are considered the most toxic, followed by fungicides and herbicides on the toxicity list, respectively. Pesticides enter ecosystems in two different ways, depending on their solubility. Water-soluble pesticides enter the soil after they dissolve in water. It harms non-targeted species through various water sources such as streams, lakes. Fat-soluble pesticides enter the bodies of animals. This process is called bioamplification. Pesticides remain in food chains for a long time as a result of their absorption from the fat tissues of animals. As a result of pesticide accumulation in food chains, the amounts of predators and raptors are directly affected and this is a major concern. In addition, pesticides can indirectly reduce the number of weeds and insects. The use of pesticides such as insecticides, herbicides, and fungicides has been associated with the depopulation of rare animal species. In addition, one of the most important consequences of long-term and frequent use of pesticides is that it causes bioaccumulation in nature (Mahmood et al. 2016). Most of the pesticides, which consist of four main groups according to their chemical structures, are synthetic and organic compounds. These groups are organochlorines, organophosphorus, carbamates, and pyrethrins and finally are pyrethroids. Examples of organochlorines are DDT and BHC, examples of organophosphorus are malathion, fenthion, dichlorvos, pirimiphos-methyl, examples of carbamates and pyrethrins are propoxur, bendiocarb and carbaryl, and pyrethroids, for example, cyfluthrin, bifenthrin, lambda-cyhalothrin. Organophosphate pesticides, one of the pesticide groups, are the most toxic to vertebrates. A very small percentage (~0.1%) of pesticides used can eliminate target pests, while the rest is released into the ecosystem, causing various effects (Sarlak et al. 2021).

Organochlorine pesticides were the first-generation synthetic organic pesticides used for pest and vector control. They have low toxicity and lasting effects. Due to their stable chemical structure, they are difficult to decompose in the natural environment. Due to environmental pollution and accumulation in mammals, causing various health problems, their use in large quantities and for a long time has been banned and left its place to other pesticides. DDT, endosulfan, and lindane are examples of this pesticide class. Organophosphate pesticides have multiple functions and are capable of controlling a large number of pests. Organophosphate pesticides are biodegradable, cause little environmental pollution, and slow down pest resistance. Methyl parathion, phosphamidon, and fenitrothion are examples of organophosphate pesticides. Carbamates work on the same principle as organophosphate pesticides by affecting the transmission of nerve signals, poisoning and causing the death of the insect. Carbamates can be used as fumigants as well as stomach and contact poisons. Since their molecular structures are very similar to those of natural organic substances, they can be easily degraded with minimal environmental pollution. Propoxur is an example of a carbamate pesticide.

Synthetic pyrethroid pesticides are synthesized by imitating the structure of natural pyrethrins. They are relatively more stable compared to natural pyrethrins. While synthetic pyrethroid pesticides are more toxic to insects, they cause less toxicity to mammals. Allethrin and permethrin are examples of synthetic pyrethroid pesticides (Ahmad and Ahmad 2014). Insecticides that are frequently used against aphids and viral diseases are organophosphorus compounds. Organochlorine, carbamate, and pyrethroid pesticides destroy pests, namely Lepidoptera, Hemiptera, and Diptera. The majority of these pesticides are used to eliminate crop-damaging insects. Pesticides can be classified according to their use as insecticides used against insect pests, nematicides used against nematodes, fungicides used against fungi, herbicides used against weed pests, etc. There is another class of pesticides made from natural materials called biopesticides (Odukkathil and Vasudevan 2013). Biopesticides refer to a method of biological control through the interaction of living organisms. Biopesticides consist of microbial pesticides, biochemical pesticides, and plant-derived preservatives (PIPs). Plants, insects, microorganisms are the source of readily available, inexpensive, versatile, and easily degradable biopesticides.

Target-specific biopesticides are not toxic to humans. With the use of biopesticides, sustainability has been increased and any pollution caused by synthetic pesticides has been reduced. Biopesticides, which are used in integrated crop management practices around the world, are compatible with other chemical pesticides and play a very important role in plant protection. Bioinsecticides, bioherbicides, and biofungicides are commonly used biopesticides (Thakur et al. 2020). Synthetic chemical compounds such as pesticides are used extensively in a variety of agricultural and household applications around the world to meet food, feed, household needs, and reduce the pest load. Pesticides are frequently used in homes and public places to reduce pathogenic vectors and pests in agricultural systems (Bhatt et al. 2021). In order to meet the increasing nutritional needs of the ever-increasing world population, plant production must also increase. With the right pesticide and pest management, the reduction in crop yield (approximately 40% reduction) caused by approximately 67,000 different crop pests can be greatly altered and the number of nutrients can be increased (Oaya et al. 2019). Globally, a total of about 9000 insect and mite species, 50,000 plant pathogen species, and 8000 weed species damage crops. Pests that cause the most damage to plants can be listed as insect pests, plant pathogens, and weeds. To eliminate these damages, pesticide use is necessary for plant production. Crop loss from pest damage can be up to 78% if pesticides are not used. With pesticide application, crop loss caused by pests can be reduced by close to 42% (Zhang 2018). Synthetic chemicals are commonly used to enhance crop productivity. Although synthetic chemicals have these and many other beneficial properties, their widespread use has also caused negative consequences such as environmental and health problems. (Chapalamadugu and Chaudhry 1992).

The most widely used pesticides for experimental study can be listed as chlorpyrifos, cypermethrin, fenvalerate, and triclopyr butoxyethyl ester (Geetha and Fulekar 2008). Adverse factors such as pollution and loss of biodiversity resulting from the heavy use of pesticides are major concerns. Chlorpyrifos, which belongs to the organophosphate group of pesticides, has toxic properties. Chlorpyrifos changes the structure of microbial in the soil and causes negative effects on the health of living things. Chlorpyrifos pesticide is very common in food and water (John and Shaike 2015). Cypermethrin is a synthetic pyrethroid pesticide. It is highly toxic to aquatic invertebrates. It adversely affects human health and cypermethrin has been classified as a human carcinogen (Tallur et al. 2008). Fenvalerate (FEN) can be absorbed by animals through the skin, respiratory tract, or digestive tract. FEN shows both acute and cumulative toxicity (Liu et al. 2010). When pesticides enter the body, they can reach every organ in the body through the bloodstream and cause accumulation there. After pesticides enter the cells, cell function balances change drastically and pesticides cause cell stress. For example, some pesticides have proven to be inhibitors or agonists of mitochondrial enzymes that alter energy expenditure by impairing mitochondrial function. Some pesticides contain endocrine-disrupting chemicals and can bind or abnormally activate proteins, which are key mediators of the endocrine system, to disrupt the function of the endocrine system. Pesticides can also cause a variety of cell stresses, including cell cycle arrest and endoplasmic reticulum stress (He et al. 2020).

9.4 Bioremediation

Bioremediation is an event that uses organisms and enzymes to detoxify the polluted environment. Bioremediation, a biotechnology approach, can be used to decontaminate certain pollutants such as pesticides, organic liquids, oils, and organic sludge. Bioremediation processes can be listed as: mineralization, biotransformation, reduction of highly electrophilic halo and nitro groups, and bioremediation can be aerobic or anaerobic. The use of sequential anaerobic-aerobic bioremediation processes in contaminated areas reduces the limitations of the mentioned methods previously. Depending on the application area and the contaminated soil to be treated, bioremediation is grouped as in situ and ex situ technology. The in situ technique is often chosen in areas where treatment with conventional methods would result in high costs, and where excavation is technically difficult or impossible. The in situ method is mainly suitable for soils with sufficient hydraulic conductivity and low to medium pollution concentration. Advantages of in situ bioremediation are summarized as: the bioremediation process is implemented without significant disruption, eliminates the burden of transportation for purification, the end products are harmless products, the spread of pollutants is completely avoided as there is no handling in the process.

On the contrary, the disadvantages of this process are that as the depth of the soil increases, the availability of oxygen, water, and nutrients decreases, the process is uncontrolled, making it difficult to determine the extent of remediation of the contaminated area, and the overall cost of comprehensive intensive monitoring increases. Ex situ bioremediation requires excavating the contaminated area and then treating it in a bioreactor or on-site or a treatment plant. Depending on the state of the contaminant, ex situ treatment can be applied as a solid phase system or a slurry phase system. The advantages of ex situ bioremediation are that the treatment process is subject to control and predictability, biodegradation kinetics can be increased, pretreatment is possible to increase process efficiency, operating factors can be optimized for efficient results. Applications are made on-site to eliminate transportation costs and reduce contamination of healthy soil. Disadvantages of ex situ bioremediation: it causes extra cost due to transportation cost, there is a possibility of spreading contamination during transportation, it requires technological equipment to bring the process to the required level of cleanliness (Fenibo 2021). Many modern physical, chemical, and biological treatment methods are used to remove pollution, but these methods are not sufficient to remove pollution. Bioremediation is a very fast, easy, environmentally friendly, and acceptable method for removing such compounds causing pollution in the environment (Sharma et al. 2018). Bioremediation can be defined as a process that can destroy a wide variety of pollutants themselves or the harmful properties of pollutants by biological activity. It is the process by which impurities are biodegraded to a harmless state under certain conditions or to levels below the concentration values determined by the authorities (Mueller et al. 1996). With bioremediation, the negative effects of environmental pollutants are eliminated by using living organisms such as microorganisms. It uses living organisms that occur naturally in nature to break down harmful substances or reduce their toxicity. Where environmental conditions are suitable for microbial growth and activity, microorganisms enzymatically attack pollutants to convert them into harmless products, resulting in effective bioremediation. Thanks to bioremediation, many dangerous compounds can be converted into harmless products. One of the advantages of bioremediation is that it is possible to completely destroy the target pollutants instead of transferring them from one environmental medium to another. Bioremediation is considered a suitable waste treatment process for contaminated materials. Treatment residues are mostly harmless products. Bioremediation is limited to the application of biodegradable compounds. Rapid and complete degradation may not be suitable for all compounds. Biodegradation products have the potential to be more persistent or toxic than the main compound. Biological processes have high specificity. For the bioremediation process to be successful, skilled microbial populations, suitable environmental conditions, and appropriate nutrient and pollutant levels factors are needed (Vidali 2001).

A large number of researchers have recently focused their attention on the degradation of hazardous chemicals by microbial populations. Microbial degradation has numerous other advantages besides being inexpensive, high cleaning efficiency, and environmental friendliness. Microorganisms used to degrade various pesticides have been isolated from various environments and identified. Microbial degradation encompasses the microbial mechanisms involved in the biodegradation and bioremediation of pesticide-induced pollution (Huang and Lu 2021). The bioremediation process is defined as the microbial degradation of xenobiotics and is an economical method to remove contaminants. With biodegradation, biological reactions take place that causes a reduction in toxicity by changing the chemical structure of the compound. When pesticide degradation occurs, it involves a large number of microorganisms. Although each microorganism contributes to biodegradation reactions in pesticides, no single strain mineralization pattern has been identified. Bacteria are widely used in bioremediation processes (Doolotkeldieva et al. 2017). Microbial degradation can be defined as the use of pesticides by microorganisms as a food source. There are more than 100 million bacteria (5000–7000 different species) and about 10,000 fungal colonies in 1 g of soil. A safe and economical alternative to other commonly used physicochemical strategies to remove soil pollutants is the use of microbial metabolic potential (Anjum et al. 2012). The persistence of pesticides in the environment is affected by the microbial degradation process. The presence, number, and enzymatic ability of microorganisms affect the dispersion of unwanted residues and impurities (Villaverde et al. 2017). Bioremediation technology is basically the breakdown of pollutants through microbial metabolic activities. Most of the microorganisms used in the healing process are native microorganisms (Zhang et al. 2020).

Compared with other physicochemical approaches, bioremediation is a nondestructive, cost-effective, and highly efficient approach to removing pollution. Contaminated areas are often contaminated with more than one type of pollutant and host a variety of different environmental conditions. Therefore, bioremediation using a single microorganism strain often fails because of the low biodegradability, adaptability, and viability of microorganisms applied in a contaminated area with different environmental conditions. To successfully perform bioremediation, many issues must be addressed, including available organic compounds, the use of suitable biodegradable microorganisms and their biodegradation properties, and various environmental factors. To overcome these limitations, a microbial consortium of multiple strains with diverse biodegradation abilities and physiological properties is implemented (Lee et al. 2018).

Many highly efficient chemical pesticides have been produced on a large scale after the discovery of some synthetic pesticides and are widely used to control various agricultural pests. Pesticides play an important role in maintaining product quality and yield, but their unconscious, intense, and continuous use causes serious problems. The rate of biodegradation of pesticides is very slow compared to other techniques. Specific microorganisms must be selected to ensure an adequate degradation rate. In bioremediation, the isolation of effective microorganisms naturally found in a contaminated area is very important (Geed et al. 2017a). *Lysinibacillus*, *Acinetobacter johnsonii*, *Pseudomonas* sp., and *Bacillus* sp. strains have been used for the degradation of pesticides (Geed et al. 2017b). Highly efficient colonization of fungal populations in polluted soils can be achieved with highly branching and filamentous growth modes (Verdin et al. 2004). White rot fungi, one of the highly filamentous types of fungi, have an advantage over other bacterial strains as they can oxidize very dangerous chemicals (Pointing 2001). Degradation of pesticides by fungi is generally dependent on ligninolytic enzymes, and fungal degradation of pesticides that are not very efficient requires long acclimatization and incubation times (Espinosa-Ortiz et al. 2021). Therefore, many genetically modified fungi species have been already patented, and they are seen as a vigorous biotechnological approach in the biodegradation of soil pollutants (Steffen et al. 2007). The fungi species reported in pesticide bioremediation are *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, *Aspergillus niger*, *Fusarium proliferatum*, *Candida* sp., *Trametes versicolor*, *Cunninghamella elegans*, *and Penicillium* sp. (Conde-Avila et al. 2020). Besides, bacterial strains of Arthrobacter, Flavobacterium, Micrococcus, Pseudomonas, Rhizobium, and Sphingomonas genera consume pesticides as sources of carbon, nitrogen, and phosphorus.

9.5 Developments and Applications of Bioremediation Techniques

In situ and ex situ bioremediation are the two main approaches named according to the region selected for the pesticide treatment. The techniques that treat the toxic pollutants on-site are called in situ bioremediation, while the techniques that treat hazardous material off-site are called ex situ bioremediation (Giri et al. 2021). The in situ approach includes stimulating microbial activity by adding microbes and nutrients and optimizing environmental-related parameters in polluted areas (Seech et al. 2008). In situ bioremediation, which is a low-maintenance, economical, sustainable, and environmentally friendly approach, involves the biodegradation of organic pollutants. It is a process in which organic pollutants are reduced to CO_2, water, or other minimally toxic products biologically for the detoxification of contaminated regions (Giri et al. 2021).

In situ bioremediation is preferable to ex situ bioremediation for environmental rehabilitation of watery ecosystems and polluted soils (Jorgensen 2007). The condition of the contaminated area depends on many parameters such as the natural microbial populations, pesticide amount, the level of toxicity, and the applicability of a specific biotechnological approach. The addition of oxygen, substrates, vitamins, and organic/inorganic additives such as phosphate and nitrate stimulates microbial activity in bio-stimulation. Bioaugmentation is a process where exogenous microbial populations with certain catabolic activities are added to the polluted area or means a biological reactor to support the biodegradation process. In bioaugmentation, adding pre-grown microbial cultures to increase microbial populations in a region improves contaminant elimination and reduces cleaning time and cost (Giri et al. 2021).

The microbial strains as axenic cultures are important in the study of the metabolism, physiology, and molecular assembly associated with pesticide degradation. To date, approximately 99% of environmental microbes cannot be cultured in laboratories using traditional culture-dependent techniques. So, researchers suppose that there is a strong possibility that the study of mixed microbial cultures from various environments can help elucidate their potential impact on pesticide degradation (Fig. 9.1) (Qian et al. 2020; Bhatt et al. 2021). The degradation studies of atrazine, 2,4-dichlorophenoxyacetic acid, carbofuran, diazinon, and glyphosate have been evaluated by a bacterial consortium (Góngora-Echeverría et al. 2020). Chlorpyrifos and 3,5,6-trichloro 2-pyridinol were completely degraded within 9 days using the consortium (MC-BSPK) of *Bacillus* sp. MCB, *Serratia* sp. MC-S, *Pseudomonas* sp. MC-S, and *Klebsiella* sp. MC-K (Sun et al. 2020). A consortium of *Staphylococcus warneri*, *Pseudomonas putida*, and *Stenotrophomonas maltophilia* was found to be effective in the degradation of chlorpyrifos (John et al. 2020).

The development of a synthetic microbial consortium in the environment will require precise control of its growth, yield, and function so that it does not harm the

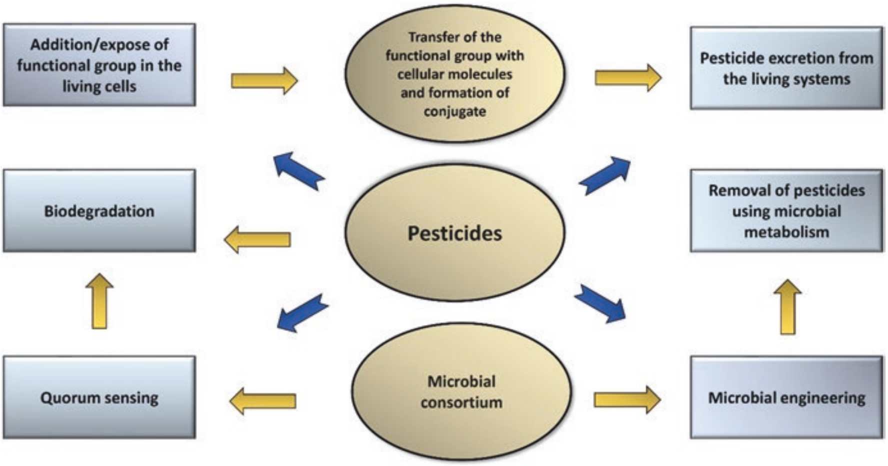

Fig. 9.1 Schematic representation of the pesticide toxicity and application of the microbial consortia. (Reproduced from REF (Bhatt et al. 2021))

natural environment. Honjo et al. designed a synthetic microbial consortium by enzyme-producing *Escherichia coli* and chemical-producing strains (Fig. 9.2) (Honjo et al. 2019). They used a synthetic quorum sensing (QS) system to enable task execution through cell-to-cell communication among consortia. The enzyme-producing strain was programmed to release the saccharification enzyme according to the strain QS signal. The main task of the strain used to produce the target chemical is to produce the desired chemical after saccharification.

Genetic circuits that enable specific protein release and QS-dependent cell lysis have the potential for a variety of bioengineering applications such as useful protein production, agriculture, and bioremediation. In environments where complex pollutants, soil and water are present, QS helps in improving biodegradation by coordinating the movement of microbes against pollutants.

The process of removing different types of pollutants, such as persistent organic pollutants (POPs), oil spills, pesticides, xenobiotics, and heavy metals, through bioremediation and biofilm has been used frequently in recent years. QS systems regulate enzyme production during biofilm-mediated degradation. Most bacteria remain in the biofilm mode, coated with an extracellular polymeric substance (EPS) under natural environmental conditions. In the bioremediation process, EPS matrix is a useful structure of biofilm-forming microbes. The environmental conditions in which the microbes are found determine the structure of bacterial biofilms and the content of EPS production (Yadav and Chandra 2020).

In a study, Raimondo et al. (2020) constructed an actinobacteria-rich consortium that was found to be capable of degrading lindane more efficiently following bio-stimulation with a sugarcane filter cake. The study conclusion was that the simultaneous application of bioaugmentation to a bacterial consortium and bio-stimulation could lead to the degradation of lindane from contaminated soil.

Villaverde et al. (2017) applied the consortium tested in a soil solution having diuron, the only carbon source and more than 98.8% of the diuron initially added was found to be mineralized after a few days. Diuron was degraded in contaminated soil using the microbial consortium of bacterial strains, viz. *Arthrobacter*

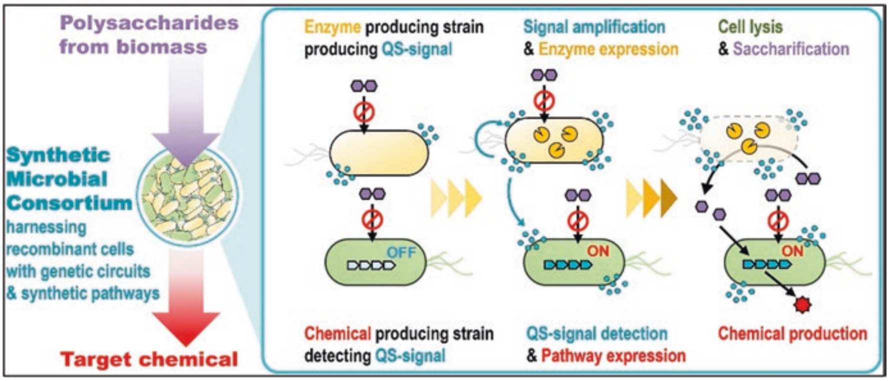

Fig. 9.2 Synthetic microbial consortium for cooperative chemical production (Honjo et al. 2019)

sulfonivorans, *Variovorax soli*, and *Advenella* sp. (Villaverde et al. 2017). The binary bacterial consortium of *Pseudomonas fluorescens* and *Bacillus polymyxa* is able to rapidly degrade aldrin when compared to axenic cultures (Doolotkeldieva et al. 2017). In a study, Jiang and coworkers performed the degradation of acetamiprid by consortium ACE-3 at a broader range of temperatures and pH values and proved that making such mixed cultures applicable to the bioremediation of various acetamiprid-contaminated environments. The presence of acetamiprid was observed in the control sample as seen from the HPLC-MS analysis. Mass spectrometry revealed the presence of four intermediates formed as a result of the biodegradation of acetamiprid (Xu et al. 2020).

9.6 Conclusion and Future Outlook

Physicochemical methods such as extraction, adsorption, coagulation/flocculation used for the removal of pesticide contaminants are mostly costly. In addition, many physical, biological, and chemical methods used for pesticide treatment are not sufficient to remove pollution. Of all the available methods for the effective degradation of various pesticides in the environment, bioremediation is the most environmentally friendly and cost-effective method as it uses a variety of living organisms that occur naturally and are readily available. Various microorganisms have been used to convert pesticides into their non-toxic or less toxic or harmless product forms. Performing bioremediation through microbial consortia is highly advantageous in terms of target-specific elimination of various pesticides, thanks to their ability to contain a large number of enzymatic potentials. Bioremediation processes combined with legacy methods to eliminate or mitigate the negative effects of pesticides in high pollution areas have proven to be a promising method, but their sustainability is questionable. The biochemical pathways of microbial species are largely dependent on the various physicochemical properties of the soil, so it is very difficult to completely destroy pesticides in nature. Therefore, further studies are needed to comment on the degradation processes of microbes and their interactions with soils with different pollutants and different environmental conditions. Since the degradation rate of pesticides is quite slow, it takes a long time. Pesticide treatment, investigation of microbes specific to target pesticides, optimization of process parameters, development of a highly efficient bioreactor, and validation of natural, easily accessible, and highly porous packaging media should be further explored.

Since biological processes are highly specific, the presence of microbial populations, suitable environmental growth conditions, and appropriate amounts of nutrients and pollutants must be known. There is a need to develop and design suitable bioremediation technologies for complex mixtures of pollutants that may exist in the environment in various forms such as solids, liquids, and gases. Genetic engineering and advanced biotechnology/microbiological approaches while inspiring rapid advances in pesticide bioremediation improve powerful and highly adaptable microbial strains and existing treatment facilities/technology. Genes responsible for biodegradation can be targeted using these tools. The rapid development of technology has made it easier to implement microbial consortia in biotechnology. Large-scale degradation of pesticides can be achieved with the development of synthetic microbial consortia with the collaboration of biochemists, microbiologists, environmental engineers, and genetic engineers to solve problems in current bioremediation methods.

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Chapter 10
Advances in Biological Treatment Technologies for Some Emerging Pesticides

Buzayehu Desisa, Alemayehu Getahun, and Diriba Muleta

Abstract Although pesticides are highly helpful for crop production, environmental contamination with persistent and potentially eco-toxic pollutants discourage their utilization. Soil is full of pesticides with significant environmental and human health problems. The contaminants' behavior, types, complexity, toxicity, and their transformation products have an environmental concern. Pesticides are the known emerging contaminants (ECs) identified in different environmental sources. Tackling these pollutants is vital in creating healthy environment in order to ensure food security and proper water supplies to feed the growing world population. Additional contaminants are released via physical and chemical remediation methods and are considered destructive and highly expensive. Thus, bioremediation is an economical and eco-friendly tool since it uses bacteria, fungi, algae, plants, and their interactions in removing toxicants. Revolutions in genetic engineering techniques aid to explore pollutant-degrading microbes. Therefore, this review mainly focuses on portraying pesticides as ECs, the different types and classes of pesticides, and their fate in the environment. Moreover, the pivotal focus of this review is on the eco-friendly bioremediation technologies available for the removal of these pollutants to maintain a sustainable environment with a healthy and productive ecosystem.

Keywords Bioremediation · Emerging contaminants · In situ · Pesticides · Phytoremediation · Treatment technologies

10.1 Introduction

Global industrialization releases contaminants that can cause harm to all life forms (Quintella et al. 2019). The quality of the environment outlines the quality of life on the planet. As stated by Azubuike et al. (2016), unsafe agricultural and ecological practices can potentially bring environmental pollution. There is also a continuous application of synthetic fertilizers and other agrochemicals to feed a rapidly growing global population (Carvalho 2017). Consequently, several toxic

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contaminants enter into the productive farmlands from multiple sources (Raghunandan et al. 2018). Patel et al. (2020) have indicated emerging contaminants (ECs) that are used on the daily basis including pesticides, plasticizers, pharmaceuticals, personal care products (PCPs), and chemical surfactants. More than 80% of pesticides are in use for a food production system. This amount of pesticides on the total environment needs immediate bioremediation options in the era of sustainable agriculture.

Crops are severely affected by diverse pests. Accordingly, Pimentel et al. (2001) have reported that each year China lost 40 million tons (8.8%) of the country's total grain output. Likewise, India loses also 11–15% of its total output yearly due to pests and other causes (Walter et al. 2016). Thus, to ensure food security, pesticides are extensively used in modern agriculture. Generally, different types of crops are seriously affected by pests with significant yield losses (Fig. 10.1) and need the application of agrochemicals. A growing body of evidence shows that pesticides application can reduce 35–42% crop loss from pests (Pimentel and Burgess 2014). Sharma et al. (2019) have estimated 3.5 million tons of pesticides usage in 2020 with concomitant pollution of the environment. The complex structure and existence at low concentrations make these pollutants untraceable and difficult to remove from the environment (Patel et al. 2020).

The quality of soil and its processes are affected by the use of pesticides in agricultural production systems. Runoff, leaching, and/or vaporization determine the persistence and movements of pesticides in soil, air, and water (Gavrilescu 2005). The function and health of living organisms are greatly influenced by the accumulation and magnification of pesticides in the food chain. Due to these threats, pesticides degradation (remediation) is of great importance (Zulfiqar and Yasmin 2020).

The physical, chemical, and biological pesticides treatment techniques are used (Saleh et al. 2020). The environmental risks of chemical and physical methods may pose low public acceptance, as well as excavation, handling, transportation, and removal costs, are not always sufficient. Thus, eco-friendly remediation approaches are needed to destroy and transform pesticides into harmless substances (Morillo and Villaverde 2017). Likewise, Patel et al. (2020) have presented bioremediation as an important and eco-friendly technology in pollutants treatment. In this paper, the

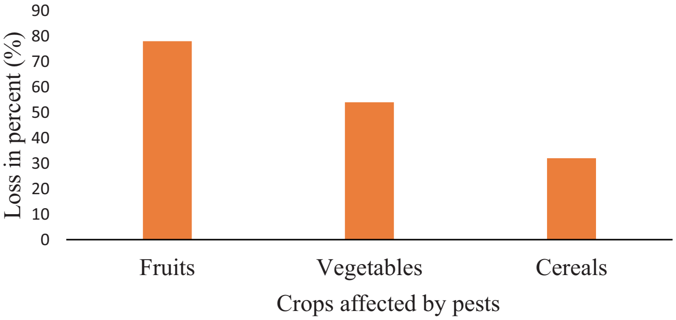

Fig. 10.1 Loss of crop yields by pests. (Modified from Pimentel and Burgess 2014)

negative impact of pesticides on the natural environment is discussed. The chemical and physical treatment options are usually costly and are not eco-friendly as well as aggressive to soil and soil microbiota. Hence, this review provides more insight into the bioremediation techniques using mainly microbes that have proven effectiveness and reliability in removing toxicants from the environment.

10.2 Pesticides as Emerging Contaminants (ECs)

Emerging contaminants (ECs) are unregulated compounds discovered in the environment. ECs are not yet widely regulated by national or international laws and are named emerging for the rising level of concern (Glassmeyer 2007; Sauvé and Desrosiers 2014). Human-induced activities increased the release of ECs into the natural environment (Arihilam and Arihilam 2019). Such contaminants create unique and considerable challenges and deserve attention (Bell et al. 2019). Emerging contaminants cause adverse ecological and human health problems (Patel et al. 2020; Zhang et al. 2019). Neonicotinoids are a first-hand generation of pesticides applied to control pests (Tomizawa and Casida 2003) and (Cloyd and Bethke 2011).

10.2.1 Types of Emerging Pesticides

Pesticide is an umbrella term used to kill, repel, and control some forms of animal and plant life and it can apply to a wide spectrum of chemicals. These synthetic toxicants vary in their characteristics and are classified under their respective groups (Freeman 2020). Figure 10.2 indicates percentages of frequently applied pesticides for agricultural production (Mekouar 2015).

Pesticide classification based on chemical composition is the most common and useful approach that gives clues about the efficacy, physical, and chemical properties of the respective pesticides (Yadav and Devi 2017). The chemical and physical characteristics of pesticides determine their mode of application and need precautions during use (Kaur et al. 2019; Mileson et al. 1998). The chemical classification

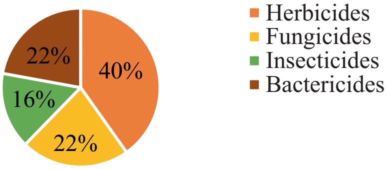

Fig. 10.2 The most applied pesticides (%) for agricultural production. (Adapted and modified from Mekouar 2015)

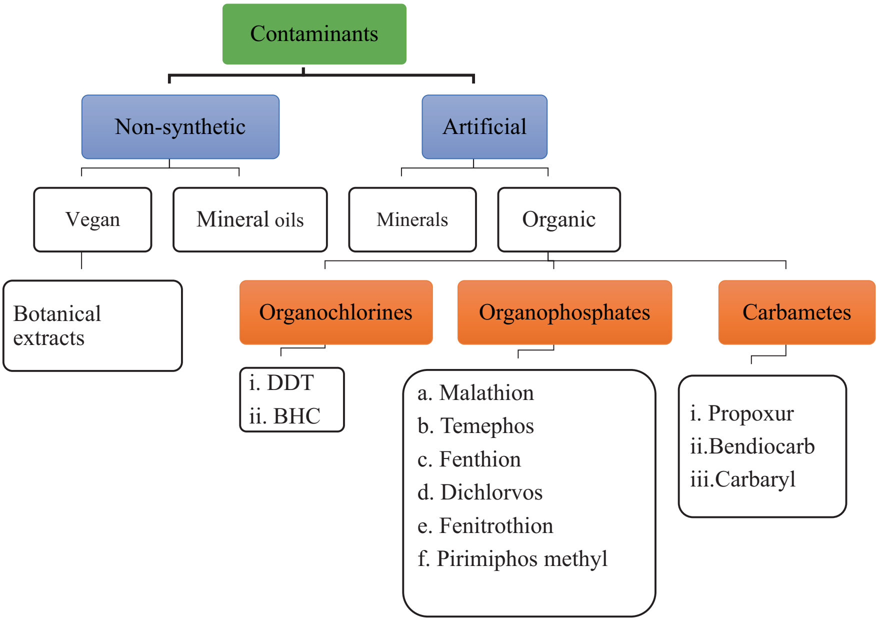

Fig. 10.3 The chemical composition of pesticides. (Adapted and modified from Kaur et al. 2019)

of pesticides is highly useful for its practical application (Gavrilescu et al., 2006; Kaur et al. 2019; Zacharia 2011) (Fig. 10.3).

10.2.2 Common Features of Pesticides

Agrochemicals have proven potential to increase the production and productivity of crops. However, damage to the environment due to the irresponsible use of these synthetic chemicals decreases their application (Meena et al. 2020). Hence, initiatives that address these questions are desirable. Understanding the common features of a pesticide allows a better pesticide formulation to apply for a particular situation to maintain the integrity of the environment. The fate of pesticides is mainly determined by their characteristics (water solubility and persistence) and soil properties (Gavrilescu 2005; Pereira et al. 2016).

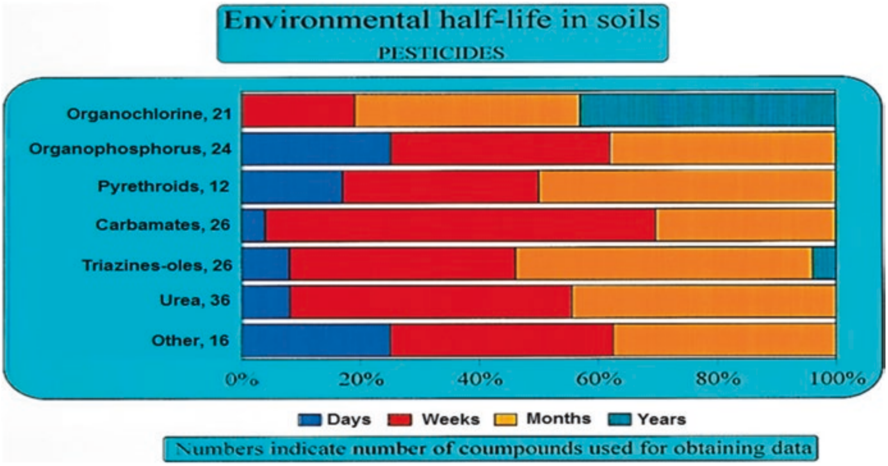

Fig. 10.4 The persistence of some pesticides in soils. (Data are available in Carvalho (2017) modified from Carvalho et al. (1997)

Table 10.1 Persistence and toxicity of pesticides. Adapted from Madigan and Martinko (2006)

Insecticide class	Example	Persistence	Toxicity to mammals
Organochlorides	DDT, dieldrin, toxaphene, chlordane, lindane	High	Relatively low
Organophosphates	Parathion, malathion, acephate, phorate, chlorpyrifos	Moderate	High
Carbamates	Carbaryl, methomyl, aldicarb, carbofuran	Low	High to moderate
Pyrethroids	Permethrin, bifenthrin, esfenvalerate, decamethrin	Low	Low

10.2.3 Persistence of Pesticides

Understanding the properties and the behavior of agrochemicals is important in the environment. These properties are linked to the products' mobility in the soil, dissociation in water, bioaccumulation, and durability in the environment (Pereira et al. 2016). The extended half-life, the more the persistent pesticide. Pesticides show considerable variations in their persistence in soils (Fig. 10.4). Persistence is affected by chemical, microbial, and photodegradation processes in the breakdown of a single pesticide (Schaafsma et al. 2016). The rate of pesticides degradation depends on its chemistry, soil environment, and microbial activities (Tiryaki and Temur 2010).

The persistent nature of pesticides in the soil is determined by their continuous applications and classifies as non-persistent, moderately persistent, or persistent

(Kerle et al. 2007; Tiryaki and Temur 2010). Less than 1% of the pesticides applied to crops attain the target pest species while an excess of them moves throughout the environment and enters marine ecosystems and keeps them there sufficiently long (Carvalho et al. 1997).

Toxicity is also another important characteristic of pesticides and it can vary depending on the target organism taken into consideration Table 10.1 (Madigan and Martinko 2006).

10.2.4 Health Effects of Pesticides

Although pesticides bring indiscriminate use resulted in serious health, they considerably improve crops production and productivity (Tudi et al. 2021). There are many routes for the entrance of pesticide residues into the food chain and can be carcinogenic or cytotoxic. This in turn causes different disorders, infertility to the affected organisms (Audrey et al. 2012). There are multiple uses of pesticides to destroy weeds, insects, fungi, and rodents (Kumar et al. 2012). Each year, 3 million insecticide poisoning, 220,000 deaths, and 2.2 million people are exposed in developing countries (Hicks 2013). The damage of pesticides to living organisms including plants is enormous (Rasheed et al. 2019). For instance, photosynthesis is impaired in susceptible plants (Tandon 2018). The author further remarked that cardiovascular, retinal, and muscle degeneration occur in humans via herbicides exposure.

Recently, pesticide poisoning caused greater than 17 million deaths from 1960 to 2019 (Karunarathne et al. 2020). Globally, the accumulation of organochlorine in the food chain distresses nearly one billion people due to hypertension (Karunarathne et al. 2020). A study in New York reported the presence of 100% and 47–78% levels of organophosphate (OP) and organochlorine pesticides (OCPs), respectively in pregnant women (Whyatt et al. 2002).

10.2.5 Environmental Outcome of Pesticides

Microbial consortia degrade and transform different pesticides and still, the resistant ones stay in the environment and food chains (García-Reyes et al. 2007). There are different modes of distribution of pesticides from target to non-targeted organisms in the environment (Tiryaki and Temur 2010). Many things happen to pesticides including the leaching of some herbicides into the root zone that can give better weed control.

The methods of pesticides application cause intoxication to the victimized individuals (Carvalho 2017). Globally, 355,000 people died each year with excessive exposure and inappropriate use of toxic chemicals (Alavanja and Bonner 2012). Pesticides may attribute to the soil, plants, move with eroded soil, dissolve in water,

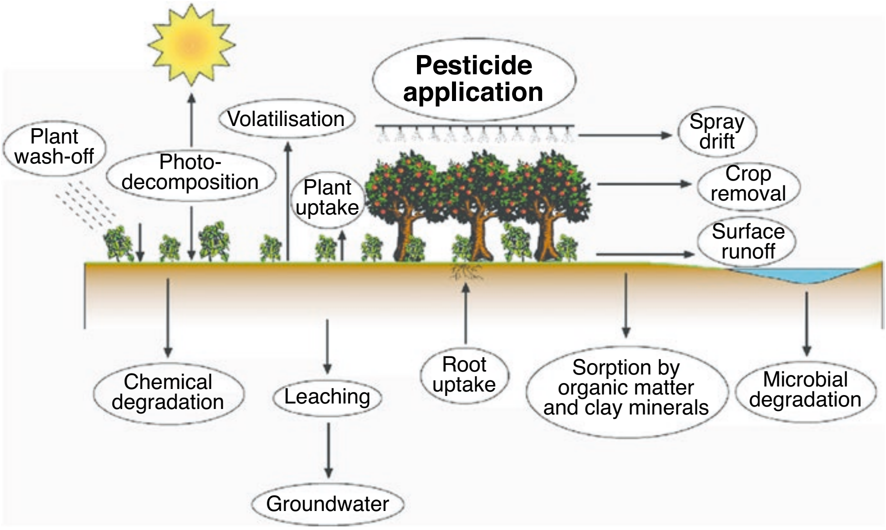

Fig. 10.5 The environmental outcome of pesticides. (Adapted from Sarmah et al. 2004)

leach, volatilize, and become airborne (Kerle et al. 2007; Tiryaki and Temur 2010). The environment is affected by pesticides via bidirectional sources, i.e., point-source and nonpoint-source pollution (Viman et al. 2010). The former is contamination that comes from a specific and identifiable place, while the latter is the contamination that comes from a wide area (Toth and Buhler 2009). Once the pesticides are disposed to the environment, they enter into physical, biological, and chemical processes which in turn affect their behavior, efficiency, and persistence (Fig. 10.5; Briggs 2018; Sarmah et al. 2004).

10.3 Removal Strategies of Pesticides

The prominent stability and water solubility of pesticide residues determine their persistence in the ecosystem. The physical, chemical, or biological technologies are used to reduce, eliminate, or stabilize pesticides in the soil (Marican and Durán-Lara 2018; Saleh et al. 2020). Each treatment technique has its limitations in operational costs, efficiency, operability, reliability, and toxic byproducts (Khalid et al. 2017; Saleh et al. 2020). The generations of many emerging contaminants that led to the development of eco-friendly treatment techniques are presented in (Fig. 10.6). Site characteristics, concentration, and type of pesticides should be considered during designing pesticides removal strategies (Morillo and Villaverde 2017).

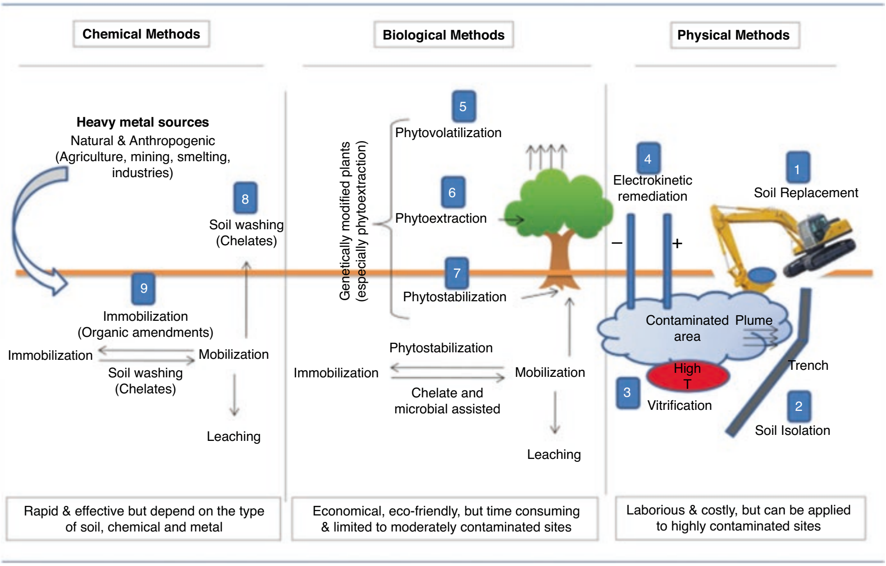

Fig. 10.6 Different soil treatment approaches. (Amended from Khalid et al. 2017)

10.3.1 Physical and Chemical Methods

One way of pesticides treatment option is by using physical and chemical methods. The majority of them are costly, destructive (which may implicate some level of hazard), and time-consuming (Khalid et al. 2017; Monteiro et al. 2012). Activated carbon and oxidation systems are energy-demanding, expensive, and increase local water prices by 10–40% (Ågerstrand et al. 2015). Physical, chemical, and physico-chemical degradation have resulted in further environmental deterioration (Huang et al. 2008). This necessitates the application of economical and eco-friendly pollutants removal options (Monteiro et al. 2012).

10.3.2 Biological (Bioremediation) Processes of Remediation

Bioremediation is a process in which bacteria, algae, plants, fungi, and other biota are involved in the process of contaminant removal (Garcia-Rodríguez et al. 2014). During this process, contaminants are degraded, altered, immobilized, or detoxified. The biological method is an attractive and greener technology that completely

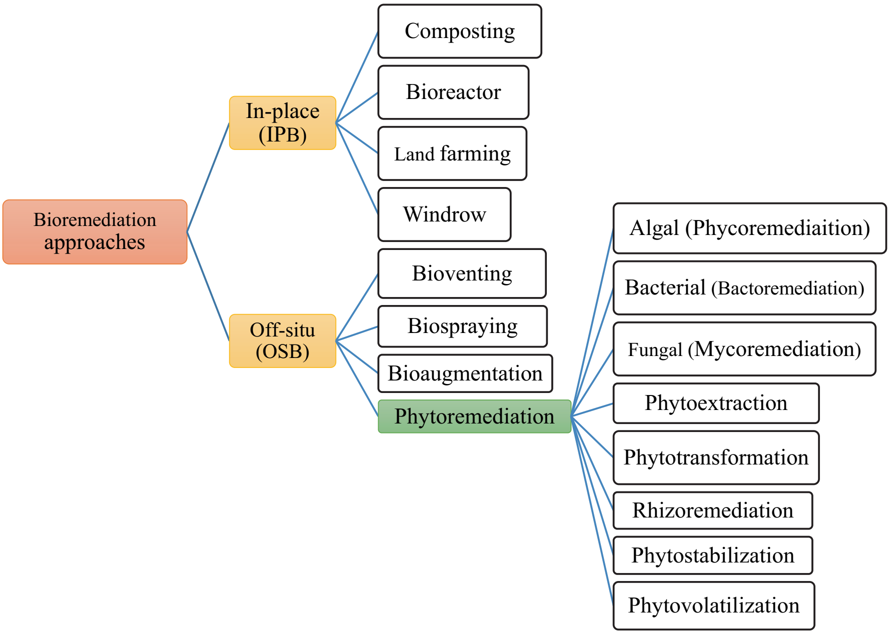

Fig. 10.7 The different types of contaminants and their bioremediation techniques

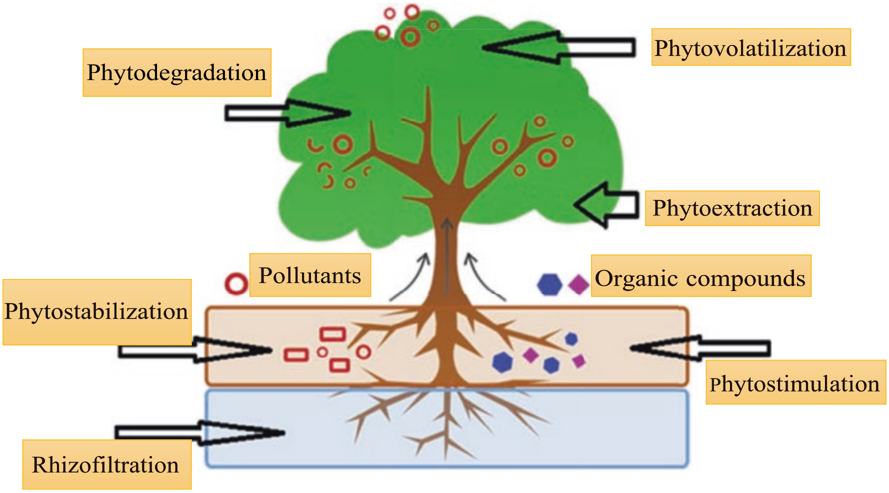

Fig. 10.8 Different types of phytoremediation practices. (Adapted and modified from Schnoor 1997)

converts neutralized contaminants and minimize their harmful effect (Nwankwegu and Onwosi 2017; Sinha et al. 2009).

Ex situ and in situ are the two major types of bioremediation techniques based on application sites (Azubuike et al. 2016). During the in situ bioremediation method, pollutants are treated on the place of contamination (natural site) but contaminants are transported from natural place during ex situ bioremediation (Caliman et al. 2011). Composting, phytoremediation, and bioaugmentation are the main bioremediation methods by involving a diverse group of organisms (Fig. 10.7). Many bacterial genera of *Alcaligenes*, *Flavobacterium*, *Pseudomonas*, and *Rhodococcus* are involved in pesticide degradation (Boricha and Fulekar 2009; Richins et al. 1997). There are various factors for the choice of the most appropriate and feasible in situ or ex situ bioremediation techniques (da Silva et al. 2020).

Phytoremediation uses plants as the main tool to remove different contaminants from the environment by involving diverse mechanisms (Fig. 10.8; Schnoor 1997).

10.3.2.1 Off-Site Bioremediation Approaches (OSB)

Off-site biotreatment (OSB) is the removal of contamination out of their natural site (Pandey et al. 2009). During OSB, contaminated soil is transported to another location for treatment and this approach makes OSB more expensive since it incurs the cost of transportation (Azubuike et al. 2016).

Contaminated Soil Treatment

Contaminated soil treatment is a land farming off-site bioremediation (OSB) technology in which contaminants are mixed with amendments in the upper soil horizon (Castelo-Grande et al. 2010). This process is a proven soil remediation technology that reduces the concentration of contaminants found in the soil (Parween et al. 2018). Soil contains microbes (fungi, algae, and bacteria) that can metabolize pesticides to enhance the remediation process. Land farming is a cost-efficient and eco-friendly approach to implement (Morillo and Villaverde 2017). The periodic turning of contaminated soil helps to increase aeration, moisture, nutrients affect pollutants biodegradation process by stimulating the activities of autochthonous microorganisms (Sharma 2020). Bhadbhade et al. (2002) have also described 83–93% of the degradation of the organophosphorus pesticide by soil bacteria. In another study, a 96% reduction in isoxathion using bacteria (Ohshiro et al. 1996). Furthermore, Tang and You (2012) have verified that bacteria were capable of degrading 33.1–95.8% of triazophos pesticides in soil indicating the efficiency of land farming in the removal of toxicants.

Composting

It is an aerobic process of degrading organic wastes into humus-like fertilizer by the involvement of microorganisms. The breakdown of contaminants is accelerated due to the heat produced during degradation (Niti et al. 2013). Microorganisms present during composting of wastes with pesticides play a significant role in bioremediation (Castelo-Grande et al. 2010; Yañez-Ocampo et al. 2016). The incorporation of different leftover wastes brings beneficial microorganisms with pesticide degradation potential (Briceño et al. 2007). Three successions of microbes occur during composting, i.e., psychrophilic, mesophilic, and thermophilic (Pavel and Gavrilescu 2008). Petruska et al. (1985) have indicated that diazinon 22% and chlordane 50% are lost during cow manure and sawdust composting due to volatilization. Singh (2008) has also identified 96.03% endosulfan degradation efficiency as a result of composting.

10.3.2.2 In-Place Bioremediation (IPB)

In-place bioremediation (IPB) remains a technology that removes contaminants under the natural environment without the need for excavation (Pandey et al. 2009). Strobel et al. (2011) have found that the effectiveness of IPB can be enhanced by improving the chemotactic behavior of the degrading microbes. White-rot fungi can be used in pesticide bioremediation due to the lignin-degrading potential of their enzyme complex (Magan et al. 2010).

Bioaugmentation

Bioaugmentation is on-site treatment practice done with the addition of cultured microorganisms to the surface of the soil for contaminant degradation (Cycoń et al. 2014). It is considered a green technology because of its eco-friendly approach to contaminant removal (Cycoń et al. 2017). The presence of a complete catabolic pathway would ensure the complete mineralization of the target pesticides (Isaac et al. 2017). Castro-Gutiérrez et al. (2019) have indicated atrazine (68.4%), carbendazim (96.7%), carbofuran (98.7%), and metalaxyl (96.7%) removal with a biomixture of the active core of bio-purification systems complemented with *Trametes versicolor*. A pesticide carbofuran is effectively removed from the contaminated site by *T. versicolor* inoculation (Madrigal-Zúñiga et al. 2016). Moreover, 85–90% atrazine reduction was achieved using *T. versicolor* (Bastos and Magan 2009). A novel bacterium (*Achromobacter xylosoxidans* PY4) had a 50% potential in metabolizing aromatic carbon rings (Nzila et al. 2018).

Phytoremediation

One of the promising cost-effective and eco-friendly strategies is phytoremediation or plant-assisted bioremediation and employed for over 300 years (Trapp and Karlson 2001; Zavoda et al. 2001). Phytoremediation is a solar power-driven technique that used pollutant scavenging potential plant species (Mir et al. 2017). In this process, contaminated sites are treated as the pesticides are take-up by plants and converted to less toxic ones (Singh and Singh 2017). Plants eliminate pollutants via phytoextraction, phytodegradation, phytovolatilization, and rhizodegradation (Truu et al. 2015). Plants deliver a promising microenvironment that facilitates contaminants degradation using both rhizospheric and endophytic bacteria (Niti et al. 2013).

Successful toxic herbicide residues reduction by bacterial endophytes in plants was investigated earlier (Germaine et al. 2006). In the contaminated soil, improved atrazine, metolachlor, and trifluralin reduction observed in the place where *Kochia* sp. was planted (Coats and Anderson 1997). Herbicides isoproturon and glyphosate are eliminated from contaminated water by planting *Lemna minor* (Dosnon-Olette et al. 2011). Genetic engineering of both microbes and plants provides a promising bioremediation approach (McGuinness and Dowling 2009). A growing body of evidence shows that transgenic plants are produced to avoid different pesticides from contaminated places (Kawahigashi 2009). Fifteen different persistent organochlorine pesticides were successfully reduced by *Ricinus communis* after 66 days of evaluation (Rissato et al. 2015).

Mycoremediation

It is the involvement of fungi in pollutant removal (Kulshreshtha et al. 2014). Toxicants/pollutants are accumulated inside fungal structures and are also used as a carbon source upon enzymatic degradation (Adenipekun and Lawal 2012). Accordingly, these transformation and detoxification processes can efficiently remove pesticides from the ecosystem (Tortella et al. 2005). The presence of an extended hyphal network and uniqueness preferred fungi in pesticide remediation (Chen et al. 2012).

Ligninolytic fungi secrete several extracellular enzymes to transform recalcitrant pollutants (Anastasi et al. 2013; Harms et al. 2017). Saprotrophic fungi produce many enzymes for pesticide degradation (Wu et al. 2015). There are many white-rot fungal strains reported as lindane, diuron, and other pesticides degraders (Sagar and Singh 2011; Singh et al. 2020).

Bactoremediation

Pesticides bioremediation uses beneficial bacterial strains as an alternative option (Gavrilescu 2005). The surging need for green technology forces in searching potential bacteria strains (Jay et al. 2011). There are many bacterial genera with a

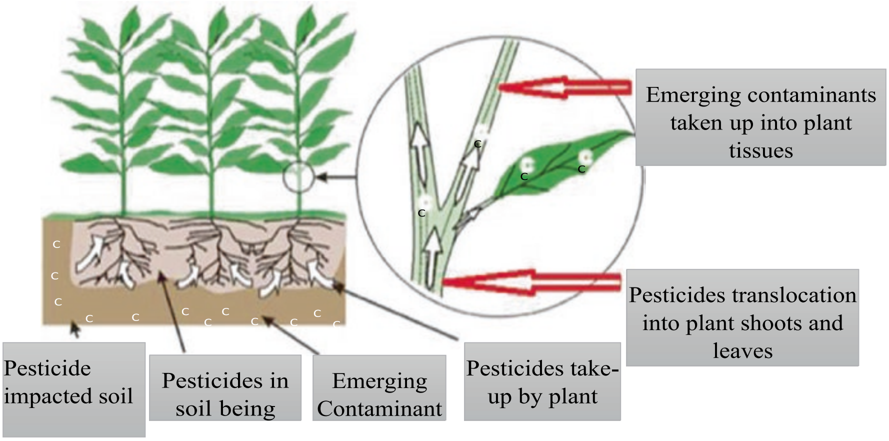

Fig. 10.9 Phytoaccumulation of organic contaminants. (Adapted and modified from Technology and Council 2009)

promising pesticides removal efficiency (Ortiz-Hernández et al. 2013). Bacterial species are known to hydrolyze bonds responsible for the enhancement of organophosphorus pesticide degradation (Singh and Walker 2006). Many bacterial species are effective in pollutant degradation (Huang et al. 2008). A 100% diazinon and organophosphate removal is seen in *Stenotrophomonas* sp. (Deng et al. 2015). *Arthrobacter*, *sulfonivorans*, *Variovorax soli*, and *Advenella* sp. bring 22–69% diuron mineralization (Morillo and Villaverde 2017). The process of degradation depends on bacterial type due to the release of different enzymes including oxygenase, hydroxylase, hydrolase, and isomerase (Karigar and Rao 2011).

Phycoremediation

Phycoremediation is one of the green technologies used to remove toxic substances via the application of microalgae or macroalgae (Rao et al. 2019). The fast growth nature, utilization of light and organic carbon offer microalgae a better pollution degradation (Dębowski et al. 2020). Internal defense mechanisms of microalgal species help to survive in contaminated sites (Torres et al. 2017). Many pollutants and different heavy metals are eliminated from the contaminated sites using microalgae (Danouche et al. 2021). During 11 days of treatment, the removal and reduction of atrazine herbicides and lindane by green algae *Selenastrum capricornutum* have been confirmed in the earlier investigation (Friesen-Pankratz et al. 2003). Moreover, chlorophenol is transformed and stored in the cells of *Chlorella* VT-1 by reducing its toxicity level (Scragg et al. 2003).

Phytoextraction/Phytoaccumulation

Phytoextraction is the ability of plants or algae to eliminate contaminants from their site via storage in their parts. The contaminants are phytoextracted in the aboveground plant parts (Singh and Singh 2017). Shoots and leaves are the plant parts where the pollutants accumulated (Abdel-Shafy and Mansour 2018). Hyperaccumulators and chelators are the main processes in phytoextraction (Utmazian and Wenzel 2006). Mukherjee and Kumar (2012) have confirmed that 47.2% and 34.5% organochlorine pesticide (endosulfan) removal using mustard (*Brassica campestris*) and maize (*Zea mays*) respectively. Transport protein inhibitors prevent the entrance of pollutants into the plant but help to be sequestered into the vacuoles of root cells (Fig. 10.9; Technology and Council 2009).

Phytodegradation (Phytotransformation)

Phytodegradation/phytotransformation is a process of pollutant degradation using microorganisms within plant tissues (Abdel-Shafy and Mansour 2018). Detoxification, transformation, and mineralization are important features involved in contaminant metabolism (Singh and Singh 2017). In this process, contaminants are degraded using microbial/plant enzymes. There is no complete breakdown (H_2O, CO_2, etc.) for complex and recalcitrant compounds by plants (Newman and Reynolds 2004). By and large, different pesticides are transformed in plants that release different enzymes (Kurasvili et al. 2014). For instance, enzyme glucosyltransferases detoxify organochlorine in *Phragmites australis* plants (San Miguel et al. 2013).

Rhizoremediation

Rhizoremediation is the process of pollutant degradation using catalytic microorganisms in association with plants around the plant rhizosphere (Khan et al. 2013; McCutcheon and Schnoor 2004). In this method, pesticides are degraded by naturally occurring rhizosphere due to the release of nutrients (Niti et al. 2013). Plant root exudates act as a carbohydrate source for microbial growth and are used as chemotactic signals for microbes (Dzantor 2007). The interaction of mycorrhizal fungi and ryegrass rhizosphere in bioremediation of chlorpyrifos is found effective (Korade and Fulekar 2009). The microbial populations near the rhizosphere of plants are stimulated by organics released from roots (Miya and Firestone 2001; Shaw and Burns 2007). The bacterial species *Klebsiella*, *Pseudoarthrobacter*, and *Pseudomonas* are known to transform lindane from 10% to 15% (Nagpal and Paknikar 2006).

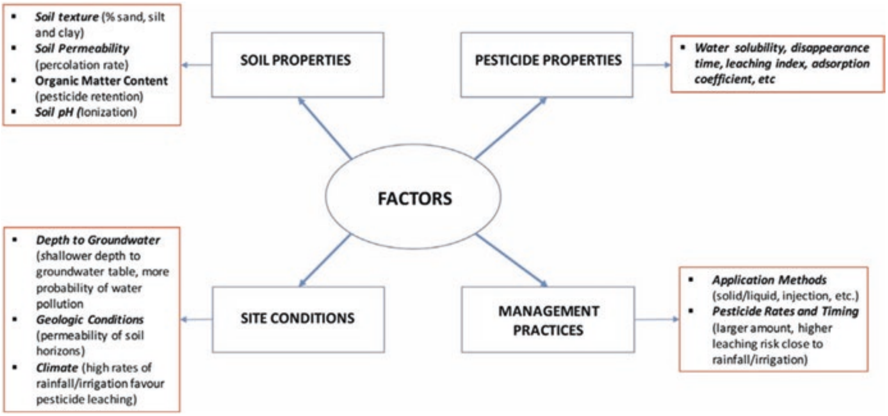

Fig. 10.10 Aspects of pesticides bioremediation in the soil. (Adapted from Gavrilescu 2005)

10.4 Detrimental Factors for Emerging Pesticides Bioremediation in Soil

The final fate of pollutant bioremediation is determined by the chemical nature and concentration of pollutants, characteristics of the environment, and microorganisms present in the soil (El Fantroussi and Agathos 2005). Soil type, temperature, pH, presence of oxygen, and nutrients are some of the factors that remarkably influence microbial pesticides degradation (Rani and Dhania 2014). Higher pollutant degradation is realized near the sub-surface soil due to higher nutrient levels (Lauber et al. 2009). Several factors potentially limit pesticides treatment strategies (Gavrilescu 2005). Soil is the ultimate sink of the pesticides applied in agriculture and acts as a storehouse of various kinds of microbes (Fig. 10.10).

Water (moisture content) is required for the biodegradation process (Riser-Roberts 1998). Generally, the optimum moisture level of 25–85% water holding capacity is needed for soil bioremediation (Niti et al. 2013). Evidence is accumulating that fluroxypyr degradation is slow under low water holding capacity (Tao and Yang 2011). Pesticides degradation is also limited if the nutrient availability and oxygen concentration are minimal. Hence, microbial augmentation can enhance nutrient availability for better pollution removal (Eskander and Saleh 2017). The pH of the soil affects the availability of nutrients and microbial activity and thus reduces the bioremediation process (Odukkathil and Vasudevan 2013). For instance, some strains of bacteria can degrade over 70% of petroleum at pH 7 and 9 (Xu 2012).

Temperature is the other influential factor affecting the rate of pesticide biodegradation by governing the speed of enzymatic reactions within microorganisms. Soil temperature less than 20 °C is not conducive for atrazine and lindane removal and causes leaching from the contaminated site (Paraíba et al. 2003). On the other hand, better oxyfluorfen biodegradation was seen at 40 °C (55.2–78.3%) than at 28 °C (17.5–36.6%) (El Hussein et al. 2012). Thus, the optimum temperature for biodegradation of pesticides may depend on the chemical nature of a pollutant and a microbe involved in the process of removal.

10.5 Merits and Demerits of Biodegradation of Pesticides

Appropriate methods, suitable environments with the right microorganism are needed for a successful bioremediation process (Cycoń et al. 2017). Residues from the treatment are usually harmless products (H_2O, CO_2, and cell biomass) (Rani and Dhania 2014; Singh 2008). In situ bioremediation is an appropriate bioremediation or phytoremediation technique and would be self-maintained through all the year. Bioremediation has also its limitations. Few bioremediations have been found for each pesticide. One important issue is the time required for remediation because biological processes are slow compared to conventional physical and chemical methods. However, bioremediation is superior to physical and chemical remediation methods since the latter is destructive, costly, and tedious.

10.6 Genetics for Pesticide Degradation

Many pollutants are recalcitrant and remain resistant to microbial attack. This condition necessitates an urgent need for microbial genetic manipulation. Correspondingly, genetic engineering is a better solution for microbial improvement for a better remediation process (Janssen and Stucki 2020). Soil contains metabolically versatile microbes but the search for new strains with potential pesticide degraders requires genetic modification of existing genetic material from metagenomic studies (Maheshwari et al. 2017). Thus, it is possible to develop bacterial strains that can adapt and immobilize pesticides with a high degradation rate (Saez et al. 2014). The modifications and manipulation of microbes to effectively remove contaminants from the site are a suitable and effective approach (Huang and Lu 2021; Ortiz-Hernández et al. 2013). Genetic alterations allow an alternative for better pesticide degradation (Zulfiqar and Yasmin 2020). Accordingly, herbicides 2,4-D and 2,4,5-T were mainly degraded by *Pseudomonas* sp. and *Alicaligenes* sp. (Huong et al. 2008).

10.7 Future Perspectives

The increased food demand to feed the global growing populations prompts the application of different pesticides to increase the production and productivity of crops by controlling plant diseases and pests. However, pesticides application brings serious harm to human and environmental health and demands eco-friendly solutions. Thus, bioremediation technologies are considered an eco-friendly strategy to overcome problems associated with synthetic agrochemicals. The understanding of the environmental fate and an integrated approach for pesticide remediation has a vital impact on the knowledge of pesticide science and biological applications. Furthermore, to avoid bioaugmentation, it is essential to find the most satisfactory bioremediation strategies.

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Chapter 11
Role of Metal Nanomaterials in Bioremediation of Pesticides

Rekha Goswami, Barkha Kamal, and Abhilasha Mishra

Abstract Due to increased global demand in agriculture, pesticides are broadly used in agricultural field for controlling pests that infest crops. The overall use of pesticides in the world has reached approximately 2 million tons. The World Health Organization classified itself as very dangerous and highly hazardous. Use of more chemical pesticides in agriculture causes more pollution and also leads to biomagnifications in different trophic level of organisms that affect biodiversity. Several technologies are being used for controlling pollution, among them nano-biotechnology is an alternative technology for remediation of pollution. Bioremediation method utilizes microbes to dispose of pollutants. Carbon nanomaterials, metal nanoparticles, magnetic nanoparticles, and quantum dots are examples of nanomaterials used for water exceptional monitoring, including those used to detect trace contamination and pathogens. Nanosized elemental or zero-valent metallic nanoparticles, i.e., of iron, silver, gold, copper palladium, and nickel have proven promoting effects towards contaminated sites with different hazardous pesticides. This chapter is an effort to consciousness on the promising application of metal nanomaterial-based technology and its assimilation with diverse essential tactics related to the bioremediation of pesticides.

Keywords Pesticides · Metal nanomaterial · Bioremediation · Agriculture · Pollution

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11.1 Introduction

Population growth is making more demand in agriculture manufacturing for both industrial advancement and urbanization which are being important resources of environmental pollution in the course of the twentieth century. Pesticides are being used to manage or control the pest populations below the economic injury level. Pesticides are chemical compounds that are broadly used in agricultural field for controlling pests that infest crops. These are the substance or mixture of substance which differ in their physicochemical properties. Hence, they could be classified on the basis of their properties. Moreover, numerous pesticides based on the demands are categorized into different classes. Presently, the three most popular classifications of common pesticides are entry mode, pesticide-based function, and pesticide-based organism. The overall use of pesticides in the world has reached approximately 2 million tons. The World Health Organization classified itself as very dangerous, highly hazardous, and moderately dangerous in four different classes based on the toxicity of pesticides (Pimentel 2002). Due to developing industries and use of chemical pesticides in agriculture, which causes more pollution and also leads biomagnifications in different trophic level of organisms that affect biodiversity. Several technologies are being used for controlling pollution, among them nanobiotechnology is an excellent approach for the environmental remediation. In the present scenario, many pollutants like hydrocarbons, heavy metals, pesticides, and other toxic substances are being more threat to our surroundings. Among these pollutants, contamination of soils, reduction of soil fertility, air and water are polluted with various dangerous substances. Although many conventional methods, i.e., precipitation, electrocoagulation, and adsorption on various substrates are in use, but a safer and cost-effective and environmentally sustainable approach is highly recommended for environment contaminant remediation (Fomina and Gadd 2014). Microorganisms are popularly used in bioremediation as it is economical method compared to other conventional methods. Bioremediation using microorganisms is greatly dependent on the availability of particular microbial species and combination of favorable environmental conditions (Adams et al. 2015). Bioremediation methods are effective for the treatment of contaminated water and soil due to its ability to degrade contaminates by using natural microbial activities which can be easily controlled by using different strains. Bioremediation includes any method that utilizes plants, microbes and their extracts or enzymes to restore the natural world after it has been contaminated (Rathore et al. 2014; El Amrani et al. 2015).

Nanotechnology has the capacity to offer a sustainable option to the worldwide demanding situations associated with defensive soil, water, and providing air cleaner. Nanoscience allows materials to be engineered and controlled at the molecular and atomic levels. Nanomaterials can be produced with specific functions that enable it to identify a specific contaminant within a mixture. The length of nanomaterial along with their excessive floor-to-quantity ratio results very precise detection

(Das et al. 2015; Asztemborska et al. 2015). Carbon nanomaterials, metal nanoparticles, magnetic nanoparticles, quantum dots are examples of nanomaterials used for water exceptional monitoring, including those used to detect trace contamination and pathogens (Xue et al. 2016, 2017). Zero-valent metallic nanoparticles or nanosized elements, such as of iron, silver, gold, copper palladium, and nickel have proven promoting effects towards contaminated sites with different hazardous pesticides. (Li et al. 2016). Despite the fact that technology has received a lot of studies and awareness, there is still a demand to analyze the trends that have emerged in investigating bioremediation during the last decade; some of the areas of focusing include the comparability of existing data, the appropriate use of existing technique, accessibility of in-depth laboratory investigations, geographical diversity, and a lack of knowledge in the field (Adams et al. 2015).

Bioremediation-related nanotechnology is a technological field that can examine several components to help clean the environment and to support life-growth situations. Due to distinctive characteristics of nanomaterial, it attains immense attention from researchers and scientist in various fields like water remediation, biomedical application, degradation of pesticides residue, etc. To increase the annual production of agricultural crops farmers mostly apply or spray pesticides over agricultural fields to control crops from pests, weeds, and any disease. Excessive use of pesticides degrades the soil profile and nearby water bodies. This may lead to negative influence in the growth pattern of flora and fauna. To avoid the drastic effects of pesticides, residue was majorly done by means of bioremediation. To enhance the potentiality of bioremediation technology, it will combine with nanotechnology for an effective reduction of the toxicological effects of pesticides (Rizwan et al. 2014). This method is known as nano-bioremediation which found to be more sustainable and cost effective in nature (Koul and Taak 2018). The degradation of pesticides residue by means of biological processes combining with nanomaterials provides more surface area for binding, less toxic effect on microorganism, enhances the activity of microorganism during eradication of pesticides contamination and found to be more suitable (Kumari and Singh 2016).

Additionally, some researchers name it on the basis of organism used to remediate the contaminants, such as phyto-nanoremediation (plant based), microbial nanoremediation (microbes based), and animal-based remediation (El-Ramady et al. 2017). It is reported that the working mechanism in between nanoparticles, biota/microbes, and contaminants depends on many factors such as morphology of nanoparticles, chemical behavior of nanomaterials and pollutant, pH value, temperature, media, microbes types, etc., which play a vital role during nano-bioremediation (Tan et al. 2018). Various metal, bimetallic, and metal oxides-based nanoparticles are the major categories which have been used for the removal and detection of hazardous pesticides contaminations in different regions. The existing chapter is an effort to consciousness on the promising application of metal nanomaterial-based technology and its assimilation with diverse essential tactics related to the bioremediation of pesticides.

11.2 Main Classes of Chemical Pesticides Utilized in Agriculture and Their Harmful Effects

The use of various synthetic pesticides has increased greatly and contributes to excessive crop yield growth. Soil, groundwater, and sediments constitute the ultimate sink for these contaminants, which are divided into simpler forms or persistent. According to the Stockholm Convention on Persistent Organic Pollutants, pesticides account for 9 out of 12 persistent organic compounds. For synthetic pest control, more than 1000 insecticides have been promoted. Pesticides incorporate herbicides, insect sprays, bactericides, and fungicides and so forth (Adams et al. 2015). Artificially, pesticides are of an extensive assortment, including chlorinated compounds, sweet-smelling rings, nitrogen and phosphorous-containing mixtures, and others. The degree of chlorination and lipophilicity of chlorophenol increases its toxicity and bioaccumulation capacity, Benzene's subordinates are used in a wide range of pesticides. Since the aromatic ring has a large negative reverberation force, benzene and its derivatives are constantly accumulating mixtures (Igbinosa et al. 2013). Adverse effects on water, air, and soil due to extreme use of chemical pesticides are shown in (Fig. 11.1). Major chemical pesticides classes include organochlorine, organophosphate, synthetic pyrethroids, and carbamates (Xue et al. 2016, 2017).

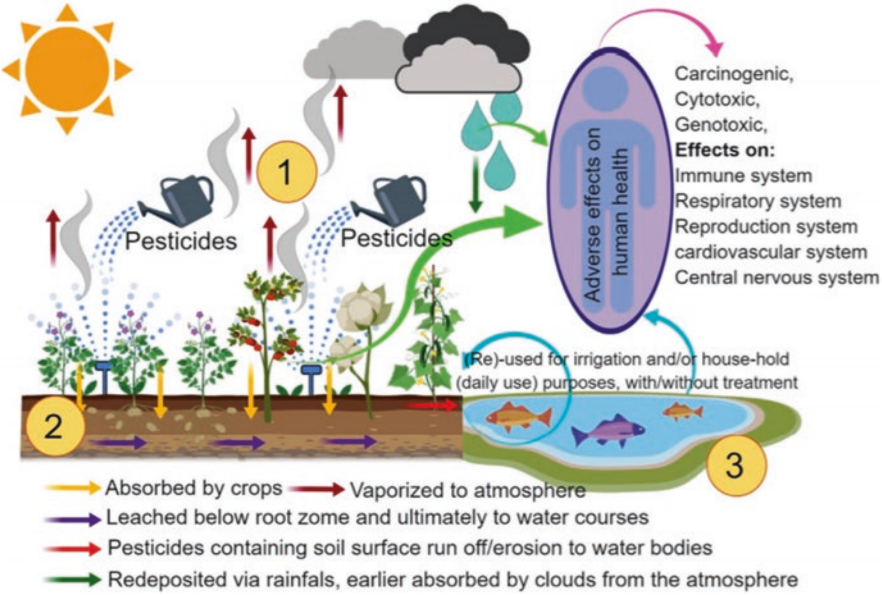

Fig. 11.1 Excessive use of chemical pesticides and adverse effect in modern agriculture; (1) air, (2) soil, and (3) water. (Reproduced with permission from Liu et al. 2019)

11.2.1 Organochlorine Pesticides

The first organic chemicals to be used to control pests and vectors were these. In broad spectrum, they have long-lasting low toxicity effects. They are, however, difficult to degrade in the natural environment due to their chemical stability. Their extensive use polluted the atmosphere and contributed to accumulation in mammals, resulting in poisoning or damage over time. As a result, organochlorine pesticides were outlawed in most cases and were eventually replaced by other pesticides. Organochlorine pesticides include endosulfan, DDT, and lindane, to name a few (Barragán-Huerta et al. 2007).

11.2.2 Organophosphate Pesticides

These toxins are distinguished by their various purpose and capability to control a wide range of pests. They are nerve toxic which used as a stomach toxic, a contact poison, or a fumigant. These biodegradable pesticides are pollutant-free, and slow the development of pest resistance. Organophosphate pesticides include methyl parathion, phosphamidon, and fenitrothion (Das et al. 2015).

11.2.3 Carbamates

These pesticides act in the same way as organophosphate pesticides, disrupting nerve signal transmission and causing the pest to die from poisoning. Carbamates can also be used as stomach poisons, touch poisons, and fumigants. Furthermore, since their molecular structures are largely identical to those of natural organic compounds, they can be degraded naturally with minimal emissions. Carbamate pesticides like propoxur (Tewari et al. 2012).

11.2.4 Synthetic-Pyrethroid Pesticide

These pesticides are combined by imitating the structure of natural pyrethrins. When compared to natural pyrethrins, they are stable and have longer residual effects. Artificial pyrethroid pesticides are more harmful to insects as compared to mammals. Permethrin and allethrin are the example of synthetic-pyrethroid pesticides. The pyrethroids are utilitarian poisons that produce unfriendly impacts in an optional manner as a result of neuronal hyper edginess.

Harmful impacts of carbamate and organophosphate pesticides happen in the sensory system where synthetics disturb the protein that controls acetylcholinesterase, a synapse. World Health Organization (WHO) assesses that 1,000,000 pesticide harming cases happen each year worldwide. Not just this, a drawn-out proficient openness to these pesticides additionally brings about expanded danger of a few ongoing and deadly illnesses like malignancy. Around 100 dynamic fixings in pesticides have been found to cause disease in exploratory creatures or people (Pimentel 2002).

11.3 Pesticide Bioremediation

Advances in research and ingenuity have enabled us to use natural variety's capacity to reduce pollutants, a process known as bioremediation. The guideline of this strategy is to eliminate poisonous toxins from the climate or convert the harmful items to nontoxic items by utilizing microorganisms (Nawaz et al. 2011). This methodology is at present applied to disinfect soil, dregs, surface water, groundwater, and air. Due to comparatively low capital costs, least disruptive techniques, and inherently aesthetic design, this technique has become desirable alternatives to conventional cleanup technologies as compared to traditional physicochemical methods (Rajendran et al. 2003; Wasi et al. 2011a, b).

Pesticide consistency in nature results either of their physical and chemical properties or the absence of life forms capable of degrading them. Certain pesticides may be lost due to volatilization or corruption as a result of light, warmth, or stickiness. On the other hand, degradation caused by living things (biodegradation) may be able to significantly reduce pesticides' persistent presence in the environment. This knowledge could be used to enhance the disposal of the harmful effects of contaminations by using living organisms; this process is known as bioremediation. The organism's ability to clean up pesticides is basically founded on their biodegradation movement. In spite of the fact that bioremediation has been first and foremost accomplished utilizing microorganisms (microbes or growths), different organic entities like plants or green growth can be utilized (Núñez et al. 2020). Elimination of pollutants would be valuable but not always possible; however, it could be confined or immobilized by some organisms. Organisms, for example, can accumulate contaminants and reduce, but do not eliminate, their presence and environmental effect. That strategy, which is indeed employed, should be included in the concept of "bioremediation" (Tyagi et al. 2011). Bioremediators would be called those organisms which can bioremediate, for example, Algicides–Algae, Fungicides–Fungi. The strategy of Bioremediatory organism like Micro bioremediation or Bioremediation for Microorganism Phytoremediation for plants.

A fruitful bioremediation procedure requires a proficient bacterial strain that can degrade the biggest contamination to the least level. The rate of soil biodegradation is dependent on four parameters, i.e., microorganism physiological condition, pesticide or microorganisms availability, survival or proliferation at a contamination site of pesticide degrading microorganisms, and the sustained population. The biodegrading in surface soil is oxygen consuming and fast because soils have an enormous number of vigorous microorganisms and their number typically diminishes (Tewari et al. 2012).

11.3.1 In Situ Bioremediation

This technique is very effective and desirable because of cost effective and creates less disturbance as they remove toxins in the environment instead of exploring and transporting them. The soil depth that can be effectively decontaminated limits in situ treatment. By the circulation of aqueous solutions naturally occurring bacteria stimulate to degrade contaminants, biodegradation adds oxygen and nutrients to polluted soils. The most significant treatments are bioventing, biosparging, and bioaugmentation (Adams et al. 2015).

11.3.2 Ex Situ Bioremediation

Land farming is a simple procedure in which degraded soil is unearthed, spread over a prepared bed, and intermittently ploughed until toxins are corrupted. Composting is a procedure that combines polluted soil with nontoxic organic contaminants such as excrement or rural waste. Biopiles are a hybrid of soil fertilization and agro farming that provide an ideal environment for native oxygen consuming and anaerobic microorganisms (Philp and Atlas 2005). Ex situ treatment of water and soil syphoned up from a polluted tuft is accomplished using slurry reactors or fluid reactors.

Various methods used for ex situ and in situ bioremediation are shown in (Fig. 11.2). Most bioremediation technologies are intended to remove pollutants after they have been produced or released into the environment. Studies of the microbial population, activities, and enzymes in the soil can provide a mirror image of the soil's functional status. Bioaugmentation (adding an organism or enzyme to a contaminant) and biostimulation are two examples (Tyagi et al. 2011).

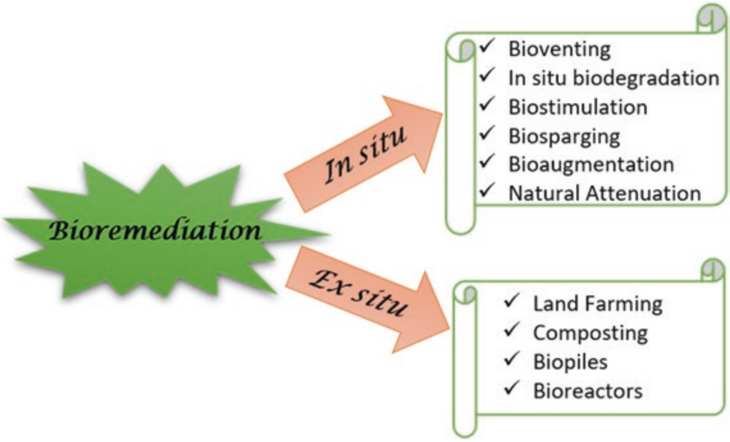

Fig. 11.2 Various bioremediation approaches for pesticides

11.4 Nano-Based Approaches for Pesticide Bioremediation

A series of technologies have been studied to identify systemic procedures to remove harmful pesticides from environmental matrices, including nanotechnology-based bioremediation. Understanding the interplay between the pollutant, nanomaterials (NMs), and microorganism is crucial because negative and positive impacts can occur. For instance, some nanomaterials are microorganism stimulants, whereas others are toxic. Therefore, it is crucial to select properly. For complete and effective pesticide bioremediation, detection, degradation, and removal of pesticide are three most important parameters. In physical and chemical processes, nanotechnology has remarkable advantages. Nanotechnology has a potential impact in above mentioned three categories: detection, degradation, and removal (Fig. 11.3).

Applications of various metal nanoparticles can effectively remove many hazardous substances from the environment in a shorter duration (Kalyani et al. 2021). Nowadays various nanomaterials are popularly used for bioremediation (Fig. 11.4). Metal nanomaterials are largely utilized for the detection of pesticides along with its elimination and degradation . These nanomaterials have been broadly categorized into the nanotubes, nanoparticles, and nanocomposites. Various forms of nanoparticles such as metal nanoparticles, bimetal nanoparticles, and nanoparticles metal oxide have been used in the detection and degradation of pesticide and are shown in (Fig. 11.4).

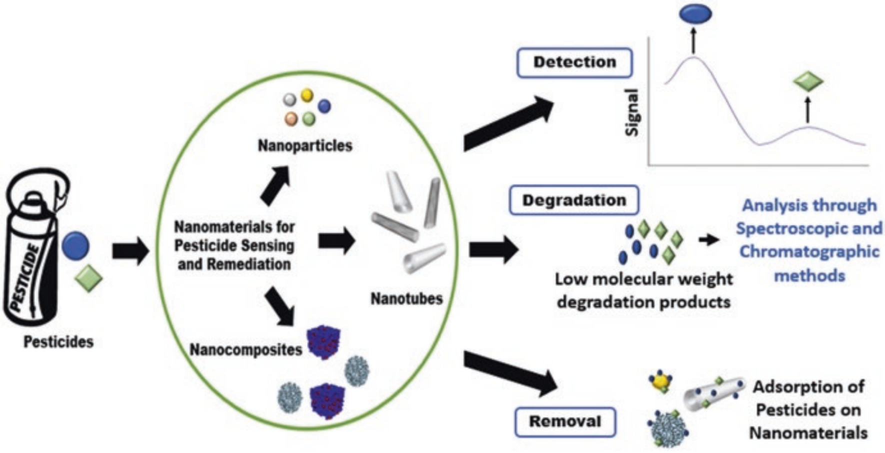

Fig. 11.3 A diagram depicting the use of nanomaterials for pesticide detection, degradation, and removal. (Reproduced with permission from Rawtani et al. 2018)

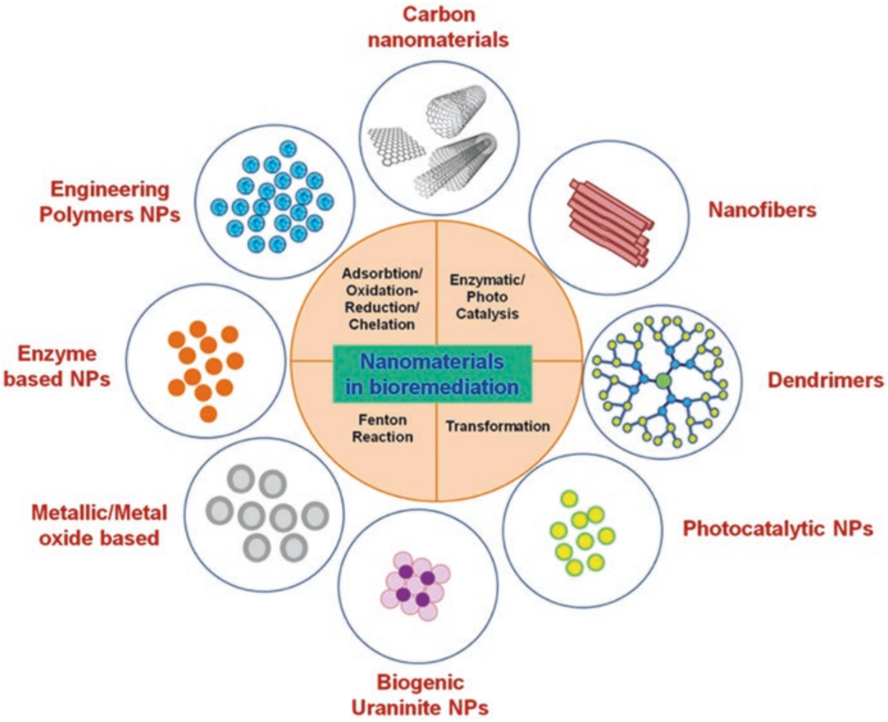

Fig. 11.4 Various types of nanomaterials used in bioremediation technique. (Reproduced with permission from Singh et al. 2020)

11.5 Role of Different Metal Nanomaterials in Detection of Pesticide Levels

Detection of pesticide levels before and after remediation is very important factor for deciding need and efficiency of any remediation technique. Pesticide identification is of great concern because of their toxicity, extensive use, and proclivity for bioaccumulation. Commercial pesticides already include over 800 active ingredients in over 100 separate substance groups. Carbamates, triazines, organophosphorus (OP), and neonicotinoids are the most common groups, and they have been the focus of nano-enabled pesticide detection till date (Kalyani et al. 2021). High insecticide level is a common source of pesticides (fungicides, herbicides, insecticides) in industry and agriculture. Not only is the trace content being measured, but also the section of high efficiency and low environmental pesticides present in food safety attractive (Das et al. 2015). Today's methods of detection are difficult and costly, limiting their uses. Applications of enzymes immobilized on various carriers such as mesoporous magnetic nanoparticles, nanoparticles, metal oxide and metal nanoparticles, and many other forms of nanomaterials are emerging in order to simplify the detection procedure. Experimentally successful in pesticide detection, the new biosensor based on the electrochemical method (Du et al. 2008) was demonstrated. Silicon nanoparticles (SiNPs), also used in biosensor fields, are widely used nanomaterials (Kalyani et al. 2021). Many of them are sensitive and can be used as a sensor care point in different sensors based on different physical principles and with rapid progress in instruments (Xu et al. 2016).

11.5.1 Nanosensor

The development of nanosensors in contaminant environments is growing rapidly and nanomaterials and identification agents are continually united in latest and innovative ways. Latest developments in sensor design have been designed to address the limitations of sensors of first generation like unspecific binding, nano parts aggregation, variation in particle size, and stabilization of nanoparticles. There remain issues of test sensitivity and selectivity in multifaceted environmental matrices, but rising numbers of reports indicate the stability and selectivity of their sensors using representative matrices. Robust sensors are a must when individuals are deployed (Kaushal and Wani 2017).

Main focus of researchers is to improve the specificity, sensitivity, and selectivity, of environmental monitoring sensors, either by focusing on the contaminant-recognition factor binding or by revamping the transduction and electronic interface to the sensing layer. Nano-based technique is helping to solve these problems in many ways. First, the nanoparticles' capacity to be immobilized with a broad variety of chemical and biological ligands aids in the sensor's specificity. Several researchers have documented coating nanoparticles with variety of ligands such as enzymes, DNA, proteins, and many more (Nune et al. 2009). The interaction of these ligands with the analyte is highly precise. Finally, the ability to make nanoparticles out of various metals improves conductivity and thus sensitivity. To detect organic contaminants, scientists have proposed employing porous silicon semiconductor nanostructures (Stefano et al. 2005). Photoluminescence is produced in porous silicone and in the presence of inorganic or organic molecules, this luminescence is quenched. This technology allows the detection of very low pesticide concentrations such as 1 ppm (Stefano et al. 2005). Nanosensors and nanoscale coatings are on the verge of marketing to replace more resistant and thicker polymer coating, nanosensors for the decommissioning of aquatic toxins, nanoscale biopolymers that improve the recycling and decontamination of heavy metals and nanosized metals that break down toxic organic matter at room temperature (Homaeigohar 2020). Furthermore, nanotechnology-based methods are less expensive and more efficient.

11.6 Green Synthesis of Metal Nanomaterial for Pesticide Bioremediation

Metal nanoparticles prepared by green synthesis methods are excellent for bioremediation of pesticide as it already has capping of biological material utilized for bioremediation. Microorganisms have potential to reduce the metal ions to form nanomaterials. Extracellular enzymes secreted by microorganism have tendency to synthesize pure nanoparticles (Kalishwaralal et al. 2010; Durán et al. 2011; Kumar et al. 2011; Alani et al. 2012; Tripathi et al. 2015). These metal nanomaterials are very effective in accelerating conventional bioremediation in which only microbes or plants are used. Figure 11.5 showing a schematic representation of the green synthesis process for the preparation of metal nanoparticles.

Specifically bacterial species have unique property of metal binding which makes them valuable for synthesizing metal nanoparticles having potential for bioremediation. Due to characteristics of having high volume of protein, fungi generally used when large amount of nanomaterials is needed to be synthesized. Comparatively for the synthesis of nanomaterials microbial method is slower than techniques using plants extract (Saravanan and Nanda 2010; Mishra et al. 2011). *Zingiber officinale*, *Abelmoschus esculentus*, *Eucalyptus*, *Mentha*, *Angelica*, *hypericum*, etc. were used for synthesizing the gold nanoparticles (Mishra et al. 2010; Pasca et al. 2014; Subbaiya et al. 2014; Suman et al. 2014; Sinha et al. 2015). For the extraction of iron nanomaterial through green synthesis by phytoextract species

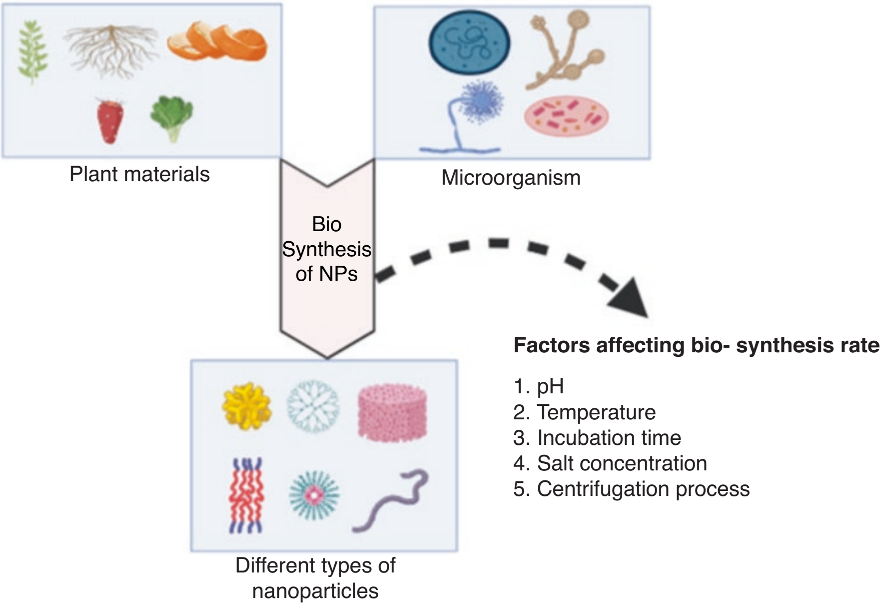

Fig. 11.5 Green synthesis process for the preparation of metal nanoparticles

of *Dodonaea viscose*, *Aloe vera*, *green tea*, *Rosmarinus officinalis*, etc. (Kumar et al. 2012; Phumying et al. 2013; Mahdavi et al. 2013; Pattanayak and Nayak 2013; Latha and Gowri 2014). Table 11.1 represents different plant species and microbes used for extracting various nanoparticles.

11.7 Metal Nanomaterials in Bioremediation of Pesticides

Metal Nps like gold, silver, iron, palladium, and platinum are highly used in different environmental concerns. Nanoparticles have unique chemistry and morphology which makes them suitable candidate to be used in pesticides removal through nano-bioremediation. The reaction that occurs over the surface of the nanomaterials plays a vital role in degrading pesticides and converts the hazardous material to simpler or less toxic compounds (Street et al. 2014). Nowadays, nanotechnological enabled approach is popularly used to remove the pesticides from contaminated soil or water. Researchers investigated the combination of metal nanoparticles with microbial cells for the degradation of pesticides (Wang and Tseng 2009). Figure 11.6 shows different type of metal nanomaterials used for nano-bioremediation of pesticides.

11.7.1 Metal Nanoparticles

11.7.1.1 Iron Nanoparticles

Nanoscale iron particles and their derivatives provide a number of remediation technologies with more alternatives. Commonly iron found under two valence states in nature, one is water soluble, i.e., ferrous iron Fe(II) and another is ferric iron Fe(III) which is water soluble below pH 3.5 and become insoluble above this pH. Under neutral to alkaline pH, it become stable with oxygen rich environment and precipitate as yellow/orange compound. Due to its retained magnetic properties, iron nanoparticles possess increased binding site during the removal of pollutant (Andrew et al. 2008). Researchers observed the potential of magnetic iron nanoparticles (MNPs) using laccase enzyme to degrade the chlorpyrifos an organophosphate pesticide. For this magnetic iron nanoparticles are developed by using co-precipitation method and nanoparticles size was about in between 10 and 15 nm. Results revealed that magnetic iron nanoparticle immobilized with laccase enzyme effectively degraded about 99% pesticides over 12 h at 60 °C and 7.0 pH. It has been also reported that 2,4-bis (1,1 dimethylethyl) phenol is the by-product obtained after the degradation process (Das et al. 2017).

Table 11.1 Different biotic components used in green synthesis of nanoparticles

Sources used for extracting metal nanoparticles		Nanoparticles synthesized	Morphology		References
			Size (nm)	Structure	
Bacterial strains	*Pseudomonas rhodesiae*	AgNP	20–100	Spherical	Hossain et al. (2019a, b)
	Bacillus siamensis		25–50		Ibrahim et al. (2019)
	Bacillus cereus		18–39		Ahmed et al. (2020)
	Pseudomonas poae		20–45		Ibrahim et al. (2020)
	Bacillus sp.		7–21		Gopinath and Velusamy (2013)
	Serratia sp.		10–20		Mishra et al. (2014)
	Pseudomonas sp., *and Achromobacter* sp.		20–50		Kaur et al. (2018)
	Aeromonas hydrophila	ZnO	57–72	Crystalline	Jayaseelan et al. (2012)
	Streptomyces spp.	CuO	78–80	Spherical	Hassan et al. (2019)
	Streptomyces capillispiralis	Cu	4–59		Hassan et al. (2018)
Plants	*Citrus limon*	ZnO and TiO_2	20–200	Polymorphic	Hossain et al. (2019a, b)
	Phyllanthus emblica	Ag	20–93	Spherical	Masum et al. (2019)
	Rosmarinus officinalis	MgO	<20	Flower	Abdallah et al. (2019)
	Matricaria chamomilla	MgO and MnO_2	9–112	Disc shaped	Ogunyemi et al. (2019a, b)
	Matricaria chamomilla	ZnO	50–190	Crystalline	Ogunyemi et al. (2019a, b)
	Lycopersicon esculentum		66–133		Ogunyemi et al. (2019a, b)
	Piper nigrum	Ag	9–30		Paulkumar et al. (2014)
	Artemisia absinthium		5–100	Spherical	Ali et al. (2015)
	Abelmoschus esculentus	Au	45–75		Jayaseelan et al. (2013)
	Syzygium aromaticum	Cu	15		Rajesh et al. (2018)

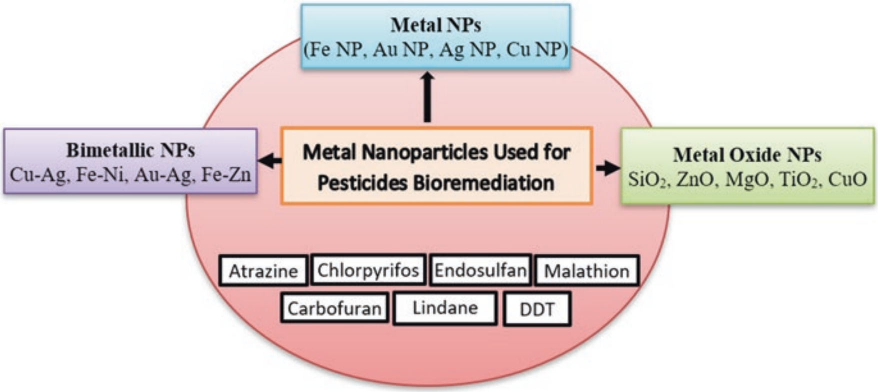

Fig. 11.6 Different types of metal nanomaterials used for nano-bioremediation of pesticides

Some study showed that iron nanoparticles are also used as catalyst for the removal of environment pollutant. Researchers evaluated the prospective of the iron nanoparticles synthesized using extract of *Euphorbia cochinchinensis* leaves for the degradation of 2,4-dichlorophenol pesticides. It was determined that the removal efficiency gets improved by 52% when iron-based nanoparticle was used as catalyst in the presence of hydrogen peroxide (H_2O_2) (Guo et al. 2017).

Zero-Valent Iron (ZVI)

Presently zero-valent iron (ZVI) is widely utilized for the management of pollutants due to its ease of use, effective pollutant degradation, low waste production, and secondary pollutants (Joo and Cheng 2006; Thompson et al. 2010). ZVI are classified into two types of ZVI (nZVI) nanoscale and iron reactive nanoscale (RNIP). nZVI particulates are 100–200 nm in diameter and consist of iron (Fe) with zero valence, whereas 50/50 wt% of RNIP particles consist of Fe and Fe_3O_4 (Yunus et al. 2012). Research has demonstrated that numerous pesticides are susceptible to ZVI degradation.

Many scientists used zero-valent iron nanoparticles for the elimination of lindane in which benzene, chlorobenzene, and dichlorobenzene are the by-product obtained (San Román et al. 2013). Zero-valent iron nanoparticles were utilized for the removal of nitrogen heteroatom compounds such as atrazine, olinate, picloram, chlorpyrifos, diazinon, and diuron (Joo and Cheng 2006; Kim et al. 2007; Jiang et al. 2018) to a limited extent. As the major reduction products, nitroaromatic pesticides with zero-valent iron were rapidly reduced to the corresponding amines. Only very small concentrations of intermediate products were found in certain reactions. Furthermore, analysis indicated a significant lower aromatic dechlorination than a reduction in nitrogen (Keum and Li 2004).

11.7.1.2 Gold Nanoparticles

Gold nanoparticles (AuNPs) due to different states of agglomeration show variation in color according to their size which makes it ideal for used in detecting various contamination level in the environment (Tsai et al. 2005). Due to ability of developing different coloration, the AuNPs were used in dipstick immunoassay for the detection of DDT (Dichlorodiphenyltrichloroethane). In this study, AuNPs were conjugated with anti-DDT antibodies to check its potentiality for decreasing the DDT concentration in the sample. The result was analyzed calorimetrically and intensity of the developed red color (due to AuNPs) was observed. Results demonstrated that the intensity of the developed color was increased with decrease in DDT concentration and reported with maximum intensity in absence of zero DDT concentration. Overall results showed that this kind of techniques may be used for rapid on-site testing to detect toxicity level of the pesticides (Lisa et al. 2009). Other researchers also used same techniques for detecting the organophosphorus pesticides (kitazine) in various samples like tomato, cucumber, grapes, etc. Here the detection of targeted pesticides was done on the basis of purple color development over the strips which were further confirmed by using ELISA (Enzyme Linked Immunoassay). Results showed that grape juice has highest color intensity during detection of pesticides (kitazine) (Malarkodi et al. 2017). Abd El-Aziz et al. (2018) prepared AuNPs with henna (*Lawsonia inermis*) extract. In this study also the degradation of DDT was monitored by evaluating the initial concentration taken, i.e., 10 or 20 mg/L. Result showed that after 72 h maximum degradation was found in the sample with starting concentration of 20 mg/L, i.e., 77% than 10 mg/L, i.e., 64%. The GC/MS spectra also confirm the presence of DDT by-product during degradation, i.e., (DDE), dichlorodiphenyldichloroethane (DDD), dichlorodiphenylmethane (DDM), and dichlorophenylethane (DCE). Researchers concluded that AuNPs have high potential for the cleanup of environmental toxic elements.

11.7.1.3 Silver Nanoparticles

Silver nanoparticles (AgNPs) showed versatile and fascinating properties among various metallic nanoparticles that involve in the bioremediation of the pesticides. The working efficiency of the AgNPs generally depends on the properties like surface properties, morphology, particles distribution, shape, composition, caping, etc. (Carlson et al. 2008). Various plant and microorganisms such as *Artemisia nilagirica*, *Sinapis arvensis*, *Nerium oleander*, *Trigonella foenum-graecum*, *Lantana camara*, *Pithophora oedogonia* were utilized to synthesize silver NPs (Kavitha et al. 2013; Vijayakumar et al. 2013; Rasheed et al. 2017; Lam et al. 2018). Some researchers used citrate for capping AgNPs for the prompt detection of dipterex, type of an organophosphorus pesticides found in different waste sample. Pink color masses were observed over citrate-capped AgNPs immobilized with acetylcholinesterase due to formation of thiocholine from acetylthiocholine through the enzymatic action of acetylcholinesterase. Study revealed that if the samples contain some concentration of pesticides, then the enzymatic based action of acetylcholine esterase was suppressed due to which thiocholine was not formed. Results confirmed that due to the presence of dipterex in the samples, there is no any color variation observed, which confirmed the presence of pesticides contamination in the water sample (Lia et al. 2014; Luo et al. 2017).

Siangproh et al. (2017) prepared a simple, rapid, economical detecting tool for detecting the concentration of herbicides contamination in canal water and groundwater samples. In this study AgNPs are coated with citrate to form colorimetry probe. Silica gel was used to adsorbed pesticides contamination. The presence of contamination was detected by color change mechanism from yellowish green to pale yellow. Other studies also showed that AgNPs were also used in combination with SERS (Surface Enhanced Raman Scattering) technique which helps in detecting the pesticides contamination at a very low level, this type of combined techniques is used to detect paraoxon and thiram type of pesticides (Wang et al. 2014). Same method was done in which cellulose nanofibers coated with AgNPs in combination with SERS used to detect thiabendazole in the samples (Liou et al. 2017).

11.7.2 Metal Oxide Nanomaterials

Crystalline metal oxides nanoparticles such as ferric oxide (Fe_2O_3), manganese oxides (MnO_2), aluminum oxide (Al_2O_3), titanium oxide (TiO_2), magnesium oxides (MgO), and ceric oxides (CeO_2) are very efficacious adsorbents used for the wide range of pesticides. Due to versatile properties of metal oxides nanoparticles such as fast kinetics due to nano size, high adsorption rate, less intraparticle diffusion distance, etc. (Cheng 2013; Bardajee and Hooshyar 2013; Tavakkoli and Yazdanbakhsh 2013; Dehaghi et al. 2014), nanocrystalline metal oxides also have tendency to abrade the hazardous pesticides contamination into the less toxic compounds (Fryxell and Cao 2012).

11.7.2.1 Titanium Oxide Nanoparticles

Titanium oxide ($TiO_{2)}$ nanoparticles are used for the removal of different types of pesticides found in the various samples. TiO_2 was used as photocatalyst for the removal of monocrotophos and chlorpyrifos pesticides from the water sample. During degradation process of the pesticides, various parameters such as pesticides concentration, pH of the examined solution, photocatalysts, etc. are also observed. Results showed that on increasing the illumination time, the photodegradation activity of TiO_2 also enhanced (Amalraj and Pius 2015; Selvakumar et al. 2018). Liu et al. (2015) prepared mesoporous TiO_2 NPs for the extraction of some organochlorine pesticides such as *trans* and *cis* chlordane, hexachlorobenzene (HCB), *p*,*p*-DDT, *o*,*p*-DDT, and mirex in the water samples. Prepared mesoporous TiO_2 NPs were used to prepare solid phase microextraction fiber and it was analyzed that prepared fiber shows greater efficiency in comparison to commercial based fibers towards the degradation of pesticides. Doping method is also with different metal ions (iron and silica) in combination with TiO_2 NPs for analyzing the degradation potentiality for carbendazim, type of fungicide. Due to adopting doping method, the photocatalytic behavior was boosted very high and removed about 98% of the fungicides under solar light (Kaur et al. 2016). Same technique of doping was used to prepare Cobal doped TiO_2 NPs used as photocatalyst to enhance the reaction rate of degradation for dichlorophenols in visible light (Hoseini et al. 2017). Schematic illustration of pesticide degradation mechanism of TiO_2 is shown in (Fig. 11.7).

Photocatalytic oxidation is a process that is eco sustainable for removing a broad variety of chemical toxins. It is a pre-treatment method which is appropriate to improve biodegradability of harmful and non-biodegradable contaminants. The treatment of the recalcitrant organic compounds can also be done using photocatalysis as a polishing step (Lasa and Rosales 2009). During photocatalysis, solid surfaces are photo-excited by radiation either near solar light or UV. Mobile electrons are therefore generated and positive surface charges. These electrons excited sites are essential steps for accelerating the oxidation and reduction reactions to degradation of pollutants (Reddy et al. 2013; Coronado et al. 2013). The advancement of nanotechnology has altered the reactivity and the detection limit of semiconductor photocatalysts. Based on this principle, photocatalytic degradation has treated a wide range of pesticides. The semi-manufacturing materials are different, such as ZnO, TiO_2, Fe_2O_3, CdS, and WO_3. Among all of these chemical stability, low toxicity, low cost, and high abundance of raw materials are main features that have made titanium dioxide most used. Many scientists reported photodecomposition of pesticides with TiO_2. The photodegradation of organochlorine pesticides on TiO_2 coated films exposed to airborne UV irradiation was investigated. Yu et al. (2007) investigated the photocatalytic activity of TiO_2 coated film for the degradation of organochlorine pesticides in air when exposed to UV irradiation. In a short period, all pesticides can be degraded. Under high power UV lamp, the degradation

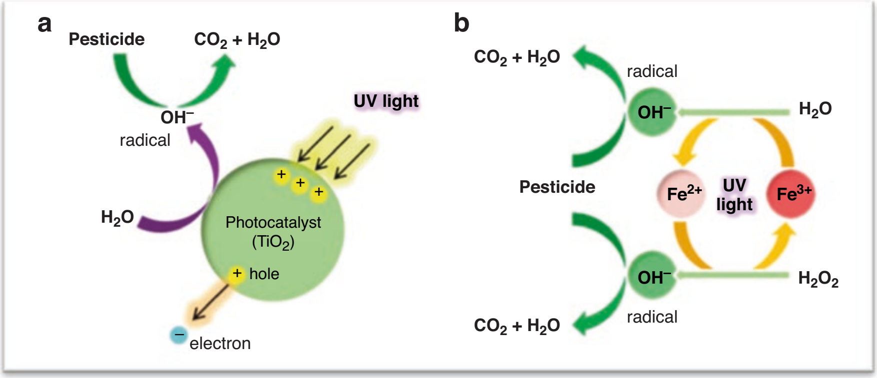

Fig. 11.7 Schematic illustration of pesticide degradation by TiO_2 (**a**) photocatalytic oxidation and (**b**) photo-Fenton degradation. (Reproduced with permission from Aragay et al. 2012)

rate was greatly increased. Another dicofol degradation photocatalytic study of TiO_2 UV-light-irradiation nanoparticles showed that dicofol could react with dicofol to produce chloride ions and lower chlorine-containing toxic compounds and could be completely damaged by active hydroxy radicals. By optimizing particle shape and dimension, maximizing reactive facets, reducing e^-/h^+ recombination through noble metal doping, and surface treatment to develop adsorption capacity, the photoactivity of nano-TiO_2 may be improved (Fujishima et al. 2008). The prepared catalysts are nanosized particles and anatase type according to the consequences. The catalysts had a redshift in the adsorption edge and showed greater absorption in the visible light field. In comparison to nonmetal doped titania, metal doping tends to be more effective in moving the absorbance spectrum to a visible area. Under UV and solar light illumination, the degradation behavior of Th-doped photocatalytic TiO_2 was investigated. These findings suggest that Th-doped photocatalytic TiO_2 with altered electronic properties is an adequate photocatalyst for oryzalin degradation in contaminated water when exposed to sunlight. Under UV irradiation, however, these modifications display only small variations in photocatalytic rates. First-order kinetics govern all photodegradation reactions. Many other photocatalysts such as WO_3, ZnO, etc. have been utilized to degrade pesticides in addition to titania (Mohagheghian et al. 2015). Eight pesticides were degraded to pilot plant size by the use of tandem $ZnO/Na_2S_2O_8$, as a photo-sensitive/poisoning sensitive and parabolic collector compound in natural sunlight (Navarro et al. 2009), in leaching water having pesticides and other solubilized chemicals as they penetrate through the ground. The results revealed that ZnO as a photosensitizer is a successful solution when using solar photocatalysis.

11.7.2.2 Zinc Oxide Nanoparticles

Nanoparticles of zinc oxide (ZnO) exhibit distinctive chemical and physical behavior. Due to surface modification, it shows enhanced sensing and catalytic behavior to effectively remove different contaminants present in the soil and water. Sharma et al. (2016) studied the degradation rate of methyl parathion and parathion, types of organophosphorus pesticides by the comparative effect of direct photolysis and by UV-ZnO nanocrystal. Recorded results showed that photocatalytic crystals were found to be more effective in degrading the pesticides.

Kaur et al. (2017) evaluated the effect of surface functionalization on ZnO nanoparticles for adsorbing the pesticides from the aqueous solution. ZnO nanoparticles were modified by 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF-IL), CTAB functionalized and bare ZnO nanoparticles. It was observed that 1-butyl-3-methylimidazolium tetrafluoroborate modified ZnO showed high adsorption (148.3 mg/g) followed by CTAB functionalized (90 mg/g) and bare ZnO nanoparticles (76 mg/g). Dehaghi et al. (2014) prepared chitosan/ZnO-based composite beads to analyze its potential towards removal of permethrin, vastly used neurotoxic pesticides in agricultural fields. Adsorption method was adopted to detect the change in initial concentration of the targeted pesticides. It was observed that only 0.5 g of bio-nanocomposite used up at pH 7 and normal room temperature which showed about 99% removal rate of pesticides from the sample. After three cleaning cycles it showed 56% regeneration capacity proved to be a new potential candidate for the removal of pesticides. Salam and Das (2015) developed a bionano hybrid system using *Candida* VITJzN04 and nanosized ZnO for lindane degradation. They studied the lindane degradation efficacy of *Candida* VITJzN04 along with ZnO nanoparticle and found more effective degradation of lindane by hybrid compared to native yeast alone. The lindane was completely removed within 3 days from the sample.

11.7.2.3 Silica Oxide Nanoparticles

For bioremediation of pesticides, use of microbes and enzymes as biotic component is more powerful as they are very much effective under normal atmospheric conditions. After immobilizing microbes and/or enzymes on some inert supports such as metal nanomaterials, they can be used repeatedly. Silica nanoparticles possess desirable properties to be used as support to immobilize different enzymes. Microbes expressing recombinant proteins and various enzymes such as carboxyesterases, organophosphate hydrolases, laccases, etc. have been successfully immobilized on silica nanomaterials for bioremediation of pesticides. Figure 11.8 depicts use of silica nanomaterials as immobilization matrices for enzymes and whole cell to enhance bioremediation. Basically, chemical and biological methods are adopted to synthesize spherical silica nanoparticles (SiO_2) which are porous in nature (Rao et al. 2005). The porous behavior of the SiO_2 nanoparticles majorly depends upon

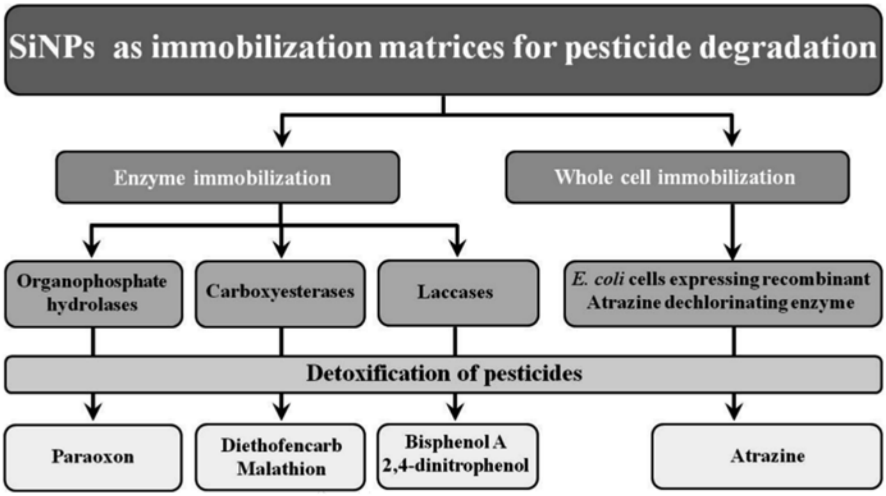

Fig. 11.8 Use of SiNPs as immobilization matrices for enzymes or recombinant whole cells for pesticide degradation. (Reproduced with permission from Bapat et al. 2016)

the surface functionality. The rage of porosity in SiO_2 particle ranges from microporous, mesoporous, and hollow porous (Bapat et al. 2016). Due to nanostructure and highly porous behavior, these nanoparticles are highly used for the remediation of various pollutant (Khung and Narducci 2015).

Boubbou et al. (2012) immobilized organophosphate hydrolases (OPH) derived from *Flavibacterium* species. They studied degradation of organophosphate pesticide paraoxon by using this immobilized enzyme and found excellent highest hydrolysis rate of paraoxon with immobilized enzyme on mesoporous silica with 6 nm diameter (Boubbou et al. 2012). Lerma-García et al. (2013) observed the enhance effect of SiO_2 nanoparticle modified by *N*-methylimidazole to detect the sulfonylurea in the water sample. It was observed that due to change in surface chemistry the rate of degradation was increased up to the mark. Other scientist also modified the surface of SiO_2 nanoparticles with polar and non-polar compound to check the efficiency towards removal of organophosphate pesticides (Ibrahim et al. 2013). In some studies mesoporous silica nano particles were used for the immobilization of enzymes such as organophosphorus hydrolase (OPH) to check the hydrolysis rate of paraoxon (diethyl-4-nitrophenyl phosphate). Results showed that OPH with silica nanoparticle shows higher tendency to hydrolyze the paraoxon comparative to the plain one (Boubbou et al. 2012). Wang et al. (2013) prepared silica colloidal crystals beads depend on photonic suspension array for the detection of chlorpyrifos-methyl and fenitrothion. During detecting the pesticides residual concentration, the binding capacity and the stability of the surface increased due to nanostructured silica particles. The prepared suspension array able to detect the pesticides in the ranges of 0.40–735.37 ng/mL and 0.25–1024 ng/mL, respectively. Observed results showed that this technique proved to be possible detecting tool for the pesticides residual present in the samples.

11.7.2.4 Iron Oxide Nanoparticles

Generally, different oxides of iron were largely exploited in the preparation of nanoparticles with unique features which are further incorporated into different matrices to removal of pollutant from the samples. Iron oxide (Fe_3O_4 and Fe_2O_3) based NPs are vastly applicable to remediate different kinds of contaminants present in various samples. Different matrices are used to immobilize the iron oxides-based NPs for eradicating the pollutants. Quali et al. (2015) used a type of clay mineral, i.e., palygorskite and modified it with the magnetic iron oxide nanoparticle for the removal of fenarimol fungicides. In this study, three composition was used, i.e., sifted palygorskite, purified palygorskite, and palygorskite modified with magnetic iron nanoparticles. The observed adsorption rate for the removal of fungicides was 11%, 50%, and 70% respectively. The clay mineral modified with magnetic iron oxide nanoparticles showed highest removal percentage and also showed 2-week stability.

Iron oxide nanoparticle embedded in mesoporous silica also has tendency to remove glyphosate from the water sample. Modification on the surface of the iron oxide nanoparticles positively increased the porosity and surface area and of the prepared adsorbent (Fiorilli et al. 2017). Fan et al. (2017) proposed quick and simple process to detect the presence of pyrethroid pesticides in various samples of contaminated water. In this method ultrasmall iron nanoparticles in combination with ionic liquid were used to detect pesticides in the water samples. The limit of detection was determined to be between 0.16 and 0.21 g/L.

11.7.3 Bimetallic Nanoparticles

As the term suggests bi means more than one, so it is basically the combination of two distinct metals within a one nanoparticle. These bimetallic nanoparticles have attracted highly due to remarkable properties which can be developing due to combining two metals. The enhanced characteristics of the bimetallic nanomaterial are generally due to the synergistic effects on conjoining (Zaleska-Medynska et al. 2016). Bimetallic nanoparticles consisting of iron and nickel (Fe/Ni) were used for the dechlorination purpose of the sulfentrazone, kind of herbicides. Various factors were also analyzed during the conversion activity such as pH, dosage, initial concentration of herbicides, etc. Recorded results showed that in 30 min about 100% conversion rate was achieved at acidic pH about 4.0 and 1.0 g/L of bimetallic NPs. It was also concluded that the dechlorination rate depends upon the temperature, dosage, and nickel content present in NPs. After dechlorination the formed by-product was less toxic and it was confirmed by mass spectrometry and toxicity assay done over the *Daphnia similis* fish species (Nascimento et al. 2016).

Shen et al. (2017) studied bimetallic nanoparticle consisting of zero-valent iron and nickel for the degradation of 4-chlorophenol. They evaluated the efficiency of the bimetallic nanoparticles towards the removal of 4-chlorophenol in the sample. Observed results confirmed that hydroxyl radicals were the most active class during the degradation process in case of iron nickel bimetallic nanoparticles. Singh et al. (2013) prepared composite of Pd/Fe bimetallic nanoparticles and carboxymethyl cellulose with *Sphingomonas* spp. (strain NM05) as biological component and used for bioremediation of lindane present in soil. They found this integrated technique very effective for bioremediation of lindane. They suggested that this integrated bio-nanocomposite system can also be used for wastewaters. Rosbero and Camacho (2017) prepared bimetallic nanoparticles of silver and copper (Ag/Cu NPs) by green synthesis method using *Carica papaya* leaf extract. The bimetallic NPs have been used as nanocatalyst to degrade chlorpyrifos in waste sample. To synthesize Ag/Cu NPs *Carica papaya* leaf extract was used by adopting co-reduction method. Observed results confirmed that bimetallic NPs have efficient potential to enhance the degradation rate of pesticides contamination from the water samples (Fig. 11.9). Some metal nanomaterials with biotic component and the removal rate of different form of pesticides by these nanomaterials are presented in (Table 11.2).

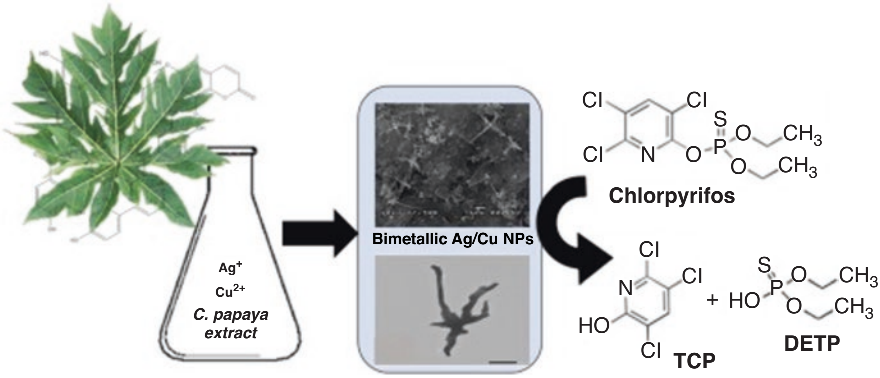

Fig. 11.9 Ag/Cu based bimetallic nanocatalyst degrading chlorpyrifos in contaminated water. (Reproduced with permission from Rosbero and Camacho 2017)

Table 11.2 Removal rate of different pesticides with different metallic nanomaterials with biotic components

S. No.	Type of nanomaterial with biotic components	Pollutant degraded	Removal rate (%)	References
1	Zero-valent iron with *Sphingomonas* sp.	Polybrominated diphenyl ethers	67	Kim et al. (2012)
2	Iron oxide nanoparticles with *Rhodococcus rhodochrous* strain	Chlorophenols	80	Hou et al. (2016)
3	nZVI and nZVI combination with microorganisms	Polychlorinated biphenyls	99	Jing et al. (2018)
4	Bimetallic iron-based NPs and tobacco plants	Hexabromocyclododecane	27	Le et al. (2019)
5	*Arthrobacter globiformis* D47 immobilized nanoparticles	Herbicides	90	Liu et al. (2018)

11.8 Conclusions and Future Prospects

Metal nanoparticles play a very important role to ameliorate conventional bioremediation techniques. Due to excellent architecture and physicochemical properties, different types of metal nanomaterials are used as support material to immobilize active microbes or enzymes. Such types of bionanocatalysts showed enhanced removal of pesticides from contaminated soil and water. Various metallic nanoparticles, bimetallic nanoparticles, metal oxide nanoparticles, and polymer metal nanocomposites are popularly used for bioremediation of pesticides. Many researchers found that rate of degradation of pesticides greatly enhanced when metal nanomaterials were used along with pesticide degrading bacteria. Metal nanomaterials also play a very important role in sensing presence of pesticide residue in environment. Iron, silver, and gold nanoparticles are most common metal nanomaterials which are utilized in bioremediation of pesticides. Due to porous nature of crystalline metal oxides based nanomaterials are very effective adsorbents used for the wide range of pesticides. Also, photocatalytic active metal oxide such as TiO_2 also provides added advantage of photodegradation which results in faster degradation of pesticide. Nowadays, bimetallic nanoparticles have attracted researchers focus for its application in bioremediation because of enhanced characteristics due to the synergistic effects on conjoining two metals in one nanoparticle. In the past decades, many metal nanomaterials and metal nanocomposites have been studied for the bioremediation of pesticide but still it is required to develop some new and greener methods for the preparation of these metal nanomaterials. Green synthesis utilizing pesticide degrading microbe or enzyme provides a single step synthesis for getting bioactive material capped metal nanoparticles.

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Chapter 12
Sensor Applications for Detection in Agricultural Products, Foods, and Water

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Abstract Pesticides are used to control pests that can destroy or reduce food production. Therefore, they are an important management tool to increase agricultural crop yield and reduce post-harvest losses, especially in a world facing hunger and famine. Although pesticides are useful in food production, they may have harmful effects such as being permanent in the environment and accumulating in living organisms, since they cannot be biodegradable. As pesticides have been widely used in agriculture for decades, concerns have been raised due to their known toxicity to human health. Thus, the determination of pesticides is of great importance due to both their increasing toxic effects on human health and the control of their use. Analytical technology methods developed using sensors are a wide-ranging field that affects industrial sectors such as medicine, health, food, agriculture, environment, and water. This chapter covers sensors and biosensors that have been developed in recent years to identify analytes sensitive to water pollution, especially used in food safety. Also, the basic principles of sensor systems used in the analysis of pollutants are mentioned.

Keywords Pesticide · Sensors · Electrochemical detection · Optical sensors · Piezoelectric sensors · Enzyme-based sensors

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12.1 Introduction

Pesticides are widely used in the agro-food industry to control, prevent, and eliminate pests. However, such compounds with high toxicity are classified as carcinogenic, neurotoxic, or teratogenic according to the World Health Organization (WHO) (WHO 2019; EPA 2019). This requires strict control of them in soil, wastewater, food, humans, and animals. In the European Union, the legal max limit (MRL) for each pesticide residue is 0.1 μg/L, while it is 0.5 μg/L for total pesticides (Caso and Plaguicidas 2012; EFSA 2013). The United Nations (UN) estimates that 200,000 deaths occur each year from acute poisoning by pesticides, 99% of which are in developing countries (OHCHR 2019). Different disease and neurological disorders can occur due to sustained exposure to these compounds.

The environmental protection agency (EPA) names substances used to prevent, destroy, spray, or mitigate any pests as pesticides (WHO 2019). Insects, mice, and other animals, as well as unwanted plants such as weeds, and also microorganisms like bacteria and viruses, are considered the target of pesticides classified as insecticides, herbicides, fungicides, acaricides, algae, and others (biopesticides, antimicrobial, and pest control devices). Among others, commercially important organophosphates, carbamates, organochlorine, and pyrethroid derivatives are widely used. Pesticides with high insecticidal activity are widely used in agriculture and industry (Du et al. 2008; Sun et al. 2013). Pesticides consisting of inorganic, synthetic, or biological compounds are classified according to their target organism, origin, and chemical structures (Obare et al. 2010). Pesticides produced by the use of synthetic chemicals are used to control pests in order to increase agricultural production by preventing crop losses and increase agricultural production, otherwise, crop yields will be reduced by a third (Pinto et al. 2010).

Quite a large number of pesticides that are routinely used in agricultural applications pollute large geographical areas by creating permanent toxic residues in the air, soil, and water (Ivanov et al. 2010). These residues cause many health problems such as sterility, allergies, acute poisoning, and even cause death due to its highly toxic effect on the acetylcholinesterase (AChE) enzyme necessary for the functioning of the central nervous system (Nicolopoulou-Stamati et al. 2016). More than 100,000 chemicals registered today (e.g., pesticides) inevitably get into freshwater, which is less than 3% of all water in the world (Schwarzenbach et al. 2010) and more than half of the total chemical production is environmentally hazardous (Gavrilescu et al. 2015).

Monitoring of freshwater quality is a priority for water quality control and ecological studies (Nikhil et al. 2018). Monitoring water quality is essential to provide clean drinking water and protect the water ecosystem (Storey et al. 2011). The most common classical methods used for pesticide determination in water samples are gas chromatography (GC) (Carneiro et al. 2013) and liquid chromatography (LC) (Sharma et al. 2010).

Instruments with highly detect and selective properties such as LC-mass spectrometry (LC-MS/MS), gas GC-mass spectrometry (GC-MS), and ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS) (Corazza et al. 2019) are required to detect pesticides in matrices (Tuzimski and Sherma 2018). There has been a major increase in the number of works conducted for the determination of pesticide in fruits/vegetables in recent years (Ferrer et al. 2017). In monitoring pesticide contamination, as a new strategy, the development of sensor and biosensor devices with several advantages over traditional methods such as simplicity, sensitivity, selectivity, and field application capabilities (Dutta and Puzari 2014) is important. Numerous sensors have been developed to detect water quality, including chemical, bio- and electronic sensors (Kruse 2018). The use of nanomaterials in sensors and biosensors to detect pesticides and other analytes is emerging as a highly efficient analytical tool (Saylan et al. 2017).

The environmentally persistent pesticides' detection used in the agricultural industry is made by traditional analysis methods such as capillary electrophoresis, high-performance liquid chromatography, and mass spectrometry (Zamora-Sequeira et al. 2019). However, although these methods have some limitations including high time-consuming, the need for highly skilled personnel, complexity, and expensive instrumentation, there are other alternative methods which allow measurements with reasonable accuracy and in a shorter time (Songa and Okonkwo 2016). Biosensor contains two different elements that include biological recognition elements such as enzymes, antibodies, lectins, receptors, and microbial cells and signal transduction elements (e.g., optical, amperometric, acoustic, or electrochemical). The signal generated by using the biological element is converted into a measurable signal (Patel 2002).

In this section, recent developments and new trends in electrochemical, optical, and piezoelectric-based biosensors used in pesticide detection are reported based on detection methods. In addition, enzyme-based biosensors will be described for pesticide detection performed by measuring enzyme inhibition or direct measurement of compounds involved in the enzymatic reaction. Biorecognition elements used in biosensors including enzymes, cells, antibodies, and DNA were evaluated. Aptamers and molecularly imprinted polymers which are used in the pesticide analysis were also presented in this chapter. Nanomaterials used in highly sensitive sensing devices allow efficient pesticides detection and merit special mention. Optical detection methods including chemiluminescence (Kochmann et al. 2012), fluorescence (Cheng et al. 2018), Surface Plasmon Resonance (SPR) (Bakhshpour and Denizli 2020), surface-enhanced Raman scattering (Nie et al. 2018), and colorimetry (Chawla et al. 2018) are used for determination of pesticide.

Chemiluminescence occurs at electrode surfaces where electron transfer reactions generate excited light emission states. The emission of any light from a substance is defined as luminescence and plasmonic nanostructures are used to control the photoluminescent properties of various emitting materials. It is well known that metal particles affect the emission of the nearby fluorophore by enhanced excitation, increasing the radiative decay rates, and quenching. The fluorescent method based on increasing and/or decreasing emissions of the fluorescent material depends on changing of the chemical environment and an analyte concentration (Zhang et al. 2007).

SPR nanosensors have been widely used in triazine pesticides detection due to their simplicity, low cost, high specificity and sensitivity, real-time measurements, no need for labeling, and ease of miniaturization (Çakir et al. 2019). The SPR as an optical technique measures the refractive index changes on the gold surface of the sensor when the target molecule is bound or absorbed to the ligand-coated sensor surface. The level of SPR curve change and the obtained response units from the shift angles are related to the analyte quantity and can be monitored in real-time (Scarano et al. 2010). SPR biosensors have been used to investigate interactions between protein–protein, nucleotides, and drug–albumin. They are also used in cell surface marker-antibody probes to examine cellular morphological changes caused by various factors (Fathi et al. 2019). SPR occurs when a portion of the light energy couples with electrons in the metal surface layer at a certain incidence angle. The plasmon resulting from the electron movements which propagates parallel to the metal surface generates an electric field around 300 nm from the boundary between the metal surface and sample solution (Šípová and Homola 2013; Nguyen et al. 2015).

Localized surface plasmon resonance (LSPR) is the collective oscillation of electrons in the conduction band of noble metal nanoparticles. This oscillation is induced by a time-dependent electric field of an electromagnetic wave. Factors such as particle size, shape, surrounding dielectric environment, proximity to other nanoparticles strongly affect LSPR (Rycenga et al. 2011). Research on technological applications such as biological sensing, imaging, and photocatalysis has increased in the last decade. Plasmonic metal nanoparticles have both synthetically tunable plasmon wavelengths and extremely wide absorption/scattering cross-sections and also enable high local electromagnetic field enhancements (Neumann et al. 2012; Linic et al. 2015). LSPR wavelengths show high sensitivity to small changes in the dielectric medium. This sensitivity makes LSPR attractive for chemical and biological sensing applications (Dondapati et al. 2010; Wu et al. 2012).

In Raman spectroscopy, chemical molecules are identified with distinctive molecular vibration modes. Surface-enhanced Raman spectroscopy (SERS) uses this capability to allow ultra-low concentration detections (Willets and Van Duyne 2007). SERS has been applied in various devices such as nanohole array and quasi-3D. However, since the Raman enhancements of these devices are moderate (10^3–10^6), they are insufficient for detecting lower analyte concentrations (Wang et al. 2012).

Colorimetric techniques are low cost and require inexpensive less signal transmission equipment. It provides a useful approach in sensing applications as the results are easy to understand. Rapid and in situ contaminant detection by observing color changes with the naked eye would be the most appropriate mechanism. LSPRs of gold and silver colloids fall into the visible spectrum so changes in aggregation states resulting in the color changes are widely used for colorimetric sensor fabrication.

Sensor designs based on aggregation-induced detections have been applied for a range of biomolecules, heavy metal ions, and pathogens (Liu et al. 2012). Plasmonic nanoparticles are widely used in biocatalysis and biosensing applications as they exhibit adjustable optical properties due to their localized surface plasmon resonances. Dark field microscopy (DFM) as one of the optical techniques monitors the scattering spectra of single plasmonic nanoparticles. Their high signal-to-noise ratio and spatial resolution properties allow them to be used extensively in the construction of various nanosensors (Xie et al. 2017).

Piezoelectric quartz crystal-based detection is quite simple. Detection of the analyte often leads to a mass change that can be identified by a corresponding change in the quartz crystal as a result of selective binding of the adsorbate. Label-free pesticides (chlorpyrifos and phoxim OPs) detection in the vegetable samples by piezoelectric biosensor were performed by Shang and coworkers. AChE enzyme was used to immobilize macromolecular structure of polymer carbon nanotubes (MWCNTs-COOH) to the crystal surfaces coated with Ag (Shang et al. 2011).

Enzymes provide an important amplification system for sensitive substrate determination depending on the turnover number. Both the catalytic conversion of the substrate and the dose-dependent inhibition of an enzymatic reaction are important parameters in contaminant concentration analysis in foods. Enzyme-based biosensors utilize specific enzymes for the catalytic generation of the product which is directly determined by electrochemical, optical, photothermal, amperometric, and acoustic transducers and they have been widely used in contaminant analyses of organophosphorus and carbamate pesticide and herbicides. In the case of pesticides, it is the enzymatic activity that is decisive in determining pesticide concentrations in samples, especially the inhibition of enzymes such as acetylcholine esterase (AChE) and butyrylcholine esterase (BChE). However, other enzymes such as tyrosinase and alkaline phosphatase have also been used. The use of the parathion hydrolase activity to determine the parathion concentration is a recent exception. Pesticides reaction with the immobilized enzymes causes inhibition depending on the type and concentration of pesticides. Transduction mechanisms such as pH change and temperature affect the resultant product formed (Patel 2002).

12.2 Pesticide Impact on Food and Water

World population growth leads to higher food demand and a reduction in land for farming. Therefore, in order to meet the increasing demand, foods are adulterated to get more quantity in a short time. Moreover, the use of pesticides in crops above the legal maximum residue limit by farmers is to gain more profits in a shorter time. Pesticides, which are very effective on pests, can reside in the environment for a long time. So, the development of rapid tools to be used for in situ and real-time monitoring of pesticide discharge toxicity effect on ecosystems is important (Gupta et al. 2016). Almost a third of global crop production is secured by the use of pesticides. However, even a small amount of pesticide residue causes serious food contamination, thus the disrupted ecosystem poses a great danger to human life. As a result, growing concerns over increased pesticide contamination have prompted governments to set many policies to guide pesticide use, regulating maximum residue levels on food and agricultural products. Bioaccumulation and continued exposure can pose safety risks to human health, even if the concentrations of most pesticides used remain within recommended limits. Pesticides are any compound or mixture of compounds used to prevent, destroy, push, or lighten any substance. Mice, insects, unwanted plants, microorganisms, and/or fungi are considered as a target for pesticides classified as insecticides, herbicides, fungicides, acaricides, algaecides, and others (biopesticides, antimicrobial, and pest control devices). Natural resources from which biopesticides are derived are animals, plants, bacteria, and some minerals. Table 12.1 shows major pesticide classes according to the chemical structures (Aragay et al. 2012). The transfer of the pesticide residues in food enhances the potential area of their effect among the population and hence directly affects human health (Food and Agriculture Organization FAO 2010).

Agricultural pesticides and chemicals, which are widely applied in the agricultural sector, cause serious problems in terms of public health in the world by causing pollution in water, food, and environmental ecosystems. The mean lethal dose (LD50) is calculated by the acute toxicity tests. Table 12.2 shows acute toxicity levels of the pesticides estimated by WHO (Food and Agriculture Organization FAO 2010).

Water bodies adjacent to agricultural lands are often the ultimate recipient of pesticide residues (Pereira et al. 2009; Christos et al. 2011; Ba Hashwan et al. 2020). The urgent need for sensors capable of detecting pesticides with high sensitivity has increased in order to control food safety, protect ecosystem, and prevent diseases . Biosensors are defined as a device that captures reactions between the sensitive

Table 12.1 Major classes of pesticides in accordance with their chemical structure

Chemical class	Code	Pesticide group	Chemical class	Code	Pesticide group
Arsenic compounds	AS	Fungicides, insecticides, herbicides	Organotin compounds	OT	Fungicides, herbicides
Bipyridine derivatives	BP	Herbicides	Phenoxyacetic acid derivatives	PZ	Insecticides
Carbamates	C	Acaricides, fungicides	Pyrazole derivatives	PZ	Insecticides
Coumarin	CO	Rodenticides	Pyrethroids	PY	Acaricides, insecticides
Copper compounds	CU	Algaecides, fungicides, insecticides	Triazine derivatives	T	Herbicides
Inorganic and organic mercury compounds	HG	Fungicides, rodenticides	Thiocarbamates	TC	Herbicides
Organochlorine compounds	OC	Fungicides, insecticides			

Table 12.2 Acute toxicity of pesticides according to WHO classification

		LD50 for the rat (mg/kg b.w.)			
		Oral		Dermal	
Class	Classification	Solids	Liquids	Solids	Liquids
Ia	Extremely hazardous	<5	<20	<10	<40
Ib	Highly hazardous	5–50	20–200	10–100	40–400
II	Moderately hazardous	50–500	200–2000	100–1000	400–4000
III	Slightly hazardous	>501	>2001	>1001	>4001
U	Unlike to present acute hazard	>2000	>3000	–	–

element and target objects after combining biorecognition elements with a physical transducer and then converting them into continuous or discrete electrical or optical signals that can become useful information. In general, immunosensors differ from immunoassays in which the transducer is not an integral part of the analytical system. While the biorecognition element determines the degree of selectivity or specificity of the biosensor, the transducer greatly affects the sensitivity of the biosensor. Typically, biosensors are classified in some ways. Depending on the different types of biorecognition element, biosensor can be classified as enzyme sensor, microbial sensor, organelle sensor, tissue sensor, and immunosensor. According to the transduction mechanism, biosensors can also be classified as electrochemical, optical, piezoelectric, and nanomechanical immunosensors (Valera et al. 2010). Electrochemical transducers classified as amperometric, potentiometric, conductometric, capacitive, and impedimetric measure changes in current, potential (voltage), conductivity, capacitance, and impedance, respectively (Sun et al. 2013). Based on different biorecognition elements, biosensors will be described in the following sections.

12.3 Typical Sensors for Pesticide Detection

Environmental monitoring has become one of the priorities due to the close relationship between environmental pollution and human health. Pesticide residue levels in food are determined by regulatory agencies in most countries. International Maximum Residue Limits-Codex Alimentarius is used by some countries to determine residue limits (Bergesen et al. 2019). To guarantee food safety and quality and to meet consumer requirements, it is necessary to ensure that the food industry has effective analytical methodologies (Novellino et al. 2013). The classical analytical methods called "wet chemistry" used at the beginning of the twentieth century have evolved into powerful instrumental techniques used in food laboratories. Broadening the scope of practical applications in food analysis, this development has led to significant improvements in analytical accuracy, sensitivity, limits of detection, and sample throughput (Cifuentes 2012).

Traditional techniques are accurate and reliable, they require time-consuming steps including solid-phase extraction, field sample collection, analyzes of the sample, and compartment of the spectral peaks to references for identification of pesticide residues (Lesueur et al. 2008). Therefore, researchers have been looking for alternative detection and screening methods that are cheaper and more user-friendly. In recent years, interest in biosensor technology has increased to determine pesticides quickly using easy and fast procedures. Biosensors simplify or eliminate sample preparation and provide a significant reduction in cost per analysis. Also, traditional analytical methods with the potential to complement or replace make field testing easier and faster.

Electroanalysis, which offers a high potential in the field of food analysis, especially in common laboratories where there is no sophisticated analytical instrumentation, is going through a real renaissance process because of the appearance of advanced approaches such as screenprinting technology, biosensors, microchips, and nanotechnology. There are more arguments for the application of electroanalysis in the analytical chemistry of foods. Firstly, many analytes in foods are electroactive and electrochemical detection offers both good selectivity (especially after electrode modification with different (bio)/(nano) materials) and sensitivity for direct detection without the need for derivatization step. Relatively low-cost electroanalytical instrumentation can be easily miniaturized without loss of analytical performance and can be used for examining samples with low turbidity. Furthermore, electrochemical sensing can operate both in batch and in continuous regimes, coupled as detectors in advanced separation methods and as a transduction system of biosensors (Escarpa 2012). The pesticide sensor is based on the process of converting chemical information such as pesticide concentration into an analytical, readable, and useful signal. The chemical reaction takes place between the target molecule pesticide and the biorecognition element such as an aptamer, antibody, or polymer.

Extensive efforts have been made in recent years to develop pesticide biosensors for use in monitoring pesticide residue in drinking water and food. Pesticides are commonly used chemicals to increase crop yields by removing various agricultural pests. Only 1% of pesticides applied by direct spraying to plants successfully reach pests or insects and other amounts of pesticides remain adhered to vegetables and fruits. The pesticide amount remaining in food has become one of the most worrying challenges because of its harmful consequences for human health (Ba Hashwan et al. 2020). Non-agricultural applications using pesticides are pest control, weed management, pet care in shelters, and industrial vegetation control. Detection of pesticide residues is important (Kumar et al. 2015) and is considered a challenge. There are several sensors for detection of pesticide, so in this section, we will overview the latest developments in the determination of pesticides using electrochemical, optical, colorimetric, single plasmonic particles, piezoelectric and enzyme-based sensors.

Electrochemical sensor variants include potentiometric and amperometric sensors. Potentiometric sensors rely on a change in potential. Electrochemical sensors are one of the useful tools used in pesticide residue detection (Abdel-Fatah 2018).

Electrochemical techniques preferred over other analytical techniques have remarkable features such as low cost, easy to use, portable, and fast response time. Electrochemical biosensors are classified according to signals measured in impedance, current, and potential, so sensors are characterized as impedimetric, amperometric, and potentiometric sensors (Facure et al. 2017). Recently, electrochemical impedance spectroscopy (EIS) technique for residue detection of pesticides has been widely used due to its unique properties such as fast response time, easy preparation, high sensitivity, and specificity. EIS is classified into two main techniques as Faradic EIS and non-Faradic EIS (Liu et al. 2019). An amperometric biosensor based on Nafion/AChE-cSWCNT/MWCNT/Au was developed for the determination of organophosphorus compounds by Dhull (2020). Goud et al., developed the first example of a disposable electrochemical biosensor chip for the detection of diisopropyl fluorophosphate (DFP), as the stimulant compound of G-type nerve agents (e.g., Sarin and Soman), based on the integration of an all-solid-state fluoride potentiometric transducer with the enzyme organophosphorus acid anhydrolase (OPAA) (Goud et al. 2020). While photoactive materials are firmly fixed on the photoelectrode of photoelectrochemical (PEC) sensors to produce the perfect photocurrent response, obvious and constant background currents will also occur, preventing ultrasensitive detection of target molecules. Ultrasensitive organophosphorus pesticides (OPs) detection is successfully performed using a dissociable photoelectrode based on CdS nanocrystal-functionalized MnO_2 nanosheets (Qin et al. 2020). Acetylthiocholine (ATCh) is hydrolyzed to thiocholine (TCh) with the help of acetylcholinesterase (AChE). TCh can effectively etch ultrathin MnO_2 nanosheets resulting in the dissociation of MnO_2-CdS from the photoelectrode.

Optical biosensors are extensively applied to monitor pesticide contamination in the environment due to excellent advantages such as lower cost, and easy preparation, and real-time showing the result (Yan et al. 2018). However, the quantification of pesticides requires sophisticated equipment and professional workers (Citartan and Tang 2019). Optical sensors used to identify chemical and microbiological contaminants including luminescence (Yan et al. 2018), fluorescence (Cheng et al. 2018), SPR (Zhang and Fang 2010), LSPR (Bakar et al. 2012), SERS (Nie et al. 2018), single plasmonic particles (Dissanayake et al. 2019), and colorimetric methods (Chawla et al. 2018). So, the basis of optical sensors used for pesticide detection is based on wavelength changes using surface plasmon resonance technology, reflection changes using surface plasmon resonance technology, fluorescence, and SERS technology using intensity change. Single particle-based plasmonic particles and colorimetric-based sensors are also used in optical sensor technology. Also, in optical biosensor applications, researchers have always used some metal nanoparticles and also some types of polymers. For the determination of organophosphorus pesticides, coreactant-free electrochemiluminescence biosensor without any extraneous species or dissolved O^{-2} was prepared by (He et al. 2020a).

Specific dithiocarbamates detection by CTAB-encapsulated fluorescent copper nanoclusters was examined as a facile, rapid, inexpensive method (Chen et al. 2020). Li et al. (2019b) reported a direct surface plasmon resonance biosensor for chlorpyrifos residue detection in agricultural samples based on an oriented assembly of antibody. A portable LSPR-based instrument for rapid biomolecular detection of pesticides in situ was developed by Rampazzi et al. (2016). Xu et al. performed SERS-based determination of 2,4-dichlorophenoxyacetic acid in food matrices using molecularly imprinted magnetic polymers (Xu et al. 2020a). Analytical techniques that locally enhance the intensity of the electromagnetic field induced by plasmons, which cause an increase in the efficiency of some optical processes in the proximity to the plasmonic nanoparticles, were detailed by Kolataj and coworkers (2020). Sensitive label-free colorimetric detection of chlorpyrifos pesticide was performed with a silk fibroin-gold nanocomposite (Mane et al. 2020) based sensor.

Offering advantages such as high sensitivity, real-time output, cost-effectiveness, and ease of use, piezoelectric sensors have attracted the attention of researchers as an alternative to traditional immunoassay tools for detecting pesticides. A piezoelectric sensor device can be designed with materials such as quartz crystals that resonate with an external alternating electric field application without needing expensive or hazardous labels (Bakhshpour et al. 2017, 2019). Frequency change occurs as a function of the crystal mass and is measured after the interaction of an analyte in the sample with the corresponding molecule immobilized to a quartz crystal. Therefore, the increase in mass will cause a decrease in resonance frequency, which is a function of the analyte concentration (Kuchmenko and Lvova 2019). Piezoelectric immunosensors are devices containing quartz crystals immobilized with bioreceptor on their surface and resonate in the application of an external alternating electric field. Pan et al. performed the metolcarb pesticide detection in spiked apple and orange juice samples by a hybrid material including multi-wall carbon nanotube/poly (amidoamine) dendrimer (Pan et al. 2013). Pesticides polluting the environment are intentionally released into the environment through various processes. Although they pose a health hazard, pesticide pollutants are not effectively monitored.

Biosensors using acetylcholinesterase (AChE) inhibition have emerged as simple, fast, and ultrasensitive tools for the analysis of pesticides which are important in environmental monitoring, food safety, and quality control. By eliminating or simplifying sample preparation, these biosensors have provided a significant reduction in cost per analysis. There are excellent studies and reviews described in the literature involving different food and environmental applications (Arduini et al. 2010). Hu et al. (2020) proposed new and stable acetylcholinesterase (AChE) sensor with a patterned structure based on a titanium dioxide sol-gel carrier to detect organophosphorus pesticides (OPs). Yang et al. integrated 1-naphthol-linked bi-enzymatic reaction (sensor core) into the LIS (sensor device) to fabricate enzyme inhibition-based lab-in-a-syringe (EI-LIS) device for monitoring pesticide residues. In pesticide capture, esterase enzyme originated from plant mediates the hydrolysis process forming 1-naphthol (Yang et al. 2020b). In the presence of acetylthiocholine iodide (ATCh) real-time and label-free methyl parathion pesticide (MPT) detection via non-adiabatic tapered fiber-optic biosensor was presented by Arjmand et al. (2020). The limit of detection for MPT was found to be as low as 23×10^{-9} M (S/N = 3). Acetylcholinesterase biosensors prepared with the use of carbon nanotubes functionalized with ionic fluid and horseradish peroxidase were used for the determination of monocrotophos (Jiaojiao et al. 2020). This chapter reviews the latest developments about the AChE enzyme inhibition-based biosensors. Therefore, sensitive and simple methodologies developed for fabricating sensors to detect and monitor pesticides without the need for extensive sample pretreatment are summarized in (Table 12.3).

12.3.1 Electrochemical Detection

The electrochemical technique has been demonstrated to be a feasible approach for pesticides and other template detection due to its high throughput capability, high sensitivity, great miniaturizing possibility, cost-effectiveness, specificity, and simple operation. Electroanalytical methods measure changes in current when potential is applied. Current is the change in charge as a function of time.

$$I = \mathrm{d}Q / \mathrm{d}t \tag{12.1}$$

According to Faraday's law (the equation is given below), the charge is proportional to the amount of analyte that gains or loses electrons.

$$Q = nFe \tag{12.2}$$

where Q stand for total charge in coulombs unit, n is the number of moles of an analyte, F is Faraday's constant (96.487 C/mol), and e refer to the number of electrons gained or lost. Hence, the current response gives information about changes in the analyte concentration (Bakirhan et al. 2018).

Electrochemical biosensors are classified according to the signal being measured impedance, current, and potential. Therefore, they are characterized as impedimetric, amperometric, and potentiometric sensors. In recent years, capacitive-based sensors are used as an alternative way for the detection of the pesticide (Facure et al. 2017; Beloglazova et al. 2018). Electrochemical impedance spectroscopy (EIS) based biosensors in which capacitance changes are measured are called "Capacitive biosensors" (Li et al. 2017).

Besides, Field Effect Transistor (FET) (Qiu et al. 2020) and the screen-printed electrodes (Pérez-Fernández et al. 2020; Soulis et al. 2020) are other electrochemical pesticide detection methods. Nanomaterial-based molecularly imprinted polymers (Mahmoudpour et al. 2020), 2D transition metal carbides-modified support materials (Shahzad et al. 2020), boron-doped diamond material (Sarakhman and Švorc 2020), and immunosensors (Fang et al. 2020) can be used for rapid electrochemical detection of pesticide residues in food samples.

Acetylcholinesterase (AChE) enzyme is frequently used to determine the organophosphorus pesticides (OP). Dou et al. (2012) used screen-printed carbon electrodes (SPCEs) to develop a biosensor based on the inhibition of AChE. The enzyme was

Table 12.3 Biosensors used for environmental monitoring

Biosensor type	Recognition element	Sensing material	Limit of detection	Reference
Electrochemical	PtNPs/CS	GCE	7 and 20 μg/L	de De Matos et al. (2020)
Electrochemical	MWCNT/zirconia	CPE	9.0×10^{-9} mol/L	Caetano et al. (2020)
Electrochemical	CuNPs	GCE modified with MWCNT	0.33 nmol/L	Roushani et al. (2020)
Electrochemical	$WO_3 \cdot 0.33H_2O$ nanorod modified carbon-based electrode	CPE	233 nM	Ilager et al. (2020)
Electrochemical	Enzyme	Indium tin oxide (ITO) electrode with ZIF-8/MB composites	1.7 ng/mL	Li et al. (2020b)
Electrochemical	*p*-phenylenediamine	PGE	2.75 μg/mL	Şensoy et al. (2020)
Electrochemical	Hb	Reduced graphene oxide-chitosan (ERGO-CS/Hb/FTO)	79.77 nM	Kaur et al. (2020)
Electrochemical	$NiCo_2S_4$	Graphitized CNF	20 nM	He et al. (2020b)
Electrochemical	CNT-H-IMZ	GCE	120 nM^{-1}	de Oliveira et al. (2020)
Electrochemical	NiO nanoparticles	GCE	0.5 μM	Baksh et al. (2020)
Electrochemical	$Au\text{-}ZrO_2$ nanocomposites	GECT	0.1 ng/mL	Tao et al. (2020)
Electrochemical	MXene/CNHs/β-CD-MOFs	Graphene	1.0 nM	Tu et al. (2020)
Electrochemical	Stearic acid/nanosilver composite	GCE	0.1 nM	Kumaravel et al. (2020)
Electrochemical	Enzyme	ITO electrode	8.8 ng/L	Nagabooshanam et al. (2020)
Electrochemical	SiO_2NP-CNT-μPs	GCE	0.092 μM	Yao et al. (2020a)
Electrochemical	Aptamer	Au-TAN	0.077 pM	Yao et al. (2020b)
Electrochemical	NiAl-LDH	CPE	1×10^{-9} M	Tcheumi et al. (2020)
Electrochemical	Poly-L-cysteine-gold nanoparticles (PLC-AuNPs/PGE)	PGE	1.83×10^{-10} M	Amouzad and Zarei (2020)
Electrochemical	SnS_2/NS–RGO	GCE	0.17 nM	Shanmugam et al. (2020)

(continued)

Table 12.3 (continued)

Biosensor type	Recognition element	Sensing material	Limit of detection	Reference
Electrochemical	Enzyme	MnO_2-Thi based electrode	3×10^{-10} M	Sun et al. (2020)
Electrochemical	Anti-fipronil	GCE	112 ag/mL	Kumar et al. (2020a)
Electrochemical	The Ag-ZnO/s-SWCNT	Au probe	0.27×10^{-16} M	Kumar et al. (2020b)
Electrochemical	PtNPs-MoS_2-rGO	GCE	0.07 µM	Zuo et al. (2020)
Electrochemical	Silver (Ag)-doped ZnO nanorods	GCE	0.34 nM/L	Wang et al. (2020)
Electrochemical	ZnO	Ni-foam electrode	1.2×10^{-15} M	Kamyabi and Moharramnezhad (2020)
Electrochemical	Nylon 6,6	PGE	0.94×10^{-8} M	Thanalechumi et al. (2020)
Electrochemical	Nitride (g-C_3N_4)/ graphene oxide(GO)-(Fc-TED)	GCE	8.3 nM	Xiao et al. (2020)
Electrochemical	(L-Cit)-(beta-CD)	GCE	10 nM	Li et al. (2020a)
Electrochemical	BSA/AChE-Glu-s-SWCNTs/GCE	GCE	3.75×10^{-11} M	Kumar and Sundramoorthy (2019)
Electrochemical	SWCNTs Au-ZrO_2-GNs	GCE	1 ng/mL	Gao et al. (2019)
Electrochemical	ACC-HNFs	SPCE	6 fg/mL	Jin et al. (2019)
Electrochemical	GO	TRGOPE	0.015 µmol/L	Brycht et al. (2018)
Electrochemical	*N*-methyl-2-pyrrolidone	GCE	0.78 nM	Wei et al. (2018a)
Electrochemical	Aptamer	GCE	0.35 fM	Roushani et al. (2018)
Electrochemical	Au NPs (3DG-Au)	GCE	0.0012 µM	Rahmani et al. (2018)
Electrochemical	Enzyme	GCE and Au nanorods	0.7 nM	Lang et al. (2016)
Electrochemical	Enzyme	SPE with Carbon black nanoparticles	5 µg/L	Arduini et al. (2014)
Electrochemical	Enzyme	SPE with Fe_3O_4 and Au nanoparticles	0.1 ng/mL	Bahadır and Sezgintürk (2015)
Electrochemical	Enzyme	CPE and $NiCo_2S_4$	0.42 pg/mL	Peng et al. (2017)

(continued)

Table 12.3 (continued)

Biosensor type	Recognition element	Sensing material	Limit of detection	Reference
Electrochemical	Enzyme	CPE with chitosan, Au nanoparticles, and Nafion	5 fg/mL	Deng et al. (2016)
Electrochemical	Aptamers	Carbon black and GO/Fe_3O_4	94 pM	Jiao et al. (2017)
Electrochemical	Enzyme	Pt electrode with ZnO	12 pM	Sundarmurugasan et al. (2016)
Electrochemical	Enzyme	Ionic liquids-Au nanoparticles porous carbon composite	0.3 pM	Wei and Wang (2015)
Electrochemical	Aptamers	Au nanoparticles, MWCNT and rGO nanoribbons	17 fM	Fei et al. (2015)
Electrochemical	Aptamers	Ag nanoparticles and nitrogen-doped GO	33 fM	Jiang et al. (2015)
Electrochemical	Aptamers	Pt nanoparticles	1 pM	Madianos et al. (2018)
Electrochemical	Antibodies	SWCNT	0.01 ng/mL	Belkhamssa et al. (2016)
Electrochemical	Phage/antibody (monoclonal) complex	Protein G	0.2 pg/mL	González-Techera et al. (2015)
Electrochemical	Enzyme	MWCNT and GO nanoribbons structure	1.7 nM	Liu et al. (2015a)
Electrochemical	Enzyme	Porous GCE with GO network	0.74 nM	Li et al. (2017a)
Electrochemical	Enzyme	GCE with GO and MWCNT	136 pM	Li et al. (2017b)
Optical	Rhodamine B (RhB)	Zr-MOF	0.2 μM	Yang et al. (2020a)
Optical	Enzyme	UCNPs-Cu^{2+}	0.05 ng/mL	Wang et al. (2019)
Optical	Lanthanide organic frameworks	Europium	2.07 ppb	Wei et al. (2018b)
Optical	OMT-MIP	$CsPbBr_3$ quantum dots	18.8 ng/mL	Huang et al. (2018)

(continued)

Table 12.3 (continued)

Biosensor type	Recognition element	Sensing material	Limit of detection	Reference
Optical	Enzyme	Ir(III) complex	0.37 μg/L	Lu et al. (2018)
Optical	*Ortho*-phenylene diamine	C-quantum dot	3 pM	Mohapatra et al. (2018)
Optical	Terbium-[Ethyl-4-hydroxy-1-(4-methoxyphenyl)−2-quinolinone-3-carboxylate]	Terbium	1.7 μM for Crotoxyphos	Azab et al. (2017)
Optical	Carbon dots-Cu(II)	Cu(II)	3.8×10^{-9} M	Hou et al. (2016)
Optical	Enzyme	Mn: ZnS	0.1 pM	Ban et al. (2014)
Optical	Eu^{3+} doped TiO_2 nano-powder	Eu^{3+}	3.2×10^{-11} mol/L	Yao et al. (2011)
Optical	CS/ZnO, CS/GO	Au	8 nM	Do et al. (2020)
Optical	Aptamer	Au	6.8 pM	Tan et al. (2019)
Optical	AuNPs	AuNPs	11.8 nM	Li et al. (2019a)
Optical	Antibody	Au	0.056 ng/mL	Li et al. (2019b)
Optical	Antibody	Au/Fe_3O_4	0.44 ng/mL	Li et al. (2019c)
Optical	Antibody	CM7	7.5 nM	Guo et al. (2018)
Optical	MAAsp	Au	0.7134 ng/mL	Yılmaz et al. (2017)
Optical	MAPA	Au	0.095, 0.031 and 0.091 nM for SNZ, SMZ and ATZ	Saylan et al. (2017)
Optical	Ag, Au, and Ag-Au	Ag, Au, Ag-Au nanoparticles	58 ppm for ethion	Dissanayake et al. (2019)
Optical	Ag	AgNPs	7 ng/mL	Shrivas et al. (2019)
Optical	AgNPs	AgNPs	0.015 μg/mL	Shrivas et al. (2016a)
Optical	AgNPs	AgNPs	3 ng/mL	Shrivas et al. (2016b)
Optical	Enzyme	AuNPs	0.234 ppb	Lin et al. (2006)
Optical	Si nanowire paper (SiNWP)	Si	72 ng/cm^2	Cui et al. (2017)
Optical	Conductive ink pens	Au, Ag nanospheres	20 ppb	Polavarapu et al. (2014)
Optical	Silver nanocubes and nanowires	RhB	10^{-15} M	Kumar and Soni (2020)
Optical	Au	AuNPs	260 pM	Rippa et al. (2017)
Optical	Antibody	Al_2O_3-Ag	1 ppb	Lee et al. (2016a)

(continued)

Table 12.3 (continued)

Biosensor type	Recognition element	Sensing material	Limit of detection	Reference
Optical	Ag	Ag nanowires (NWs)	250 ng	Lee et al. (2016b)
Optical	6-aza-2-thiothymine	AuNPs	0.42 μM	Kailasa et al. (2019)
Optical	ABT	Ag NPs	1.04 μM	Patel et al. (2015)
Optical	Graphene quantum dot/Au(III)	Au	0.007 ppm	Babazadeh et al. (2020)
Optical	Aptamer	AuNPs	5.6×10^{-10} M	Qi et al. (2020)
Optical	Enzyme	3DRGO-$NiFe_2O_4$/NiO NPs	10 μg/mL	Wei et al. (2019)
Optical	Ag	AgNPs	0.3 μM	Yaqoob et al. (2019)
Optical	MnO_2	AuNCs	0.125 μg/L	Yan et al. (2019)
Optical	Au	AuNPs	37.0 nM	Li et al. (2018)
Optical	Ag	AgNPs	0.04 μM	Zheng et al. (2018)
Optical	Au	AuNPs	20 nM for DMT	Chen et al. (2018a)
Optical	Au	AuNPs	80 nM	Kang et al. (2018)
Optical	Au	AuNPs	3.4 ppb	Ma et al. (2017)
Optical	Aptamer	AuNPs	0.01 nM	Bala et al. (2016b)
Piezoelectric	BNT-BKT-BT ceramic immunosensor	Bismuth	0.11 μg/L	Fernández-Benavides et al. (2019)
Piezoelectric	Antibody	Au	17 μg/L	Cervera-Chiner et al. (2018)
Piezoelectric	HCB and DDT	Au	0.75 for DDT and 0.69 for HCB	Prasad and Jauhari (2015)
Piezoelectric	Enzyme	Au	1.55×10^{-8} M for EPN	Kim et al. (2007)
Piezoelectric	Pirimicarb-MIP	Au	5×10^{-7} mol/L	Sun and Fung (2006)
Piezoelectric	Enzyme	Au	10^{-10} mol/L	Halámek et al. (2005)
Piezoelectric	Antibody	Au electrode	30 μg/L	March et al. (2015)

immobilized by polyacrylamide polymerization after the manufacturing of the SPCEs. The detection limits of dichlorvos, monocrotophos, and parathion pesticides were 18.1, 26.4, and 14.4 nM, respectively. In both studies, a simple and fast sensor response was obtained via enzymes fixed on unmodified working electrodes. Gu et al. (2020) reported a strategy to fabricate a non-enzymatic pesticide electrochemical sensor for the detection of pesticides. They used an ultrasensitive non-enzymatic pesticide sensor based on glass carbon electrode (GCE) modified by copper oxide @ mesoporous carbon (CuOx@mC) composite derived from directly pyrolyzing metal-organic framework HKUST-1 (Fig. 12.1). They demonstrated a sensitive result with CuOx@mC composite towards glyphosate. The linear range of glyphosate was showed between 1.0×10^{-15} and 1.0×10^{-4} M and the detection limit value was reported 7.69×10^{-16} M. They showed an excellent stable, reproducible, and anti-interference able system.

In another study, an electrochemical immunosensor was developed for the detection of pyrethroid, neonicotinoid, and organophosphates. Bhardwaj et al. (2020) used successfully polyclonal antibody (rIgG) based nano immuno-hybrid with MOF modified ITO substrate also, they used molecular docking methods to give an insight of interactions between the pesticides and the polyclonal antibody (Fig. 12.2). They developed a sensitive method to measure total pesticide load using cyclic voltammetry at 0.410 V.

Ahmed et al. (2020) successfully synthesized the atrazine-imprinted reduced graphene oxide composite having enhanced functionalities and applied it for the selective detection of atrazine in complex matrices. At optimized parameters for atrazine limit of detection (LOD) and limit of quantification (LOQ) values were recorded to be 0.4 nmol/dm^3 and 1.2 nmol/dm^3, respectively.

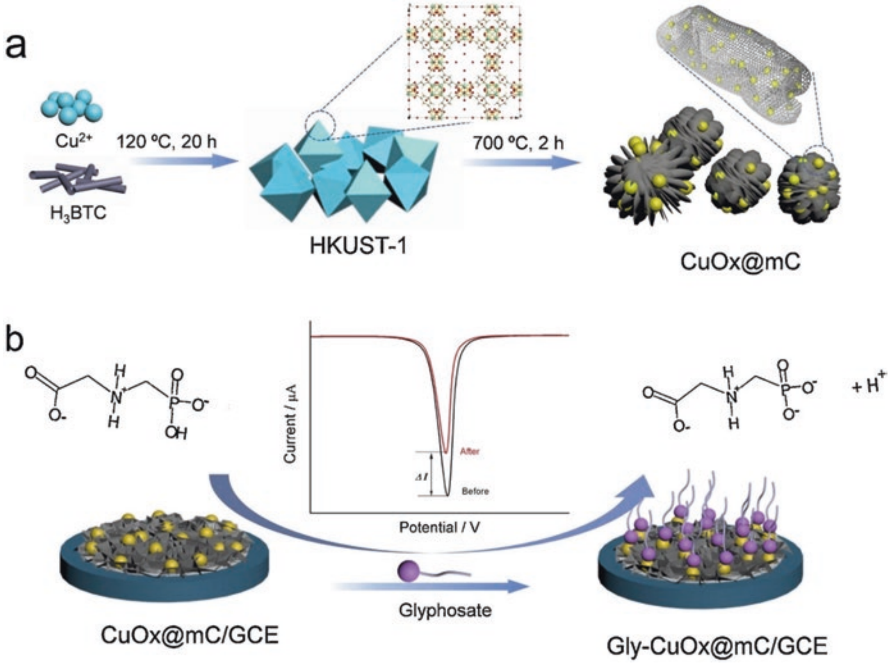

Fig. 12.1 (**a**) Illustration of the formation of CuOx@mC composite. (**b**) Analytical principle of the electrochemical sensor based on the CuOx@mC composite (Gu et al. 2020)

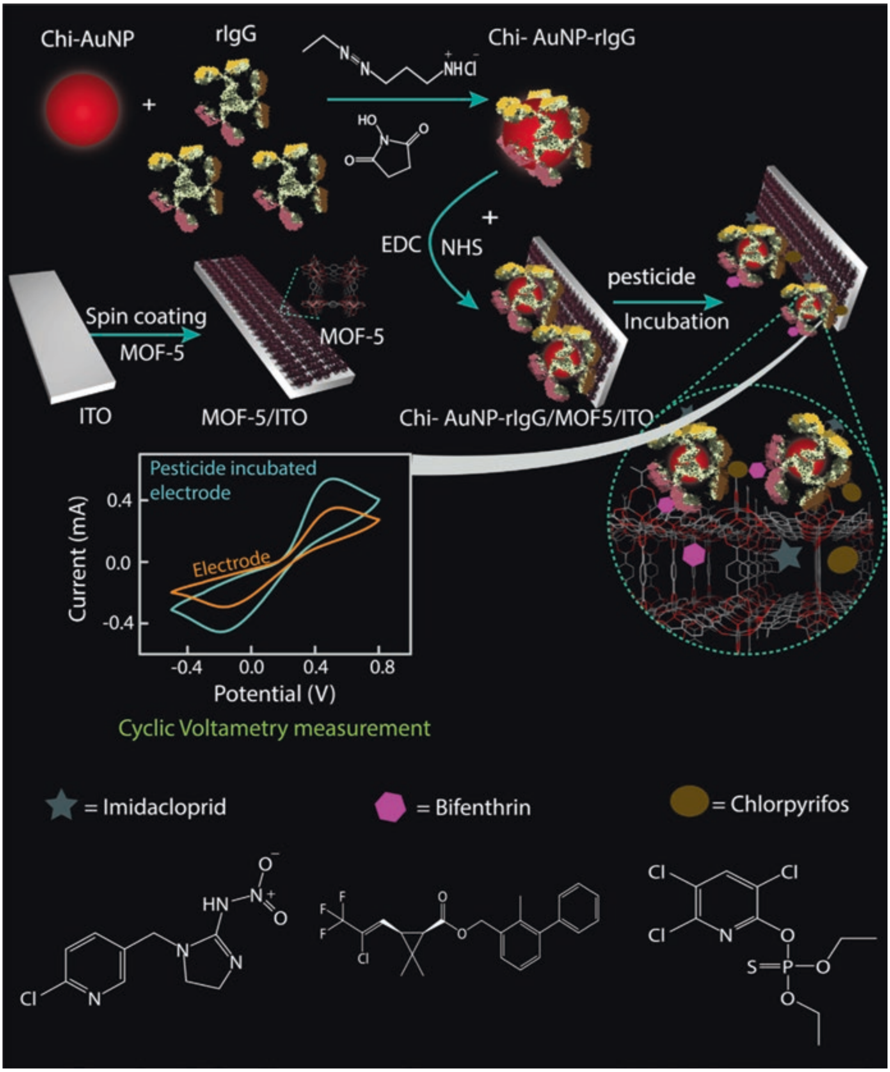

Fig. 12.2 Schematic representation on the mechanism of fabrication and detection of pesticide by immuno-electrode (Bhardwaj et al. 2020)

12.3.2 *Optical Sensors*

The optical sensor ensures a low-cost, facile, sensitive, and rapid detection of a pesticide including luminescence and fluorescence, SPR, LSPR, SERS, colorimetric, single plasmonic particle sensors. Largely, an optical sensor includes a special unit for recognition of the desired target that can interact with the target and transducer component and then a signal is obtained by the binding event. Recognition elements such as an antibody, enzyme, molecularly imprinted polymers, host–guest recognizer, and aptamer attract increasing attention of the researcher to develop the performance of the optical sensors. In this chapter, we aim to highlight the detection of pesticides via various optical sensors.

12.3.2.1 Luminescence and Fluorescence-Based Sensors

Fluorescent dissolved organic matter is derived from naturally occurring organic compounds (bacteria, algae, and higher plants) as well as a wide range of various compounds from the petroleum industry, paper, and pulp mills, agrochemical industries, and domestic wastewater constituents. Many aromatic and double-bonded structures produced by diverse organic compounds are fluorescent. Therefore, portable fluorescent sensors have the potential to provide instantaneous measurements of fluorescent organic compounds found in chemical and biological contaminants (Wasswa et al. 2019).

The sensing material undergoes a chemical reaction with the agent causing a measurable change in the luminescence called fluorescence-based detection which is a method for sensing and identifying. Fluorescence-based detection has several potential advantages over colorimetric detection in terms of speed, sensitivity, and mode of detection. It can be achieved using a change in the steady-state photoluminescence (PL) intensity (“turn on” or “turn off”), PL color, or PL lifetime. Therefore, it is possible to monitor multiple characteristics of the PL simultaneously (e.g., color and intensity) to improve selectivity (Fan et al. 2020). Enzymatic reactions are mostly used in the fluorescence enzymatic bioassays are glucose oxidase (GOx)- and AChE-based detection systems. PL of low-dimensional photoluminescent semiconductor nanoparticles, known as quantum dots (QDs) change by the product of the enzymatic reaction is used for the determination of analyte concentration. QDs PL quenching by a product of an enzymatic reaction is considered a promising candidate for the development of commercial on-site tests that can be performed by non-professionals due to their simplicity, little equipment investment, cost-effectiveness, and the absence of the sample pretreatment (Speranskaya et al. 2020). One of the most used fluorescence enzymatic bioassays is acetylcholine hydrolysis by acetylcholinesterase following by choline oxidation catalyzed with choline oxidase (AChE) for acetylcholine, organophosphorus, and carbamate pesticides detection (Yu et al. 2014; Sun et al. 2011a, b).

Trace amounts of OPs and carbamate type pesticides can inhibit the activity of the choline oxidase (ChOx) (the mechanism which leads to the paralysis and death of insects) leading to an increase in PL intensity of the conjugated QDs. The ability of the enzyme to recognize pesticide molecules has allowed for the development of QD-based sensors for these target analytes. The structurally similar pesticides, parathion-methyl, paraoxon, and parathion have been extensively and successfully targeted using this type of sensor possibly due to similar interactions that they have with the enzyme (Nsibande and Forbes 2016). As shown in Fig. 12.3, choline was obtained by hydrolysis of acetylcholine chloride (Ach) via the AChE enzyme. After

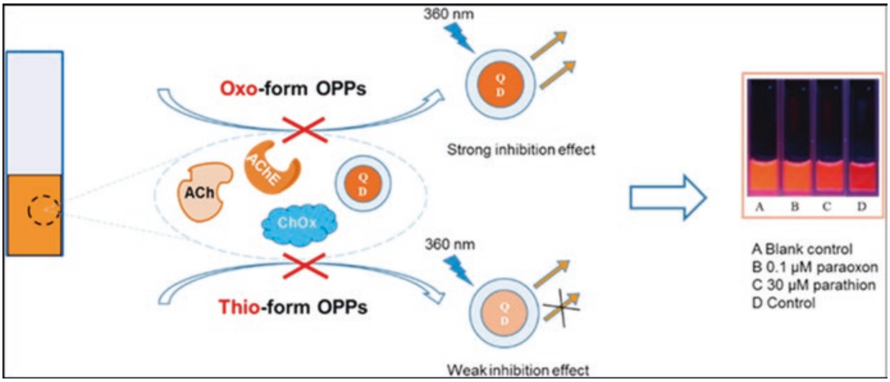

Fig. 12.3 The illustration of the biosensor for organophosphorus pesticides detection (OPPs) (Wei et al. 2017)

the oxidation process to betaine, H_2O_2 is produced in the presence of ChOx. Fluorescence quenching was observed in the presence of H_2O_2 produced by enzymes. Pesticides could inhibit the active centers of AChE. As a result of this, the generated H_2O_2 decreases, and the fluorescence intensity of QDs increases. The measuring of the fluorescence changes shows the inhibition efficiency of pesticide to AChE activity (Wei et al. 2017).

On the other hand, the samples are complex matrices containing several components which significantly impact the accuracy of analyte quantification. Besides, the samples are typically only diluted without any additional pretreatment before mixing with the assay reagents. Consequently, the interfering compounds of the matrix can quench QDs PL or influence enzyme activity (Speranskaya et al. 2020).

12.3.2.2 SPR and LSPR Based Sensors

LSPR and SPR based sensors have been used to detect biological and chemical compounds such as nucleic acid, enzymes, pesticides, etc. (Chegel et al. 1998; Obando et al. 2004). The technique of the SPR sensor has shown a reliable procedure and high sensitivity among the several sensing techniques (Wu and Lin 2004). A p-polarized light plays an important role in the SPR technique and satisfies a certain resonance condition. This light is the reason for the excitation of a charge density oscillation along with the metal–dielectric interface. Therefore, incident photon energy is transferred to the surface plasmon wave. The resonance is monitored by a sharp dip in output optical signal at either resonance wavelength or resonance angle. The Kretschmann configuration is frequently utilized in which a thin layer of metals such as gold or silver are directly placed on the base of a coupling prism (Kretschmann 1971) (Fig. 12.4).

The most advantage of optical fiber is the small diameter of its core, so, this advantage allows it to be employed in simplified optical design, very small areas,

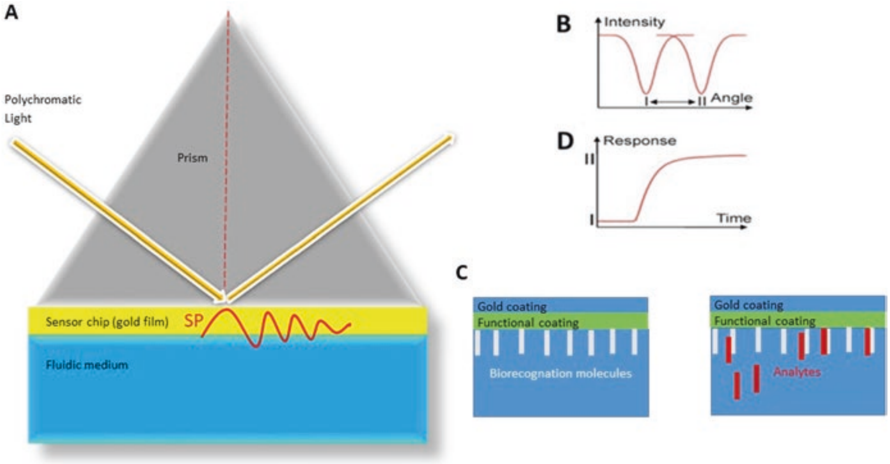

Fig. 12.4 Concept of the SPR sensor (**a**) Kretschmann geometry of the ATR method; (**b**) changing the refractive index before and after binding the target; (**c**) binding the target on the SPR biosensor; and (**d**) changing the refractive index. (Adapted from Šípová and Homola 2013)

and the capability for remote sensing. The concept of SPR has been usually used for analyzing the conformational of proteins, the interaction between molecules, detection of the pesticides, biomolecular interactions, and other biological samples. Here, the detection process occurs by changing the refractive index in all the cases (Matsubara et al. 1990).

Yao et al. integrated SPR sensor with surface molecular imprinting methods for sensitive detection (Yao et al. 2013). They used magnetic nanoparticles for amplifying the response of the SPR sensor. They developed a magnetic polymeric-based nanoparticles by self-polymerization of dopamine on the Fe_3O_4 NPs surface using chlorpyrifos (CPF) as a template. Figure 12.5a has shown the schematic preparation of magnetic imprinted NPs, and Fig. 12.5b has shown the preparation of magnetic nanoparticles-based SPR sensor. Also, they implied the recognition and separation of chlorpyrifos with the designed SPR sensor. After obtained the CPF imprinted magnetic nanoparticles (Fe3O4@PDA NPs), they used transmission electron microscopy, UV−vis absorption spectroscopy, and Fourier transform infrared spectroscopy for characterization of the NPs. In this study, the concentration of CPF was detected from 0.001 to 10 μM and the limit of detection value was reported 0.76 nM. The selectivity, sensitivity, and stability of the magnetic NPs based SPR sensor were demonstrated an excellent recognition for pesticide residuals and other environmentally deleterious chemicals.

Saylan et al. (2017) prepared molecularly imprinted nanofilms-based SPR sensors for fast, real-time, selective, and sensitive detection of multiple pesticides. They used atrazine (ATZ), simazine (SMZ), and cyanazine (SNZ) as template molecules in molecularly imprinted technology using *N*-methacryloyl-l-phenylalanine methyl ester, ethylene glycol dimethacrylate, and 1-vinyl imidazole as a functional

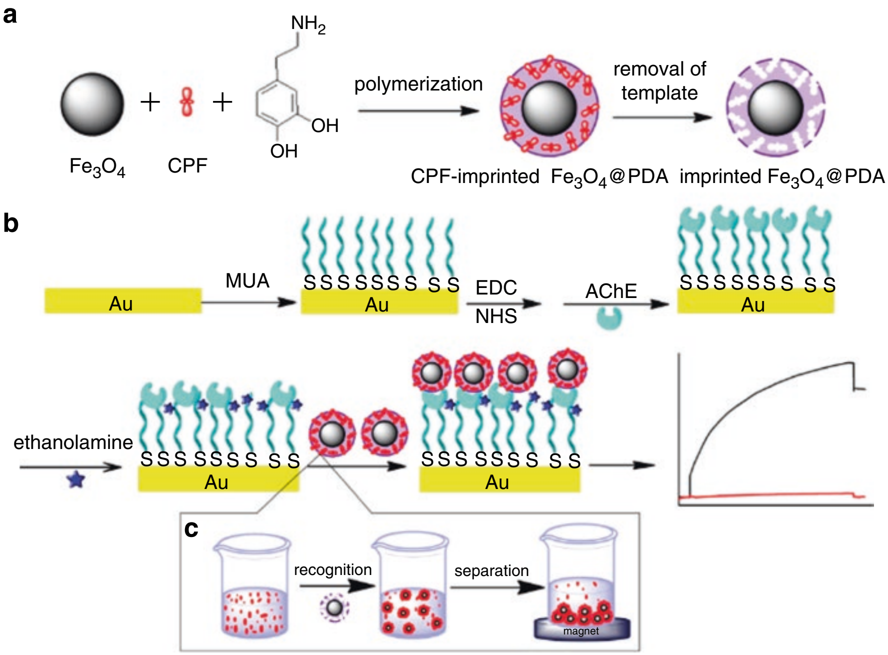

Fig. 12.5 The preparation of magnetic nanoparticles and SPR sensor response (Yao et al. 2013)

monomer, cross-linker, and co-monomer, respectively. They reported 0.095 nM limit of detection value for SNZ, 0.031 nM for SMZ, and 0.091 nM for ATZ. Also, they showed a selective SPR platform for multiple pesticides where ATZ, SMZ, and SNZ were investigated as competitor molecules.

In another study, Lin et al. (2006) developed the AChE immobilized LSPR biosensor for the detention of the organophosphorus pesticide. They used a self-assembling technique via absorption characteristics of Au nanoparticles for sensitive detection. The optimal incubating conditions were reported 12.5 mU/mL AChE for the immobilization of AChE onto the LSPR sensor. They demonstrated 1–100 ppb concentration of paraoxon via LSPR biosensor and successfully reported a 0.234 ppb limit of the detection value.

12.3.2.3 SERS Based Sensors

Primarily SERS has appeared from the LSPR of metal nanostructures (Au and Ag nanoparticles) (Ameer et al. 2014). SERS has been used in a large range of physics and chemistry, as well as life and material science with unique characteristics such as rapid response, ultrasensitive detection, narrow peak bandwidth, and non-destructive detection. Therefore, SERS has been utilized for the determination of pesticide residues in food (He et al. 2015).

In this field, Tang and their coworkers used Ag nanoparticles as a SERS substrate for the detection of chlorpyrifos and imidacloprid. They reported sensitive detection for both pesticides and obtained 50 ng/mL imidacloprid and 10 ng/mL for chlorpyrifos. They showed a simple method to produce a low-cost and non-planar SERS substrate. The low detection results in the chlorpyrifos and imidacloprid can be allowed using this technology for the analysis of pollutants with high sensitivity in the environment and food (Tang et al. 2019). In another work, Xu et al. (2020b) developed a novel sensor using Au nanoparticles templated from mesoporous silica film. They used the air–water interface as a promising SERS substrate for sensitive 2,4-dichlorophenoxyacetic acid, thiamethoxam, and pymetrozine detection. They reported 5.15 nm size of Au nanoparticles and reported 0.79 pg/mL limit of the detection value for 2,4-dichlorophenoxyacetic acid. Also, they obtained 1.21 and 1.04 pg/mL of detection limit of thiamethoxam and pymetrozine, respectively. They showed highly sensitive and stable methods for the detection of pesticides via Au nanoparticles SERS technology.

12.3.2.4 Colorimetric Sensor

The main feature of colorimetric sensors which is the behavior of transforming response into detectable color change makes these methods promising candidates for the development of point of care devices. For the development of rapid and sensitive colorimetric sensors in order to achieve the efficient detection of pesticides in foods and water sources, advances in nanotechnology such as modifications of nanoparticles are enormously utilized. The modifications and functionalizations performed on the surface of metal nanoparticles (silver and gold) affect the localized surface plasmon resonance characteristics of nanoparticles. Due to the changes in the surface chemistry of nanoparticles, when the interaction occurred between the analyte and metal nanoparticles, a color change that is based on the LPSR change can be detected by naked eyes or with the use of a spectrophotometer (Yan et al. 2018). On the other hand, when the target binding is established, gold nanoparticles (AuNPs) constitute aggregates that lead to surface plasmon resonance coupling, and the color of AuNPs changes (Liu et al. 2018).

Recently, many different applications have been realized for pesticide detection by the use of metal nanoparticles to develop colorimetric sensors. Bai et al. (2015) used ssDNA functionalized AuNPs as an aptamer for the selective detection of six different organophosphorus pesticides (OP). The mechanism of this assay is based on the color change of AuNPs from red to blue-purple because of the aggregation of nanoparticles caused by target binding. Similarly, poly(diallyldimethylammonium chloride) (PDDA) interacted aptamers and AuNPs used for the investigation of a novel system to detect malathion colorimetrically (Bala et al. 2016a). After the modifications that applied to the surface of AuNPs, the shift occurred on the maximum absorption wavelength of NPs by the changes in the particle shape, size, and interparticle distance can cause a large color change (Liu et al. 2018). For instance, to detect glyphosate existed in water sources, the colorimetric assay was developed by using cysteamine modified AuNPs (Cs-AuNPs). The presence of glyphosate was observed with the naked eye by the color change of Cs-AuNPs from red to blue after aggregation. Also, the quantity of glyphosate was determined using UV visible spectrophotometer with an LOD of 5.88×10^{-8} M (Zheng et al. 2013). Similarly, lipoic acid-functionalized AuNPs and catalytic activity of acetylcholine esterase (AchE) based sensor systems have shown high potential to achieve rapid and on-site detection of organophosphate compounds with an LOD. The color of lipoic acid-functionalized AuNPs turns red to blue due to the aggregation of NPs induced by AchE activity in the presence of pesticides (Sun et al. 2011a, b). Additionally, using binding capacity between atrazine and melamine through the interactions of the hydrogen bond, the colorimetric sensor based on melamine modified AuNPs has been utilized to monitor herbicide pesticide contamination (Liu et al. 2015b). As a result, the change in the form of AuNPs from dispersion to aggregation form or modifications applied to AuNPs leads to color change (Chen et al. 2018b).

Moreover, a rapid and highly selective detection method was reported by Menon et al. monitoring dimethoate pesticides contamination in wastewater using modified AgNPs with *p*-sulphonate calix resorcinarene. The principle of this method is based on the strong electrostatic interactions between the pSC_4R and dimethoate which cause the aggregation of pSC_4R AgNPs and finally visible color change from yellow to red. When the selectivity studies were examined by using various pesticides, no color change was observed other than dimethoate (Menon et al. 2013). For the successful analysis of rice samples, a colorimetric sensor to detect tricyclazole fungicide has been developed by using 5-sulpho anthranilic acid dithiocarbamate-modified silver nanoparticles (SAADTC-AgNPs). In this method, as a result of the aggregation of SAADTC-AgNPs due to the electron donor–acceptor interactions with tricyclazole, the color change has occurred from yellow to red. Thus, tricyclazole fungicide was detected with LOD of 1.8×10^{-7} M (Rohit and Kailasa 2014).

Also, in recent years, paper-based sensor systems can be used for the colorimetric detection of several pesticides. Bordbar et al. (2020) constructed a paper-based colorimetric sensor by using modified AuNPs and AgNPs on the surface of the paper for monitoring pesticide contamination in the real samples including rice samples, apple juice, and tap water. To modify NPs, polyglutamic acid, L-arginine, and quercetin were used. The color change was observed for modified AuNPs from red to purple and for AgNPs from yellow to brown due to the interactions between the analyte and functional groups of capping agents. Each NPs modified with different capping agents can discriminate different pesticides due to the active sites that contain in their chemical structure. With the development of this method, the discrimination and determination of six different pesticides including carbaryl, paraoxon, parathion, malathion, diazinon, and chlorpyrifos were achieved with LOD of 29.0, 22.0, 32.0, 17.0, 45.0, and 36.0 ng/mL, respectively. Additionally, Shrivas et al. (2020) reported a paper-based nanosensor supported with the smartphone in order to detect phenthoate pesticides from food and water samples with a limit of detection of 15 μg/L. Citrate capped Cu@Ag core-shell NPs were preferred for the selective determination study. The detection mechanism is based on the high binding affinity of phenthoate to AgNPs that existed on the surface of CuNPs which leads to aggregation and color change on the paper. Consequently, it has been proved that colorimetric sensors have a capacity for rapid monitoring and discriminating pesticides in order to prevent the entry of these hazardous pollutants into the human body.

12.3.3 Piezoelectric Sensor

Piezoelectric sensors are applied to detect commonly used pesticides from food and environmental sources also called quartz crystal microbalance (QCM). Due to a mass change that occurred at piezoelectric (quartz) crystal after the partial or complete immersion of crystal into a liquid solution, these crystals can be used to fabricate sensor systems by combining with the recognition elements such as an antigen, antibody, enzyme, aptamer, MIP polymer (Pundir and Malik 2019). As a result of affinity interactions, the oscillation frequency of quartz changes due to the increase in the mass of the surface layer. The detection of target analytes without label-free methods makes this sensor system attractive for various analysis. Several applications especially immunosensor based approaches have been performed for pesticide analysis by using QCM sensor devices (Ermolaeva et al. 2019).

QCM immunosensor using monoclonal antibodies was investigated to detect carbaryl that is a carbamate pesticide and 3,5,6-trichloro-2-pyridinol (TCP) in fruit juices. The detection limits of 11 and 7 μg/L were recorded for carbaryl and TCP, respectively, with the use of this immunosensor system (March et al. 2009). Likewise, Pan et al. (2013) fabricated piezoelectric immunosensing chip by using multi-wall carbon nanotube/poly(amidoamine) dendrimer (MWCNT-PAMAM) hybrid material to enhance the antibody immobilization. They developed a sensitive and stable immunoassay-based QCM method capable to detect metolcarb that is a carbamate group pesticide in apple and orange juices with a detection limit of 0.019 mg/L. Additionally, High Fundamental Frequency QCM biosensor based upon immunoassay constituting with the use of monoclonal antibodies specific to analyte molecule was developed to detect sulfathiazole in honey by Cervera-Chiner et al. (2020). They can detect 40–50 times lower sulfathiazole amount with LOD of 0.10 μg/kg than the other studies performed for antibiotic analysis.

In the past decades, several methods have been realized using QCM immunosensors or enzyme sensors based upon specific antigen–antibody interaction in order to determine the pesticide residues in food or water samples with low detection limits (Karousos et al. 2002; March et al. 2015). Currently, piezoelectric sensors that combined with molecular imprinting technology are applied to obtain more accurate, easily performed, and cost-effective methods for detecting pesticides. Using sensitive QCM with molecular imprinting technique which is based on the synthesis of polymer materials capable of binding to target molecules to create synthetic recognition units provides great convenience in measuring the amounts of pesticide residues (Liu et al. 2020). Moreover, 2,4-dichlorophenoxyacetic acid imprinted [ethylene glycol dimethacrylate-*N*-methacryloyl-(l)-tryptophan methyl ester-p(EGDMA-MATrp)] polymeric nanofilms have been synthesized to determine pesticide amount in apple sample by using QCM sensor system. This study revealed that the developed MIP-based QCM sensor system is a good candidate for pesticides detection with a fast response time, high sensitivity, selectivity, and low detection limit at 20.17 ng/L (Çakir et al. 2019).

Another sensible approach for pesticide detection is using the molecular imprinted (MIP) polymers as a recognition element, which has been discussed by Sroysee et al. Two different MIP polymers were fabricated for selective determination of carbofuran (CBF) and profenofos (PFF) that belong to insecticide family. While methacrylic acid (MAA) based imprinted polymer was synthesized for recognition of carbofuran, poly(4-vinylphenol) (PVP) and diphenyl methane-4,4′-di-isocyanate (DPDI) were used as functional monomers to create synthetic recognition sides for profenofos. LOD was recorded as 0.21 μM and 0.38 μM for CBF-imprinted and PFF-imprinted, respectively, with the use of MIP-QCM sensor system (Sroysee et al. 2019).

12.3.4 Enzyme-Based Sensor

Various types of recognition elements can be used to develop a sensitive biosensing system for the detection of pesticides from water and food samples. One of them is enzymes which are utilized to develop sensor systems for pesticide determination designed on the principle of enzyme inhibitory effects of pesticides (Table 12.4).

In order to develop enzyme-based sensors, inhibition of different enzymes were exploited such as cholinesterases (Doong and Tsai 2001), peroxidase (Oliveira et al. 2012), laccase (Zapp et al. 2011), photosynthetic system II (Giardi et al. 2001), cytochrome P450A1 (Wu 2011), alkaline phosphatase (Sánchez et al. 2003), aldehyde dehydrogenase (Noguer et al. 2001), urease (Vaghela et al. 2018), and tyrosinase (Kim et al. 2008). Another approach of a designing biosensor for pesticide determination is based on the utilization of enzymes that use pesticides to act as a substrate. The advantages of this method over the method described above are that it is direct, more selective, simple, and suitable for real-time monitoring. For instance, organophosphorus hydrolase (OPH) and organophosphorus acid anhydrolase (OPAA) which catalyze the hydrolysis of organophosphorous pesticides can be used to develop enzyme-based biosensor by using combined with several transducers such as optical and electrochemical for the detection of organophosphorus pesticides (OP). Moreover, Methyl parathion hydrolase (MPH) which catalyzes the hydrolysis of a wide range of OP, can be used to fabricate enzyme-based sensor systems for sensitive and selective detection of OP. By exploiting the catalytic activity of enzymes can be exceeded the limitations of enzyme inhibition-based sensor systems (Verma and Bhardwaj 2015; Pundir and Malik 2019). Due to the nonreusable features of enzyme inhibition-based sensors caused by the inhibitory effects of OPs and carbamates against the enzymes, catalytic sensors should be preferred for the selective determination of OPs. Furthermore, while OPH enzyme shows

Table 12.4 Applied enzyme inhibition-based biosensors for pesticide determination

Pesticide	Enzyme	Method	Sensing device	Sample	LOD	Reference
Paraoxon	AChE	AChE immobilized on the multi-wall carbon nanotubes	Electrochemical	Water	0.5 nmol/L	Joshi et al. (2005)
Paraoxon	AChE	AChE immobilized on the nylon membrane surface	Electrochemical	Grape	0.1 μg/L	Boni et al. (2004)
Paraoxon Carbaryl	AChE variant	Cross-linked with GA	Electrochemical	Milk	1.20 μg/L	Zhang et al. (2005)
Organophosphorus Carbamic	AChE	AChE immobilized via glutaraldehyde on an electrochemical-deposed multilayer of cysteamine	Impedimetric	Water and lettuce samples	8 ppb 10 ppb	Malvano et al. (2017)
Ziram Carbofuran	Laccase	Laccase immobilized on graphene doped carbon paste electrode functionalized with Prussian blue films	Electrochemical	Tomato and potato crops	5.2×10^{-9} mol/L 1.0×10^{-7} mol/L	Oliveira et al. (2013)
Glyphosate	Urease	Urease conjugated with AuNPs immobilized in agarose-guar gum matrix	Potentiometric	Water	0.5 ppm	Vaghela et al. (2018)
Paraoxon	AChE	Color change of LA capped AuNPs with enzyme inhibition	Optical	Fruit	4.52×10^4 pM	Sun et al. (2011a, b)
Methamidophos Malathion	Alkaline phosphatase	Enzyme-triggered deposition of AgNPs on the surface of AuNPs	Optical	Water	0.025 μg/L 0.036 μg/L	Lv et al. (2016)

GA glutaraldehyde, *LA* lipoic acid

substrate specificity to the target OPs, AChE enzyme can respond to any kind of compound that inhibits AChE enzyme. On the other hand, catalytic sensor systems offer advantages such as high specificity, selectivity, short response time, real-time monitoring, and reusability for detecting pesticides in the food and water samples (Songa and Okonkwo 2016). Several studies based upon catalytic biosensors are given in Table 12.5 to discuss the capability of different methods in pesticide detection.

12.4 Conclusion and Outlook

Consumers today are urging their governments to take more responsibility for food safety and consumer protection (World Health Organization/FAO 2003). In modern farming practices, pesticides are primarily used for preventing, controlling, or eliminating pests and weeds to increase agricultural productivity. Recently, pesticide usage in agriculture has increased. Pollution caused by pesticides adversely affects water, food, and soil. The toxicity of pesticides is vital to humans and insects. Therefore, for this reason, it is important to determine the pesticides in water and food with sensitive, fast, and reliable methods in order to protect human health from possible dangers.

Biosensors are widely used as analytical techniques that are cost-effective, fast, in situ, and capable of real-time measurements. When the need for portable, fast, and smart biosensing devices are combined with materials in nanotechnology, the development of biosensors for pesticide detection has been accelerated.

Currently, there are several types of biosensors used to detect chemicals and pesticides (Justino et al. 2017). And in these biosensors used recognition elements such as enzyme, antibody, molecularly imprinted polymers, aptamer, and also host–guest reactions involved are mentioned. This chapter explored the key features of established strategies regarding sensors used for pesticide detection. In addition, we provided information on the drawbacks of the current sensor and future prospects and also ongoing efforts to improve pesticide sensors. The latest developments in biosensors used to monitor potentially toxic elements, pesticides, under real conditions in food and water were evaluated. Pesticides are widely used today to prevent unwanted pests from attacking crops and livestock. The overuse of pesticides widely used today to prevent unwanted pests from attacking crops and livestock has serious harmful effects on human health and all other living organisms. Various diseases are associated with exposure to pesticides, such as cancer, chronic obstructive pulmonary disease, birth defects, infertility, and further harm to human health. The Codex Alimentarius Commission and the European Union have regulated maximum pesticide residue limits to protect human health. Therefore, it is important to monitor these compounds to ensure that only allowable pesticide levels are maintained. To date, various detection techniques have been developed for pesticides, from traditional analytical techniques to advanced detection methods. Traditional analytical techniques involving gas chromatography and high-performance liquid

Table 12.5 Enzyme-based biosensors utilizing catalytic activity of enzymes developed for pesticide determination

Pesticide	Enzyme	Method	Sensing device	Sample	LOD	Reference
Parathion-methyl	OPH	OPH immobilized on $CuInS_2$ QDs	Optical	Water, rice, banana	0.06 μmol/L	Yan et al. (2015)
Parathion-methyl	MPH	MPH immobilized on *N*-doped carbon dots	Optical	River and pear	0.338 μmol/L	Song et al. (2017)
Organophosphorus	OPH^{6His}	OPH^{6His} encapsulated with Terbium-BTC-metal-organic framework	Optical	Grape and tomato	2.3 nM/L	Mehta et al. (2019a, b)
Parathion-methyl	MPH	MPH immobilized on 4-carboxyphenyl Modified AuNPs	Electrochemical	Green tea	0.07 ppb	Liu et al. (2014)
Organophosphate pesticides	OPH	Nanocomposite designed by ELP-OPH/BSA/TiO_2NFs/AuNPs	Electrochemical	Lake water	29 nM	Bao et al. (2016)
Parathion-methyl	OPH^{6His}	OPH^{6His} immobilized on the surface of UiO-66-NH_2	Optical	Orange and tomato	10 ng/mL	Mehta et al. (2019a, b)
Organophosphorus	OPH	OPH immobilized on the LIG-based electrode	Electrochemical	Spinach and apple	2.63 μg/L	Zhao et al. (2020)
Organophosphate insecticides	MPH	MPH immobilized onto a chitosan film-coated polystyrene microplate via MPH-GST	Optical	Tap water Asparagus Basil leaves	1 ppm 2 ppm 3 ppm	Senbua et al. (2020)

MPH methyl parathion hydrolase, *OPH^{6His}* hexahistidine-tagged organophosphate hydrolase, *BTC* 1,2,4-benzenetricarboxylic acid, *ELP* elastin-like polypeptide, *BSA* bovine serum albumin, *TiO_2NFs* titanium oxide nanofibers, *LIG* laser-induced graphene, *MPH-GST* glutathione-*S*-transferase chromatography coupled with various detectors involve the sample preparation step before analysis.

Advanced detection methods are used in electrochemical, optical, piezoelectric, and enzyme-based sensors. In this review, traditional and advanced methods used for pesticide detection in the environment and foodstuffs are summarized. In addition, pesticide classification, toxicity, and available extraction methods are briefly discussed (Samsidar et al. 2018).

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Chapter 13
Algae Mediated Pesticides Bioremediation: Mechanisms, Approaches, Limitations, and Prospects for Future Research

Meenakshi Singh, Krupa Unadkat, Punita Parikh, and K. Chandrasekhar

Abstract The advent of the green revolution boosted agricultural practices' use to suffice the food demand. However, due to their highly accumulative and permanent nature, the repeated use of pesticides caused significant environmental problems. Microalgae technology has recently made enormous progress in the effective treatments of contamination from pesticides. This chapter brings introductory insights on pesticides and their inevitable need in agricultural practices to control pest's population. The global pesticide market share according to geographic region and their commercial consumption by the key manufacturers are discussed briefly. Based on previous research, the metabolic pathways involved in pesticide elimination are outlined in this chapter. Different strategies employed to increase the capability of algae to extract pesticides are discussed. Also, the reuse of algae biomass after pesticide removal for charcoal production and biodiesel production was also studied. Besides, we discuss probable future research lines to show the prospects for microalgae research in pesticide removal and value-added product manufacture.

Keywords Pesticides · Green remediation methods · Microalgae · Biodiesel · Biodegradation

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13.1 Introduction

The alarming rise of global food demand is affecting conventional agriculture practices, which are under tremendous pressure to meet sufficient food demand. The farmers are dependent on chemical substances to increase the soil vigour and plant production capacity. Consequently, advanced agricultural techniques and better management practices based on synthetic chemicals were introduced to feed the growing human population. This practice allowed control over some organisms that destroy the crops by causing the disease to crop plants, ultimately leading to economic loss and poor plant growth. These unwanted organisms are called pests which can be eradicated using certain chemicals in the early infestation period. Pesticides are considered a quick and easy solution to control weeds and insects in the agriculture field as they improve crop yield (Pandya 2018; Gulliya et al. 2020; Gonçalves 2021).

The recent years witnessed progress in the research and development activities focused on agricultural techniques, and thus resulted in potential market size of pesticides. The global pesticide market size is expected to achieve $70.89 billion by 2025, at a CAGR of 3.67% during the forecast period 2020–2026, by Industry ARC report on "Pesticides Market—Forecast (2020–2026)" (Pesticides Market Research Report 2021). However, the adverse impact of synthetic pesticides on natural surroundings has raised questions about their massive application. Chemical pesticides are emerging micropollutant which also causes adverse effects on the aquatic atmosphere and non-target organisms (Chavoshani et al. 2020). In the agricultural field, pesticide application has been increasing for crop improvement and remains as a residue in the field. They enter the food chain of an ecosystem and result in biomagnifications, which can harm human health (Upadhayay et al. 2020). Many technologically advanced and emerging countries are promoting awareness about microalgae cultivation that is capable to remove pollutant and thus may reduce geopolitical stress on food distribution (Molinuevo-Salces et al. 2019). The microalgae-based solutions bioremediate the environment in a highly adaptive manner, i.e., can be grown in autotrophic, heterotrophic, and mixotrophic mode because algae are photosynthetic organisms and metabolically active at certain pH, temperature, and salinity in the waterbodies (Ławniczak et al. 2020).

13.1.1 Pesticides: Why Is Their Need Inevitable?

Pesticides are chemical or biological agents that are designed to control pests and boost up the yield in the agriculture field. The first-time synthetic pesticide has been introduced in the agriculture field around the world in 1950s. Moreover, pesticides have improved crop quality, crop productivity, faster growth of plants, and control invasive species, pests, and disease vectors, thus improving the economy. In this way, pesticides help reduce food demand by enhancing agricultural production, leading to the green revolution. However, on the dark side, excessive use of pesticides can affect soil fertility, water purity which enters into the food chain resulting in biomagnifications (Aktar et al. 2009; Upadhayay et al. 2020).

13.1.2 Pesticides

Pesticides are extensively well known for their chemical and toxicological properties. Therefore, they will continue to be part of the environment to increase crop production. In addition, it helps to produce environmentally friendly food production and reduction in the annoyance produced by the pest. They are synthetic chemicals that inactive the pest or directly kill the pest. They are highly and quickly effective in controlling target pest populations. Chemical pesticides are providing greater persistent control as well as a more prolonged residual activity under field conditions. Chemical pesticides can be classified (1) based on types of pests which they kill (Fig. 13.1) and (Fig. 13.2) based on chemical structure. They are also classified based on the types of pests which they kill. For example, insecticides (killing insects), bactericides (killing bacteria), herbicides (killing weeds), fungicides (killing fungi), and rodenticides (killing rodents).

Understanding these devastating impacts on human health, the need for more efficient treatment technology is evident. As a substitute, systems are of natural origin, non-toxic, cost-effective, and environmentally sustainable (Gonçalves 2021). For example, algae-based systems offer promising results towards bioremediation of pesticide-contaminated environment (Goswami et al. 2020). These results have

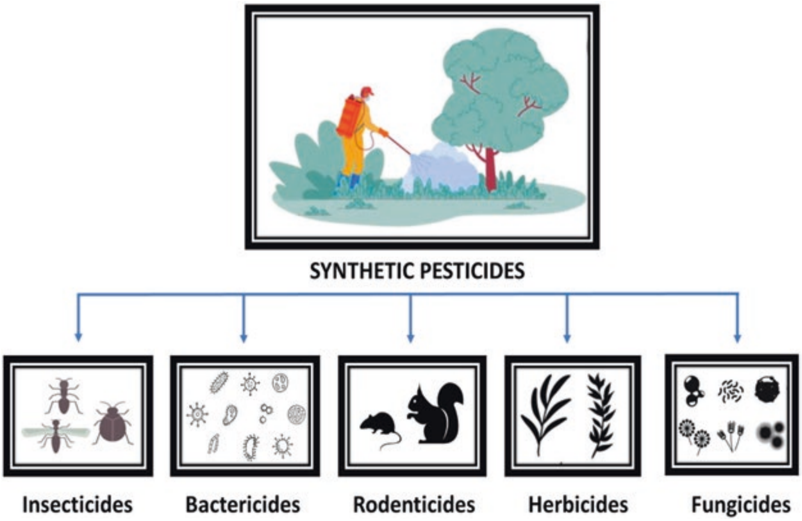

Fig. 13.1 Classification of synthetic pesticides based on types of pests

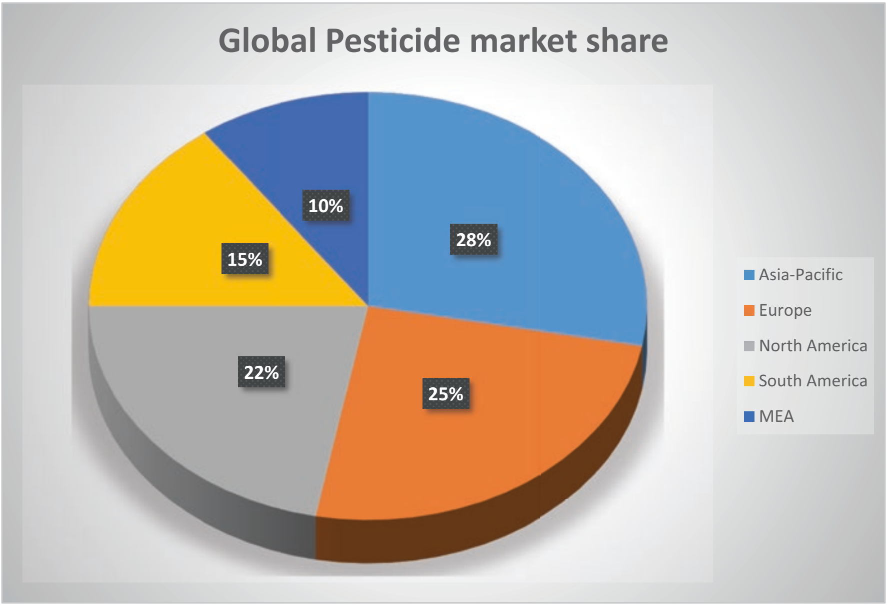

Fig. 13.2 The anticipated global pesticide market share of five major regions of the world

proved that algae-based bioremediation techniques have a colossal scope that provides major fortuity for more resilient and imperishable agriculture (Nicolopoulou-Stamati et al. 2016).

13.2 Microalgae as Biocontrol Agents of Pesticides in Agricultural Practices

13.2.1 Pesticides in Agriculture

As per the definition given by USDA, synthetic or conventional pesticides are formulated or manufactured with the help of a chemical process. It also involves changes in the chemical properties of substances obtained from sources of natural origin. Depending upon the type of pests killed by pesticides, they are classified as insecticides (insects), herbicides (plants), rodenticides—rodents (rats and mice), bactericides (bacteria), fungicides (fungi), and larvicides (larvae) (Yadav et al. 2019). Organochlorines, pyrethroids, organophosphates, and carbamates are again the pesticide categories that are in conformity with their chemical composition (Table 13.1).

Because of a wide range of spectrum activity and quick action, pesticides have become an integral part of agriculture as well as household as far as global food

Table 13.1 Classification of chemical pesticides based on the chemical group (Sciacca and Conti 2009)

Chemical group	Examples	Toxic effects
Organochlorines	DDT, toxaphene, dieldrin, aldrin	Carcinogenic, neurotoxic, hormonal agonist
Organophosphates	Diazinon, glyphosate, malathion	Neurotoxic, dermatotoxic
Carbamates	Carbofuran, aldicarb, carbaryl	Neurotoxic, dermatotoxic
Pyrethroids	Fenpropathrin, deltamethrin, cypermethrin	Hormonal agonist neurotoxic, immunotoxic
Inorganic chemical pesticides	Zinc chloride, zinc phosphide/phosphine, copper sulphate, barium carbonate	Pulmonary fibrosis, carcinogenic

demand is concerned. Among various pesticides, the most widely used for agriculture are carbofuran ($C_{12}H_{15}NO$), DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane), BHC (Benzene hexachloride; a stereoisomer of 1,2,3,4,5,6-hexachlorocyclohexane), endosulfan ($C_9H_6C_{16}O_3S$), dimethoate ($C_5H_{12}NO_3PS_2$; *O*,*O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] dithiophosphate), and acetamiprid ($C_{10}H_{11}ClN_4$). The usage of these pesticides has brought about a revolution in the field of agriculture worldwide and has proved as a boon in agricultural produce (Maryjoseph and Ketheesan 2020a, b). Nevertheless, simultaneously, they are known to harm all the forms of life that are targeted to pest and non-targeted species. It poses diverse ecological impacts ranging from chronic to acute toxic effects on major environmental components such as water, soil, air, and biota. Pesticides have gained popularity among various agrochemicals. The agrochemicals intended to enhance food production lead to the augmentation of different agrochemicals of a hydrophobic type such as dithiothreitol (DDT), endosulfan, heptachlor, lindane and their intermediates (Jayaraj et al. 2016) due to their retention capabilities in the soil which ultimately get transferred from crops and subsequently get magnified at higher trophic levels. This poses severe threats to public health (Upadhayay et al. 2020) and aquatic life (Kumar et al. 2020b). India is the 12th largest producer of synthetic pesticides in the world, wherein the maximum population depends on agriculture. The total consumption of pesticides in India is 80% insecticides, 15% herbicides, 2% fungicides, and less than 3% others (Devi et al. 2017). The three utmost normally used pesticides are hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT), and malathion; organophosphorus pesticides being the most widely used. The major challenge for the country is to enhance food production with the compatible reduction of plant pathogens and insect infestation (Avila et al. 2021).

The conventional methods involved in the treatment of pesticides have low removal efficiency, need a high level of energy input, generate a huge amount of sludge, and consume more time. Therefore, bioremediation methods using microalgal technology have gained traction due to their coherence and success in treating pesticide pollution. Besides this, bioenergy can be generated after absorbing nutrients like carbon and phosphorous, which results in the production of algal biomass.

Furthermore, during photosynthesis, algae absorb contaminants and increase oxygen content in water, which in turn increases the growth of many degraders.

13.2.2 Algae as Bioremediator of Pesticides

Pesticides, hydrocarbons, and several other compounds, including cyanides (because algae use cyanides as C and N sources), are absorbed by algae. Their cell wall is made up of carbohydrates that bind with the hazardous toxic chemicals resulting in bioabsorption and finally removing harmful chemical substances from the contaminated sites. Therefore, they are the most suitable candidates for mitigation of several contaminants like phosphorous, nitrogen, heavy metals, pesticides, etc. Reports are suggesting that in addition to having bioaccumulation capacity, microalgae also biodegrade pesticides if they are present in sublethal concentrations (Hammed et al. 2016). They can biosynthesize numerous metabolites that possess biopesticidal action and are potential biological agents that control harmful organisms to soil and plants. This proves that microalgae-based sustainable treatment of pesticides offers greater protection to aquatic as well the land ecosystem. Table 13.2 represents microalgae-based bioremediation of pesticides

13.3 The Global Scenario on the Consumption of Pesticides

The word pesticides are a composite term that includes insecticides, fungicides, and herbicides that can effectively control, abolish, and avoid crop deterioration caused by unwanted pests. Pesticides are usually applied to the plants to control harmful pests that negatively impact the plant's growth, reduce defoliation of leaves, flowers, and fruits, act as a desiccant for fleas, and reduce thinning and premature death falling of fruit. Moreover, the application of pesticides prevents the crop from deterioration during storage and distribution as well help the domesticated animals to be fleas-free and hence disease-free. This has led to rampant consumption of synthetic pesticides worldwide because of good crop yield. The experimental trials on different crops suggested good efficacy against an integrated pest management system meeting all environmental requirements that were upscaled in the market. The pesticide industry is based on several factors: the safety and reliability of pesticides, cost and performance of pest management quality, and a broad spectrum of employability and income generation (Pesticides Market Research Report 2021).

Table 13.2 Algae mediated pesticide bioremediation

Microalgae	Pesticide bioremediation	Reference
Scenedesmus sp., *Chlamydomonas* sp., *Stichococcus* sp., *Chlorella* sp., *Nostoc muscorum* and *Anabaena* sp.	Fenamiphos	Cáceres et al. (2008)
Selenastrum	Capricornutum, benzene, toluene, benzopyrene chlorobenzene, 1,2-dichlorobenzene, nitrobenzene, naphthalene, 2,6-dinitrotoluene, phenanthrene, di-nbutylphthalate, pyrene	Gavrilescu (2009)
Scenedesmus obliquus	DDT, parathion, naphthalene sulfonic acid	Tang et al. (2010)
Chlamydomonas sp.	Mirex, lindane, naphthalene	Zhang et al. (2011)
Anabaena azotica	Lindane	Zhang et al. (2012)
Anabaena sp.	Butachlor	Agrawal et al. (2015)
Anabaena oryzae and *Nostoc muscorum*	Malathion	Ibrahim et al. (2014)
Oscillatoria limnetica	Organophosphates	Salman et al. (2015)
Chlorella vulgaris	Atrazine, molinate, simazine, isoproturon, propanil, carbofuran, dimethoate, pendimethalin, metolachlor, pyriproxyfen	Hussein et al. (2016)
Spirulina sp.	DDT	Kurashvili et al. (2018)
Chlorella vulgaris, *Scenedesmus quadricauda*, and *Spirulina platensis*	Malathion	Abdel-Razek et al. (2019)
Chlorella sp. and *Scenedesmus* sp.	Hydrophobic pesticide Chlorpyrifos, cypermethrin, and oxadiazon	Avila et al. (2021)

13.3.1 Commercially Available Products to Target Species

Generally, the pesticide market potential is determined by the demand, and the last few decades have witnessed an enormous surge of pesticide sales to meet the food demand. There could be many reasons supporting this enormous global usage of synthetic pesticides: (1) As per the average population, limited agricultural land availability suggests more people are dependent on restricted land for food production. (2) Cultivation of GM (genetically modified crops) for higher yield at competitive market price. (3) Affordable rates of pesticides to farmers. (4) Wide acceptability of pesticides and their distributorship in developing countries. (5) The sales of pesticides depend on their application as an agricultural and aesthetic horticultural requirement. In Table 13.3 we have discussed the prominent commercial pesticides of the global presence.

Table 13.3 Different types of synthetic pesticides, commercial name, target species, and their mode of action

Pesticides	Chemicals	Commercial products (common name)	Target species	Mode of action	Reference
Insecticides	• Chlorinated hydrocarbons • Organophosphate • Carbamates	Permethrin, carbaryl, chlorpyrifos, methyl parathion, endosulfan, kelthane, methoxychlor	Grasshopper, beetle Caterpillars	The chlorinated cytotoxins disrupt the functioning of the nervous system	Kurihara (2000)
Fungicides	• Bordeaux mixture • Mercuric chloride • Cadmium chloride • Chloropicrin • Methyl bromide • Formaldehyde	Fosetyl-Al, vinclozolin, thiophanate-methyl, mancozeb, chlorothalonil, azoxystrobin, PCNB	Pathogenic fungus	Interrupt the function of the specific metabolic enzymes and halt cellular respiration	Kumar et al. (2018)
Herbicides	• Phenoxy and benzoic acid (2,4-D) • Sulphates and nitrates of copper and iron • Sulphuric acid	Glyphosate, pelargonic acid, trifluralin, pendimethalin, DCPA, sethoxydim, clethodim, halosulfuron, bentazon	Weed and invasive species	Inhibition of amino acid synthesis, disruption of cell membrane, and inhibition of regular plant growth	Kumar Das and Mondal (2014)
Larvicides	• Anthranilic diamide • Phthalic diamide	Permethrin, malathion	Lepidopteran larvae	Methomyl, thiodicarb, chlorantraniliprole, flubendiamide, emamectin benzoate, bifenthrin, abamectin	Liu et al. (2017)
Rodenticides	• Coumarins • 4-hydroxycoumarins • Metal phosphides	Act as anticoagulant and cause internal haemorrhaging	Rats, mice, squirrels, chipmunks, porcupines, beavers, and other rodents	Warfarin 1080 (sodium fluoroacetate), ANTU (α-naphthylthiourea), arsenic trioxide, barium carbonate, fluoroacetamide, thallium sulphate	Kumar et al. (2018)

Pesticides	Chemicals	Commercial products (common name)	Target species	Mode of action	Reference
Bactericides	• Active chlorine and oxygen • Iodine • Concentrated alcohol • Phenolic substance • Heavy metals	Destroy the cell wall synthesis	Bacteria	Wet chlorine, peroxides, lugol's solution, ethanol, phenol, mercury chloride, silver nitrate	Kumar et al. (2018)
Nematicides	• Avermectin • Carbamate • Methyl isothiocyanate • Organophosphate • Benclothiaz	Once ingested, they are toxic to the internal organs of nematodes and cause paralysis in the juveniles	Nematodes and parasitic worms	Avermectin, fosthiazate, oxamyl, fenamiphos, ethoprophos, cadusafos, chloropicrin, Vapam, paladin, mocap, nimitz	Taylor (2003), Ronald et al. (2019)
Acaricides	• Permethrin • Ivermectin • Carbamate • Organophosp • Dicofol • Lime sulphur	Inhibits the mitochondrial electron transport system and lipid biosynthesis	Arachnids—spider, mites, and ticks	Spiromesifen, chlorfenapyr, abamectin, fenpyroximate, hexythiazox, bifenazate, dicofol	Reddy et al. (2014)
Nanopesticides	• Nanoemulsions • Nanocapsules • Inorganic engineered nanoparticles (ENPs)	Target the cell wall of mould/yeast/gram-positive or gram-negative bacteria, and they accumulate in the cytoplasm causing cytotoxicity	Microbes	Carboxymethyl chitosan, chitosan-saponin, alginate, polyhydroxybutyrate-co-hydroxyvalerate (TiO_2, ZnO, SiO_2, fullerenes)	Prasad et al. (2017)

13.3.2 Market Demand

The agricultural and horticultural practices depend heavily on pesticides as the pest-free crop or fruit yield is in high demand. The businesses of buyers or distributors and sellers vastly prefer to purchase disease-free commodities to earn a good source of revenue. Because of this, farmers apply synthetic pesticides to increase their source of income and save the crop from pest infestations. Additionally, pesticides are used to clear roadside weeds, trees, and bushes; at home to kill termites and moulds and remove wasps and bees' nests. The departmental stores with grocery items regularly employ pesticide treatment to manage rodents and insects' population.

However, certain pesticide market drivers need to be addressed to meet the demands across the world. First, the farmers should adopt intensive farming techniques to increase the crop yield. This will allow mechanized tools to grow different crops at a time to get maximum output, and crop rotation practices will prevent nutrient loss due to the overuse of pesticides. Second, the farmers must apply integrated pest management practices in their farms, such as growing pest-resistant crops, employment of mechanical traps to kill rodents, regular plowing of the field to destroy the nesting areas of pests under the harvested crops. Third, use of eco-friendly pesticides such as nanopesticides, which work at the nanoscale and eliminate pests by destroying the cellular mechanisms of pests (Enamala et al. 2021). According to TechSci Research report (2018), the geographic market share of pesticides is separate out into North America, Europe, Asia-Pacific, South America, and Middle-East and Africa (MEA). The Asia-pacific market is showing the most exponential growth (28%) of pesticide sales. This can be attributed to the high population density versus limited agricultural land. In the Asia-Pacific segment, India, China, Pakistan, Bangladesh, and Sri Lanka are the prominent markets for all types of pesticides because they produce mostly cereals, fruits, and vegetables. Similarly, the rapid consumption of pesticides in Europe with an anticipated sales of 25% pesticides in 2023 (Market APCPP 2021). In European nations, the requirement for pesticides is high, based on cash crops, to boost the agricultural economy. The pesticide sales are expected to reach 22% in North America, where stakeholders are interested in promoting non-toxic synthetic pesticides and proposing a strategic framework for business growth. Latin America's data on untapped avenues of the agricultural economy is possible by using pesticides that significantly reduce crop loss and improve the quality of the crop. It is expected to be 15% by 2023 due to progressive talks of farmers and industry partners to boost the supply chain network (Market LACPC 2021). As per the Market MEAAA (2021), the Middle east and Africa (MEA) segment is anticipated to reach 10% by providing the government subsidy to small-holder farmers, agronomists, extensive agricultural dealers to use non-toxic chemical pesticides to protect the community and the environment (Fig. 13.2).

13.3.3 Key Manufacturing Companies

The agrochemical market is driven by many key manufacturing companies such as Syngenta, Bayer CropScience, Dow Agrosciences, BASF SE, DuPont Inc., FMC Corporation, Sumitomo Chemical, BioWorks, and Monsanto. As per the geography segment analysis, many competitor companies are listed in (Table 13.4), which clearly depicts the huge demand for pesticides across the globe. These industries play a vital role in the distribution of pesticides to increase agricultural productivity to ensure adequate food supply for the budding human population.

13.4 Cultivation, Screening, Identification, and Characterization of Microalgae

Algae is ubiquitous in nature and represents great diversity in its solitary and colonial forms with variable physiological attributes. Algal diversity differs as per the environmental conditions and the growth requirements, which phototrophic, heterotrophic, and mixotrophic conditions can commercially attain. Basically, rapid algal growth is influenced by several key factors such as temperature, light duration, and intensity, available micronutrients, and macronutrients, CO_2, and pH. These conditions will promote algal photosynthesis efficiency, enabling them to accumulate

Table 13.4 List of major pesticide companies in five geographic regions of the world

Geographic region	Competitive landscape of Major players	Reference
Asia-Pacific	Adama Ltd., Bayer CropScience AG, Camson Bio Technologies Ltd., FMC Corporation, Meiji Seika Pharma Co. Ltd., SomPhytopharma India Ltd., Shandong Weifang Rainbow Chemical Co. Ltd., Syngenta Crop Protection AG, Sumitomo Chemical Co., Ltd., UPL Ltd.	Market APCPP (2021)
Europe	Agrichem Ltd., AGRO International., Agropharm, Crop Protection Association, nterfarm (UK) Ltd., Pesticides Safety Directorate, Suterra	Companies L of EP (2021)
North America	Arkema Inc., BASF Corporation, Bayer Cropscience, BioWorks Inc., Certis USA LLC, Cleary Chemical Corporation, The Dow Chemical Company, Marrone Bio innovation, Monsanto, Isagro S.P.A, UPL Ltd., Nutrichem Company Ltd., Pest Control Supply Company	Company PM (2021)
South America	BASF Corporation, Bayer Cropscience, CCAB Agro Dow-DuPont, FMC Corporation, Nortox, Syngenta AG	Market LACPC (2021)
MEA (Middle east and Africa)	Agrium Inc., Bayer Cropscience, BASF SE, Dow-DuPont, Israel Chemicals Ltd., Monsanto Company, Mosaic Company, Sociedad Química Y Minera SA., Syngenta AG, Yara International ASA	Market MEAAA (2021)

high-value bioproducts within their cells (Jiang et al. 2012). This section will discuss different cultivation techniques, algal screening, identification, and characterization process to assist in the bioremediation of pesticides at nanoscale (Gour and Jain 2019).

13.4.1 Cultivation of Microalgae

Large-scale algal cultivation is majorly carried out by photoautotrophic, heterotrophic, and mixotrophic systems. The techno-economic feasibility of these cultivation systems relies on high biomass productivity as per the volume ratio, low operational and maintenance cost, simple control of growth parameters such as light, temperature, pH, CO_2, turbulence, and salinity.

13.4.2 Photoautotrophic Cultivation

It is the most primitive way of algal cultivation, in which algae are completely dependent on solar radiation as the energy source. The photosynthetic metabolism is performed using available CO_2 and water by the algae to synthesize organic compounds. A further requirement of CO_2 into nutrient growth medium is carried out by submerged aerators that can enhance CO_2 absorption (Venkata et al. 2020). Nevertheless, this method is not suitable on a large scale because it is prone to bacterial and other algae contamination. It relies on environmental temperature and light, continuous mixing either via mechanical route or machinery for CO_2 absorption, and a high operational budget.

13.4.3 Heterotrophic Cultivation

In this system, algae use organic carbon compounds such as glucose and glycerol as energy sources and the capacity to grow in dark conditions. Also, they occupy less surface to volume ratio because the light source is not compulsory. During the aerobic process, assimilation of organic substrates produces energy over oxidative phosphorylation, which goes together with O_2 utilization as a terminal electron acceptor (Morales-Sánchez et al. 2017). This method is suitable to cultivate algae in wastewater loaded with organic nutrients, hence purify it. Moreover, the heterotrophic growth results to high cell density, high lipid accumulation, and low cost of feedstock. Heterotrophic cultures are characterized by higher growth rates and final biomass/lipid concentrations as compared to phototrophic or mixotrophic cultures (Chen et al. 2020).

13.4.4 Mixotrophic Cultivation

It is a two-stage system in which algae use uninterrupted inorganic CO_2 and organic carbon sources as the energy source under solar irradiation. Assimilation of high organic carbon takes place during the dark phase (respiration), resulting in cessation of normal growth by the catabolism of organic compounds for cellular biosynthesis. Therefore, to attain a certain level of carbon source, algae undergo a photoautotrophic (light) phase to assimilate CO_2 and promote the oxygen concentration in the chloroplasts. In *Chlorella protothecoides*, organic carbon assimilation and chlorophyll production to provide energy are processed together by mixotrophy, capable of switching between photoautotrophic and heterotrophic growth (Sim et al. 2019). From a technical point of view, a mixotrophic system results in optimized photosynthetic rate, improved biomass yield, and high-value metabolites production (Zhan et al. 2017; Patel et al. 2020).

13.4.5 Factors Affecting the Growth of Algae

The mass cultivation of algae is dependent on several parameters, which can be very species-specific. The most important parameters in optimal algal growth are organic and inorganic nutrients, their quantity and quality, light, CO_2, temperature, pH, turbulence, and salinity. Numerous studies by researchers (de Carvalho et al. 2019; Singh et al. 2020) have suggested different nutrient mediums with variable proportional composition for different algae species. However, the nutrient media should include a carbon and nitrogen source, macro-elements (sodium, magnesium, potassium, etc.) and chelating agents, vitamins, salts, and other ionic components based on cellular composition. The most used media are bold basal media (BBM), BG11, Guillard's F/2 medium, Walne medium, CHU medium, Zarrouk's medium, etc., for the culturing of different types of prokaryotic and eukaryotic algae. Vitamins and micronutrients like manganese, selenium, boron, zinc, copper, iron, etc. are essential elements for balanced media preparation. Light is another limiting factor to determine the growth of algae, whether present naturally or artificially. The rate of biomass production depends on the light intensity, spectral quality, and photoperiodism. In the high light duration, the algal biomass production is reduced due to the saturation effects (Kliphuis et al. 2012). The algal cultures can thrive well in the temperature range of 16–27 °C. However, the growth rate is reduced at cooler conditions, and algae cannot survive at high temperatures. The pH range of 7–9 is suitable for biomass growth, and in case pH balance is not maintained, it can inhibit cell growth. The salinity factor can induce osmotic stress and changes in cellular salt-ion concentration in the algal cell, thus disturbing the cell permeability mechanism. The gaseous exchange between the nutrient medium and surface-air maintains the pH, temperature, and cell density of the culture medium. The optimal biomass density can be achieved by aeration by mechanical stirrers or electrical rotators at laboratory scale and paddlewheel at large scale set-up (Aziz et al. 2020).

13.4.6 *Screening, Identification, and Characterization of Microalgae*

Algal selection and characterization from the aquatic environment involve sampling of periphytic algal colonies, submerged plants and pebbles, suspended water from different locations of a waterbody. The collected sample is a mixed algal sample, and to isolate an algal species, standard plating methods are conducted. In this sterilized procedure, serially diluted samples were placed over multiple nutrient agar plates, spreaded evenly across the surface, and immediately sealed. It is kept under an inoculation period of 2 weeks at the regulated temperature and light. The algal colonies are observed carefully, and a small sample is transferred to agarized medium using the streak-plate method. This microbiological procedure is repeated until the axenic unialgal cultures are isolated (Lee et al. 2014). A haematocytometer does the cell counting of isolated algae, and if the contamination of other algal or bacterial species is observed, then the serial dilution method is repeated. Finally, the isolated strain is grown in a species-specific medium and incubated at a suitable photoperiod to avoid further contamination. The morpho-taxonomic identification of each isolated algal is verified using microscopic screening and molecular approach of DNA extraction, PCR amplification, and gene sequencing (Gumbi et al. 2017).

The regular sub-culturing of isolated strains was maintained in the laboratory with proper labelling of sample location and specific nutrient media. The high-throughput screening of isolated strains for high-value metabolites such as lipids content, omega-3-fatty acids, pigments, etc., will help in the characterization of algae. The selected algae are cultivated on a large scale and harvested to maximize biomass yield with value-added products (Goswami et al. 2020) (Fig.13.3).

13.5 Algae Mediated Metabolic Mechanism for Pesticide Removal

There are numerous anthropogenic activities responsible for environmental pollution, which results in major health issues. Several organic and inorganic chemical releases in our natural resources by modern agricultural practices and industrial activities lead to environmental pollution. One of the major toxic chemicals known for a long time is pesticide residue, which markedly enters the food chain and is responsible for biomagnification (Molinuevo-Salces et al. 2019). Pesticide residues are mutagenic and carcinogenic for plants and animals and cause various adverse effects on them (Pandya 2018).

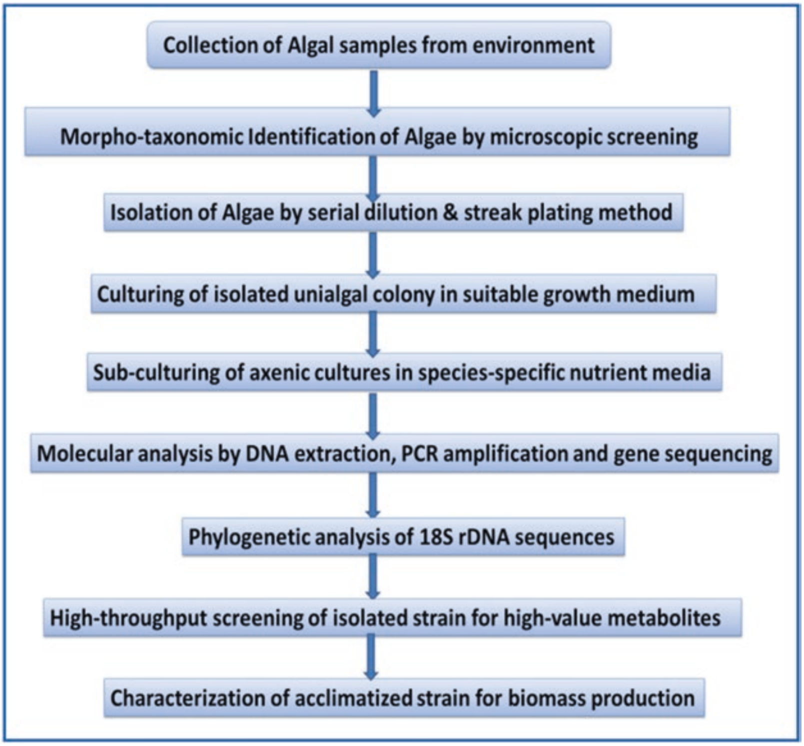

Fig. 13.3 The flowchart of screening, isolation, and characterization of algae for biomass production

Many physicochemical methods have been identified for cleaning industrial wastewater as well as our natural resources. However, they have many disadvantages in forming undesired by-products, decreasing soil quality, large use of expensive chemicals, and time-consuming. Consequently, bioremediation has been developed to defeat this alternative method, which is eco-friendly, less expensive, and more efficient (Silva et al. 2019). An important bioremediation agent is microalgae which have already been applied for effluent treatment. Algae are highly adaptive and can grow in severe ecological circumstances, low nutritional levels, and extreme temperature and pH, hence gaining more importance. Various algal species have been reported as biosorbents like freshwater green microalgae and macroalgae, marine red macroalgae, brown marine macroalgae, in which brown algae are conveyed to have the highest biosorption capability because of the existence of alginates in their cell walls. Bioremediation of contaminants using algae can reveal by biosorption, bioaccumulation, and biodegradation (Maryjoseph and Ketheesan 2020a, b).

13.5.1 Biosorption

Environmental pollutants are usually defaecated by the algal cells and unconstrained in the form of proteins, lipids, polysaccharides, and nucleic acids (Kumari et al. 2016; Saavedra et al. 2018). Biosorption involves numerous steps (Fig. 13.4). In biosorption, negatively charged algal cell wall secretions can interact with positively charged pollutants due to their spatial and electronic properties. In this way, the pollutants are adsorbed on the cell wall surface and removed from wastewater (Hansda et al. 2016). The pesticide runoff from agricultural lands and industrial effluents releases a wide variety of organochlorine compounds and heavy metals added to aquatic resources. The pesticide responses widely vary and dependent on the concentration used and duration of exposure. The pesticide residues are susceptible to a wide range of algal species used for bioremediation (Boudh and Singh 2019).

The biosorption process involves four steps: (1) transport of the sorbate after the bulk liquid phase to the hydrodynamic border layer localized around the biosorbent element, (2) transportation over the borderline layer to the boundary layer to the external surface of the biosorbent, (3) surface diffusion towards the inside of the biosorbent particle and active communication amid the sorbate molecules and the sorption sites (Maryjoseph and Ketheesan 2020a, b).

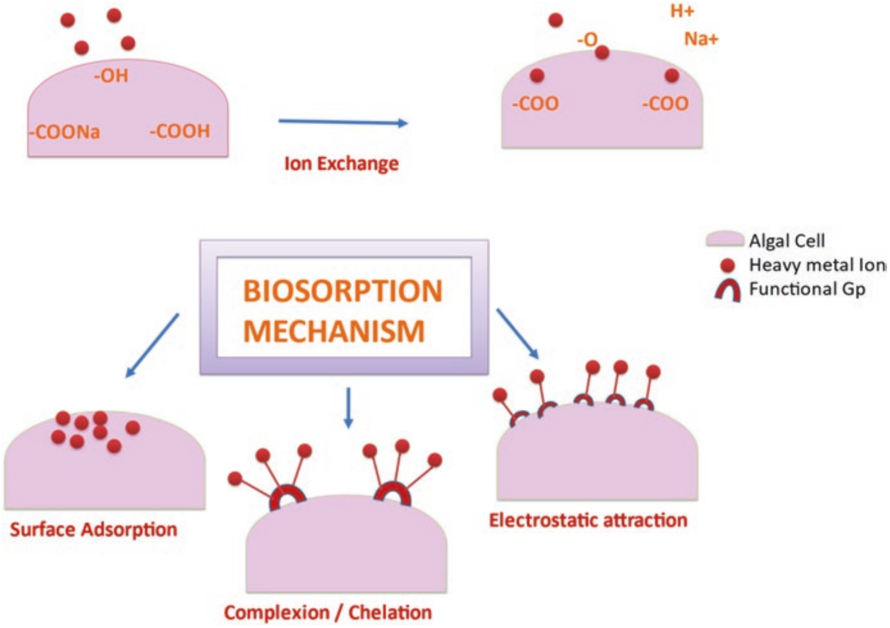

Fig. 13.4 A schematic representation of the mechanisms involved in the biosorption (Cheng et al. 2019)

13.5.2 Bioaccumulation

In the bioaccumulation process, the algal cell wall reacts with pollutants and is then transferred into inside of cells, binding to intracellular proteins and additional materials. Microalgae are proficient in bioaccumulating chemical compounds like triclosan, trimethoprim, and sulfamethoxazole (Bi et al. 2012). In addition to that, bioaccumulation of nonionic pollutants may result in oversensitive O_2 species overproduction, leading to oxidative impairment to biomolecules, cellular malfunction, and eventually cell death. Subsequently, liberated pollutants may be free back to the atmosphere and the reversal of residual pesticides into the aquatic bodies is considered harmless to the food chain (Corcoran et al. 2018). The detailed list of pesticidal compounds by different algae is given in Table 13.5.

13.5.3 Biodegradation

Intracellular or extracellular breakdown of composites into simpler molecules is biodegradation (Chandrasekhar et al. 2021; Gambino et al. 2021). Markedly biodegradation has more possible to decrease the poisonousness of pollutants inside algal cells compared to biosorption and bioaccumulation, and microalgae biomass is then converted into value-added products (Chandrasekhar et al. 2020b). The biodegradation mechanism involves metabolic breakdown and co-metabolism. During the process of metabolic degradation, pollutant serves as a carbon source for algae, while in the co-metabolism process, breakdown of pollutant mediated by enzymes in co-metabolism (Enamala et al. 2019a; Singh and Ummalyma 2020; Avila et al. 2021).

The enzymatic pathways are made to counter the poisonous properties of pollutants that result in the high tolerance of algae (Norvill et al. 2016). Biodegradation is influenced by numerous factors such as enzymatic pathways, algal species, and

Table 13.5 Bioaccumulation of pesticidal compounds by various species of algae

Algae	Pesticides residual compound	References
Chlamydomonas sp.	Naphthalene, lindane, mirex, phenol	Jin et al. (2012)
Chlamydomonas reinhardtii	Fluroxypyr	Zhang et al. (2011)
Chlamydomonas reinhardtii	Isoproturon (IPU)	Bai and Acharya (2017)
Chlorella sp.	Chlordimeform, toxaphene, methoxychlor lindane	Tang et al. (1998)
Scenedesmus obliquus	DDT, parathion, naphthalene, sulfonic acid	Tang et al. (2010)
Scenedesmus quadricauda	Atrazine	Tang et al. (1998)
Pediastrum sp.	Atrazine	Tang et al. (1998)

environmental conditions. After biodegradation, algal biomass toxicity has been reduced. Hence it is used for various purposes like biofuel, biocrude, animal feed, and biofertilizers.

13.6 Methods for the Higher Removal of Pesticides by Algae

In the future, the valuable commercial potential of algae biotechnology will increase, meaning that the production of classical strains will grow. Thus, the development and cultivation of better, more consistent strains are rapidly approaching. An enhanced performance of microalgae, coupled with other effective techniques, will be required (Li et al. 2020). As seen in (Fig. 13.5), a whole flowchart of the several stages intricate in the increased elimination of pesticides by algae was shown.

13.6.1 Acclimation

Microalgae strains must be identified and cultivated to get valuable features. Screening for native strains is recommended as these strains may sustain harsh wastewater conditions (Nie et al. 2020). The steps used for each target strain may be broadly categorized into the following: Primary screening is used to identify the dominating algae, tailed by separation, screening, amplification, and collecting

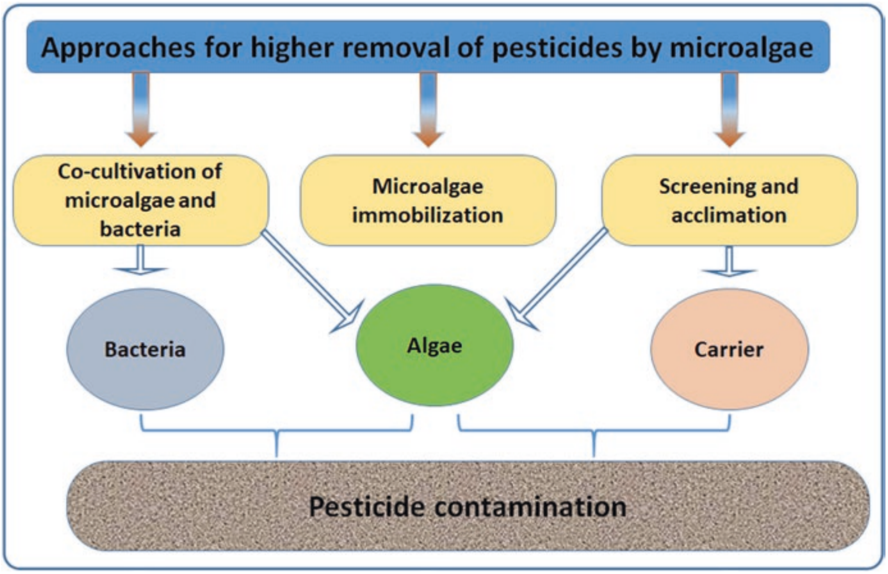

Fig. 13.5 Various processes that are involved in enhanced removal of pesticides by microalgae

(Zhou et al. 2017). Depending on the aims, the enriching of the strain is accomplished in varying concentrations of substrates. Cultivation of facultative strains can be done using both genetic modification and non-genetic means. An algae clone library could be generated by UV mutagenesis. A healthy strain could be tested by continuous or semi-continuous growth (Corcoran et al. 2018). When the conditions change, organisms use acclimatization to maintain internal equilibrium, resulting in changed gene expression. Algae exposed to harsh settings will produce enzymes capable of removing toxicants.

13.6.2 Algae and Bacteria Co-cultivation

The method for bioremediation using microalgae is frequently used in clean environments at the lab-scale; nevertheless, actual applications that use the technique are known to have microorganisms included. The use of a mix of microalgae and bacteria in wastewater treatment has been examined, therefore providing evidence for the effectiveness of that process (Nie et al. 2020). Cyanobacteria are very adaptable to severe settings, which allow them to live on autotrophic, heterotrophic, and mixed-culture media. This enables cyanobacteria to serve as the main substrate for bacteria and supply the latter with additional material. The coexistence between microalgae and bacteria depends on the intermediate products of microalgae and bacteria (Abdel-Razek et al. 2019). Photosynthesis in microalgae results in the production of oxygen, which serves to assist bacterium development, while the bacteria's metabolism results in the production of carbon dioxide, which microalgae use as a carbon source (Kumari et al. 2016; Kumar and Singh 2017). Even while it may be said that the cultivation of bacteria and algae is only a symbiotic interaction, this may be a case of antagonism instead. The outside atmosphere of the bacterium *Bacillus pumilus* influences the growth of algae in a variety of ways. Green algae, namely *Chlorella vulgaris*, had an additional growth-promoting impact on the bacteria cultivated in dry soil, leading to increased bacterial reproduction (Yadavalli et al. 2020). However, different research found that the bacterium *Bacillus pumilus* inhibits the nitrogen-fixing microorganism *Nannochloropsis* species (Fulbright et al. 2016). Existing literature indicating that co-culturing cyanobacteria and bacteria can improve the efficiency of breaking down organic contaminants. The effects of bacteria on cyanobacteria have not been studied well enough to know for sure, and as a result, more extensive research is required.

13.6.3 Microalgae Immobilization

New applications of immobilization technology are emerging in bioremediation and refer to the practice of strategically putting free microorganisms in a predetermined geographic region using either chemical or physical techniques to hold them active and reusable. While this method does have the aforementioned characteristics, the main factor to be considered is the possibility of this method as a substitute to traditional remediation because of (1) extremely sustained cell catalytic action and cell density, (2) modest parting and resiliency, and (3) enhanced existence as a result of resistance to harsh environments (Silva et al. 2019). This process has been previously documented. It may be taken as an example, like *Chlorella*, which was treated to eliminate butyltin chlorides and had more critical contaminant elimination. The covalent attachment, cross-linking, and implanting are the four most often utilized immobilization procedures. Surface adsorption is the most popular strategy because of its non-toxic, simple nature. Carrier selection is essential, and carrier technology is vital. Many characteristics are needed in picking an appropriate carrier, including non-toxic, pollution-free, affordable, strong, light, etc. (Nie et al. 2020).

13.6.4 Reprocessing of Algae After Pollutant Removal

13.6.4.1 Biodiesel and Biochar Production

There is increasing interest in microalgae as a possible biodiesel feedstock, particularly for grain replacement, such as maize, soy, and other palm species. The utilization of non-agricultural land in the growing of microalgae suggests that the land required to manufacture algal biodiesel is minimal. As of late, researchers have shown that microalgae can be cultivated in wastewater, and as a result, they are capable of breaking down organic contaminants and producing biomass (Matamoros and Rodríguez 2016). Moreover, microalgae growing using agricultural wastewater have the additional benefit of reducing the financial cost of farming land restoration during the post-restoration phases. In addition, the carbon dioxide, which comes from the atmosphere, may be used by microalgae as a carbon source for the creation of biomass and oil. According to the existing research reports, the importance of biodiesel synthesis is optimizing the culture conditions, improving the achievement of the algae lipid, and oil synthesis via transesterification response (Suganya et al. 2016). Additionally, it is assumed that the microalgae produced under heterotrophic conditions will have a greater lipid content. First, microalgae create microalgae oil by pyrolysis, and then it will be exposed to reverse esterification to transform the oil into biodiesel (Li et al. 2020).

Since the beginning of the new millennium, biochar has shown enormous potential in ecosystem services and has gained significant attention. Biochar is generated from biomass that has been partially pyrolyzed using an atmosphere of minimal oxygen concentration. The features of a high specific surface area, a formed micropore morphology, and an abundance of surface functional groups lead to biochar's exceptional capabilities as an adsorbent for water pollution removal (Tan et al. 2015). It is assumed that the raw materials for biochar manufacturing include such things as rice husks, straw, and other organic waste. Old-style waste remediation techniques will harm the atmosphere and create a significant quantity of biomass resource waste. By using waste biomass, biochar is created, which acts as a means of disposing of the garbage while simultaneously helping to restore and protect the ecosystem. Using a novel technique, a recent study discovered that a combination of hydrothermal and microwave-assisted treatment could yield hydro-char from seaweed (De Bhowmick et al. 2019).

13.6.4.2 Using as a Potential Feedstock for Biofuels Production

Although producing various biofuels from diverse biomass sources is important, it is also critical to remember that these fuels are costly, environmentally friendly, and effective at cutting down on waste output during operation (Enamala et al. 2019b; Chandrasekhar et al. 2021). Biomass production can be done at a lower cost and without negative impact on the environment through the use of microorganisms, like cyanobacteria, bacteria, and microalgae (Chandrasekhar et al. 2020a; Park et al. 2021). With these organisms, biomass production can serve to replace fossil fuel use, which saves money and has minimal impact on the environment (Yadavalli et al. 2020; Mal et al. 2021; Yadavalli et al. 2021). Aquatic photosynthetic algae include the majority of algae, though a few of them are terrestrial (Enamala et al. 2020). The product they create has a large portion of lipids, carbs, and proteins, and it is made utilizing sunlight and CO_2. Based on the above information, it has been determined that 1.83 kg of CO_2 are required to create 1 kg of algal biomass (Kumar et al. 2020a). A myriad of rewards makes algae as good applicants for biofuel production, for example, algae and cyanobacteria use water molecule to donate electrons for photosynthesis mechanism, cyanobacteria's per-acre biomass yield is excessive related to other seed crops biomass yield, determination food vs. fuel disputes. Algae cultivation has adapted to growth in brackish water, seawater, and wastewater and can produce various products (De Bhowmick et al. 2019). Several pieces of research have supported the findings that algae and cyanobacteria, for example, fatty acids produce biodiesel and jet fuel, ethanol, and hydrogen. The commercial manufacture of syngas may also be carried out by the Fischer–Tropsch process, as well as the generation of hydrogen and methane by hydrothermal gasification, methane generation through anaerobic digestion, and power generation through the co-combustion of various biomass (Venkata 2014; Das 2016). Because of this, algal biomass can be used as a feedstock for sustainable bioenergy and biomaterials production in the future, but economic feasibility is still a concern. Prior to increasing the production levels of this technology, several difficulties, including biotechnological, economic, and environmental ones, must be addressed.

13.6.4.3 Limitations in the Algae Biotechnological Pollutant Removal

Until now, the fractional development of algae biotechnology has only occurred in the laboratory. To tackle the resulting issues, an interdisciplinary approach is necessary. There are few limitations in this direction: (1) Research on algae for removing pesticides has been hampered by the high manufacturing cost, even though several researchers have explored industrial operations. While current medium and photobioreactor (PBR) level studies are carried out to create high-value products, running expenses are substantial. (2) Algae are microscopic, single-cell organisms floating in water with a hydrophilic charge on their superficial. Hence, settling by gravity is problematic (Singhal et al. 2022). Collecting algae biomass still confronts low operational effectiveness and high running expenses because of its high energy intensity. (3) Algae use wastewater comprising contaminants and nutrients for biomass production purposes. Some nutrients may be utilized to increase marketable output. Nevertheless, certain hazardous chemicals stay in the microalgal biomass after being absorbed and aggregated, which may cause process failures in the future by hindering algal growth (Ummalyma et al. 2018).

13.7 Conclusion and Future Perspectives

Water pollution from pesticides is a huge problem. Bioremediation offers a potential remedy for pesticide pollution. Successful microalgae applications make microalgae biotechnology an attractive choice for environmental remediation and wastewater treatment. Water quality might be improved by microalgae's method of pesticide removal. Furthermore, processing of the regenerated microalgal biomass renders the procedure cost-effective and ecologically friendly. This piece may encourage researchers and industrial partners to use algal technology to perform simultaneous pesticide breakdown and product creation during anaerobic digestion (Patel et al. 2021).

At present, microalgal biotechnological implications for the remediation of pesticides are limited to laboratory scale. However, the corresponding challenges need to focus on interdisciplinary research. Some investigations related to large scale application of microalgae-based remediation of pesticides in commercial operations have proved that it has been impotent due to high production cost and shows differential responses outdoor and indoor because it is affected by different climatic conditions such as temperature, intensity of illuminations, and alien organisms (Huo et al. 2018; Avila et al. 2021).

The methods of harvesting microalgae have their own pros and cons. For example, in the process of biodiesel production, the harvesting technology is taxing due to high operating costs and low operating coherences. From future perspective, it requires integration of multiple methods to be performed at a time, as single method alone would not meet the demand. Additionally, the accumulated toxic pollutants by the microalgae from the wastewater should be degraded by proper technology, else these under graded components would affect further requisition as well as the recovery and the purification of biosynthetic products (Gifuni et al. 2019). In the coming years, research focusing on life cycle analysis and its related indices have proved that along with bioremediation, the algal biomass has greater utility in the production of third generation biofuel production.

Being a hazardous environmental threat, pesticide bioremediation through microalgal biomass offers an eco-friendly, sustainable, and feasible solution. The joint venture of researchers and industrial partners to apply microalgal technology in the field of pesticide removal beside producing high-value products from recycled algal biomass would lead to the development of cost effective and better environmentally sustainable biotechnological method in the future.

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Chapter 14
Remedial Potential of Plant Growth Promoting Rhizobacteria (PGPR) for Pesticide Residues: Recent Trends and Future Challenges

Ahmed Ali Ali Romeh

Abstract Different ecosystems can be exposed to pesticide residues, which pose a huge threat to the environment and to non-target organisms which includes useful soil microorganisms, plants, and human. In addition, pesticides have a negative impact on rhizobacteria's plant-useful functions, resulting in reduced nodulation in legumes, reduced N accumulation in grains, and a poor impact on grass root improvement, because of cell death of microbial as a result of pesticides. Undoubtedly, one of the main challenges is the compatibility of pesticides and inoculants, so new procedures to resolving the pesticide-inoculant incompatibility are required. Plant growth promoting rhizobacteria (PGPR) can be utilized as excellent and effective biotechnological tools and they represent promising long-term solutions for improving plant biomass production and reducing the harmful phytotoxic effects of organic pollutants. Furthermore, PGPR can improve degradation of pesticide residues and other contaminants, increasing the bioavailability of xenobiotics in the rhizosphere area and plant uptake subsequently for providing a clean environment free of contaminant and alternative to hazardous chemical fertilizers. Interactions of both plants and bacteria with catabolic genes have resulted in the emergence of more than one catabolic enzyme able to metabolize and detoxify xenobiotics as a sole carbon source for their cell functioning and metabolism. By growing powerful, adaptable and versatile bacterial strains and improving handling facilities/processing technologies, advanced biotechnology, microbiology, and genetic engineering can contribute to solving the problem of pesticide bioremediation. More cooperation is required between scientists who contribute to the field of environmental remediation, such as genetics, biochemists, microbiologists, and the environment.

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Keywords Plant growth promoting rhizobacteria (PGPR) · Pesticide residues · Remediation · Recent trends

14.1 Introduction

Pesticides are widely used around the world, which has contributed to increase crop productivity by reducing potential crop losses related to insect attacks. This widespread prevalence is the cause of major problems in sustainable agriculture (Li et al. 2020). Pesticide residues are frequently accumulated in the environment and have negative effects on human health and the ecosystem as a result of their persistence in soil (Yadav et al. 2015; Taiwo 2019). Furthermore, the existence residual of pesticides in various crops, particularly vegetables and fruits, in concentrations greater than the allowable limits poses a risk to humans, particularly children. Soil pollution control is an important problem that needs a quick solution to maintain soil fertility while increasing productivity (Ashraf et al. 2014; Sun et al. 2018). Previous studies focused on developing physicochemical technology for the remediation of soil procedures include physical and chemical, including soil excavation, incineration or thermal degradation (thermal desorption), soil vapor extraction, soil washing/flushing to remove such residues (Hakeem et al. 2014). However, traditional technologies suffer from serious problems such as high cost, equipment complexity, high operating costs, and environmental insecurity. Furthermore, various physical and chemical technologies cause a variety of environmental complications as a result of their degradation products or side effects (Singh et al. 2020). To solve these issues, new low-cost, very selective, and safe remediation techniques are urgently needed for the removal or detoxification of organic pollutants in soils and water (Mandal and Singh 2017; Giri et al. 2021). Despite extensive research and development in the field of soil remediation from contamination with pesticide residues, the transfer of these techniques to the field is a major challenge. Scientists and engineers working in the field of remediation require effective treatment methods for polluted soil and groundwater with toxic organic compounds, such as biological methods (Aresta et al. 2015; Gupta et al. 2016; Vikrant et al. 2018; Giri et al. 2021). Bioremediation is a method of biological decomposition of pollutants, specifically/genetically, primarily based on the metabolic ability of microbes to breakdown numerous organic compounds such as pesticide residues into environmentally non-toxic products (Huang et al. 2018; Raffa and Chiampo 2021).

Plant growth promoting rhizobacteria (PGPR) refer to a group of beneficial, root-colonizing bacteria that exist naturally in the soil, associated with the roots of plants or within the plant (e.g., roots, shoots, leaves, or even fruits and seeds) by endophytes with plant growth promoting ability (Lobo et al. 2019; Alka et al. 2020). They are applied to plant roots as inocula to stimulate plant growth, improve nutrient uptake, and aid in the degradation of soil pollutants (Santoyo et al. 2016; Varma et al. 2020; Jiao et al. 2021). Therefore, it is considered PGPR as one of the leading candidates in this regard (Basu et al. 2021). PGPR have been shown to be efficient in enhancing dissipation of pesticide residues and other contaminants, primarily species of *Bacillus* and *Pseudomonas* (Gkorezis et al. 2016; Fatima et al. 2017; Yu et al. 2020). Therefore, in recent decades, new technologies for the removal of pesticide residues by PGPR have been studied.

14.2 Soil Pollution with Pesticide Residues and Its Effect on PGPR

Pesticides are employed at an unprecedented rate throughout the world, to prevent or control the pests for maintaining high agricultural production or reducing yield losses. Due to their toxicity, endurance, and breakdown of by-products, these chemicals are commonly dispersed contaminants (Giri et al. 2021). Because of lack of in-time degradation, pesticide residues will contaminate the ecosystem if they are used extensively, frequently, and continuously (Rangasamy et al. 2018; EL-Saeid and Alghamdi 2020). Because of their non-biodegradable nature and long shelf life, these toxic chemicals remain in the environment and contribute to hazardous to the ecosystem, soil pollution, leakage into groundwater, enter the food chain causing serious health risks such as biomagnifications (Morillo and Villaverde 2017). It also affects non-target organisms such as beneficial soil microorganisms, plants, and human causing danger to them (Dhananjayan et al. 2020; Khan et al. 2020), as well as a reduction in biodiversity in various ecosystems (Arora et al. 2019; Harwood 2019). Pesticide accumulation in soil and uptake by plant is affected by a variety of factors such as type of soil and pesticide's physicochemical properties including water solubility, active ingredient, formulation of the compound and the partition coefficient octanol/water, log P or K_{ow} (Bonmatin et al. 2015). Log K_{ow} should be between 0.5 and 3.0 for uptake. Compounds with a higher log K_{ow} are hydrophobic quickly cross bio-membranes and may adsorb strongly to roots, whereas compounds with a lower log K_{ow} are too hydrophilic to cross via cell membranes (Bouldin et al. 2006). Also, pesticides that have a high K_{ow} tend to bind to the soil, especially with organic matter, thus, they take much longer time to decompose and are known as slow organic pollutants such as organochlorine compounds (Taiwo 2019). These pesticides are difficult to be transported by the plant and can be degraded at the roots with the help of microorganisms, especially PGPR, which works to degrade them into carbon dioxide and water, or they dissipate into more polar metabolite products that can be moved to the upper parts of the plant (Hassen et al. 2018). Pesticides that are persistent in the environment can enter waterways and the food chain, causing biomagnification. With a high degree of stability, it can also be easily transported to long distances from its sources. On the other hand, pesticides that have a low Log K_{ow} tend to movement from the soil to groundwater or translocation to plants such as neonicotinoid insecticides (Bonmatin et al. 2015). Because of hydro-solubility, it has been proposed that a molecule be considered systemic if the partition coefficient is less than 4 (Bonmatin et al. 2015). Furthermore, traditional agricultural practices usually include chemical fertilizers and pesticide residues, both of which have negative consequences for plants. Numerous reports have found that pesticide poisoning reduces germination capacity and alters plant development patterns by inducing numerous physiological and biochemical processes, which includes destruction of membrane integrity, enzyme function, and nucleic acid harm in plants which includes *Oryza sativa*, *Brassica juncea*, and *Trigonella* (Mahapatra et al. 2019; Yüzbaşıoğlu and Dalyan 2019; Homayoonzadeh et al. 2020; Bakshi et al. 2021). In addition, pesticides cause negative manifestations on rhizobacteria plant-beneficial functions. The low compatibility of pesticides with inoculants, especially when applied to crop seeds such as soybean and maize, is a principal limitation to inoculation success. Impact of pesticides on the inoculant depends on many factors, the most important of which are the physical-chemical properties, the mechanism of pesticide action, application method, time of application, bacterial species, present in the inoculant, contact time with lively microorganisms, and the ability of the microorganism to restore its viability, the type of soil, among others. This affects the contribution of microbes to plant growth (Santos et al. 2019, 2020, 2021; Pereira et al. 2020; Hungria et al. 2020). In this respect, long-term exposure of microorganisms to pesticides has a deleterious impact on the survival of bacteria, resulting in reduced nodulation in legumes, decreased N accumulation in grains, and a poor impact on grass root development, due to cell death of microbes caused by pesticides (Rodrigues et al. 2020; Pereira et al. 2020; Santos et al. 2020).

One principal challenge is to make compatibility between the pesticides and inoculants, so new approaches to resolving the pesticide-inoculant incompatibility are required.

14.3 Compatibility of PGPR with Pesticides

Combination of crop seeds with PGPR for nitrogen fixation, fertilizers, pest control, and pesticide biodegradation are becoming increasingly important in agriculture, as the global trend seeks to increase sustainability. It is critical to assess microbial survival at the moment of inoculation and the extent of the response to plants. In the same direction, it is crucial to determine whether pesticide contact with microorganisms in the inoculant has an impact on cell survival and metabolism, reducing the efficacy of the inoculant as there have been concerns regarding the compatibility of pesticides with PGPR for decades. The compatibility of fungicides and rhizobia-carrying microbial inoculants was investigated. Because fungicides are extensively utilized in soybean plants, there are concerns about fungicide compatibility with inoculants, which may affect several stages of the symbiosis, from rhizobia survival on the seed to nodule formation and N_2 fixation efficiency (Santos et al. 2019, 2021; Rathjen et al. 2020). The pesticide Standak™ Top had a negative impact on plant morphology such as number of branches, length, and percentage of root hair appearance, in corn seeds inoculated with PGBR, *Azospirillum brasilense* (Santos et al.

2020). Furthermore, using pesticides and rhizobia, the number of nodules, dry weight, and nitrogen activity in nodules and plant biomass production were decreased (Ahemad 2014; Santos et al. 2021). The toxicity of pesticides on PGPR increases with the lengthening of the stability period of the compound and with the increase in the dose exposed to it. Organophosphate pesticides such as phorate, acephate, monocrotophos, and glyphosate can reduce the development of five soil PGPR, i.e., *Bacillus brevis*, *Salmonella typhimurium*, *Rhizobium leguminosarum*, *Azotobacter vinelandii*, and *Pseudomonas fluorescens* by decreasing siderophore production (Kumar et al. 2019). Despite the fact that herbicides are another major class of pesticides for agriculture, few studies have looked into the compatibility of herbicides with inoculants. Studies by Madhaiyan et al. (2006) cleared that only 2,4-D inhibited *Gluconacetobacter diazotrophicus* cell growth, while all herbicides, including amides (butachlor, alachlor), triazines (atrazine), and phenoxy (2,4-D), reduced nitrogenase activity, IAA and GA3 synthesis, and P and Zn solubilization (Madhaiyan et al. 2006). Herbicides are generally thought to be lower injury than fungicides and insecticides (Santos et al. 2021). A major issue has been identified as the lack of compatibility among pesticides and microbial inoculants applied to seeds. As a result, develop strategies to make microbial strains compatible with the action of pesticides, as well as new biopesticides and other environmentally friendly integrated pest management strategies are critical. One of these strategies is the utilization of microbial inoculants such as *Rhizobium leguminosarum* strain MRP1 that tolerated the action of pesticides (fipronil and pyriproxyfen) in peas crop with the highest production of IAA, exopolysaccharides (EPS), and siderophores (Ahemad and Khan 2010). Kapta et al. (2020) showed the ability of *Pseudomonas putida* J6 and *Pseudomonas putida* J8 to tolerate a greater concentration of chlorpyrifos. Study by Rodrigues et al. (2020) found acclimatize mechanism of *B. japonicum* SEMIA 5079 and *B. elkanii* SEMIA 587 in seed of soybean and exposed to the pesticides, Standak™ Top (contained pyraclostrobin and thiophanate-methyl fungicides and fipronil insecticide). According to the findings, the main constraint is the limited compatibility of insecticides and microbial inoculants used on seeds. Furthermore, the use of *Mesorhizobium ciceri* enhanced the biochemical, physiological, and antioxidant process of *Cicer arietinum* (L.) under fungicide exposure (Shahid et al. 2021). Scientific basis for reduced stress molecules and antioxidant defence enzymes in inoculated symbiotic bacteria *C. arietinum* cultivated in fungicide-contaminated soil is now better understood (Shahid et al. 2021). Other options include developing herbicides that are less hazardous to microbial bioinoculants (Santos et al. 2021). Also, instead of living bacteria, another option could be to use microbial metabolites, especially that produce secondary metabolites such as *Azospirillum* sp. (Fukami et al. 2017). Adding protective compounds such as polymers, charcoal, biochar, and peat as a formulating agent, chemicals, or microorganism-produced molecules minimizes the dangerous effects of pesticides on microbial cells (Santos et al. 2017; Jabborova et al. 2020). In-furrow inoculation of soybeans 2.5 times higher than the concentration used for seed inoculation led to prevent inoculants from coming into contact with insecticides and reduced the effects of seed treatment with agrochemicals (Galindo et al. 2019).

14.4 Remedial Potential of PGPR for Pesticide Residues

The employment of potential and degradative microorganisms, which can grow and survive with the roots of plants or within the plant under high-stress insecticide concentrations, could provide a way to remove pollutants like pesticide residues from contaminated environments (Hamada et al. 2019; Bhatt et al. 2020a). The most promising technological solution to addressing pesticide contamination is the addition of PGPR to pesticide-contaminated soil (Dar et al. 2019; Rani et al. 2019; Sun et al. 2020). The genera of *Streptomyces*, *Pseudomonas*, *Klebsiella*, *Bacillus*, and *Burkholderia*, which belonging to PGPR has been found to have the ability to breakdown the pesticides (Briceño et al. 2018; Sun et al. 2020). The bioremediation process relies on microorganisms' metabolic capacity to detoxify or convert toxic molecules through their enzymatic systems for the cleanup of hazardous materials from the environment (Khatoon et al. 2020). PGPR can play a vital role in pesticide dissipation from the soil by the enzymatic system through metabolizing those pollutants into less toxic or non-toxic products (Sidhu et al. 2019; Yadav et al. 2020). The enzyme system, temperature, pH, and nutrient availability all influence the breakdown process caused by the presence of PGPR (Singh et al. 2020). The enzymatic degradation is the most important strategy for removing pesticide residues (Gouda et al. 2018). Pesticide degradation enzymes are effective, safe, and environmentally friendly, and they can degrade a wide spectrum of pesticides (Gouda et al. 2018; Bhatt et al. 2020a). These enzymes are created by degrading cells during various metabolic pathways or are found outside of the cell. Hydrolases are a type of enzyme that is commonly used in pesticide bioremediation. These enzymes stimulate the degradation of different principle biochemical classes of pesticides that contain carbon halide, esters, tri-esters, urea bonds, and other components (Gouda et al. 2018). For example, PGPR are important in the degradation of polychlorinated biphenyl (PCB) by oxidative enzymes from different genes, resulting into CO_2 and water that provide energy to microorganisms (Terzaghi et al. 2018). Aminocyclopropane-1-carboxylate (ACC) deaminase produced by *Enterobacter cloacae* UW4 and *E. cloacae* CAL2 strains, which plays a key role in breakdown of total petroleum hydrocarbons (TPHs) pollutants by decreasing the levels of ethylene (Glick et al. 2007; Govindasamy et al. 2008). Also, dehydrogenases, dioxygenases, aldolases, hydrolases, and hydratases enzymes which produced by PGPR play a substantial role in breakdown of polycyclic aromatic hydrocarbons, PAHs (Reddy et al. 2019). Degradation of organophosphate pesticides (OPs) in the existence of microorganisms, particularly PGPR, via a shared organophosphorus degrading (opd) gene as a source of carbon, nitrogen, and phosphorus has been studied extensively (Kumar et al. 2015; Patel et al. 2017; Wijekoon and Yapa 2018; Sidhu et al. 2019; Yadav et al. 2020). In pesticide residue, biochemical detoxification is attached to the existence of specific enzymes. As a result, in organophosphate compounds, the hydrolysis of P-O-alkyl, P-F, P-S, and P-O-aryl bonds and the formation of esters are regarded as the most important step in detoxification processes (Sidhu et al. 2019; Hassen et al. 2018). Several studies described the biodegradation of organophosphate compound by specific degrading enzymes, such as hydrolases, peroxidases, oxygenases, carboxyl-esterases and phosphodiesterase, and others (Gouda et al. 2018). *Azospirillum lipoferum* (Beijerinck) supported on peat-moss and inoculated to the soil samples leading to chlorpyrifos and cyanophos degradation more than other treatments (Romeh and Hendawi 2014). Also, Nayak et al. (2019) proposed the potential use of newly isolated strain, *Ochrobactrum* sp. CPD-03 to degrade chlorpyrifos, degradation product, 3,5,6-trichloro-2-pyridinol (TCP), and other organophosphorus pesticides by aryl-esterase enzyme. Furthermore, esterases created by *Bacillus* sp. strain SG2 isolated from cypermethrin-contaminated farm fields are critical enzymes in the degradation of pyrethroid pesticides (Bhatt et al. 2020b). Inoculated rice seedlings with CPD-03 showed potential plant growth enhancing action. It was determined that *Burkholderia* sp. strain L2, isolated from the rhizosphere of *L. esculentum*, was effective in P-solubilization and IAA synthesis even at higher pesticide concentrations, and that it might be employed in agricultural fields where pesticides are persistent in the soil (Tripti et al. 2015). Chopra et al. (2017) isolated imidacloprid-degrading bacterial strain DC14 and DC16 as a sole carbon energy source with PGPR activity. The capacity of *Pseudomonas* sp., *Bacillus* sp., and a mixture of the two showed considerable growth and withstand even at high concentrations and efficiently degraded glyphosate as a sole phosphorus source (Wijekoon and Yapa 2018). Yadav and Sundari (2021) investigated the potential of rhizobacterial isolates as bioinoculants for increasing remediation of phorate residues via ester bond hydrolysis of ester bonds. Biodegradation of pyrethroid pesticides was identified as *Citrobacter freundii* CD-9. This technology will help formulate new strategies to suppress pesticide residues related to environmental pollution and serving as a future reference for the development of microbial degradation agents and environmental remediation (Tang et al. 2020).

14.5 Plant-PGPR Beneficial Interactions for Pesticides-Contaminated Soil Remediation

Given all the negative consequences that synthetic chemicals have had, creating safe techniques to address these issues is extremely important. Plant growth-promoting rhizomes (PGPR) are important components for increasing soil fertility, promoting plant growth, bioremediation of pesticide residues, and antagonistic actions against plant pathogens by a number of mechanisms (Méndez-Bravo et al. 2018; Mekonnen and Kibret 2021). Improved plant growth promotes the colonization of rhizobacteria in the rhizoplane, it increases the breakdown of organic pollutants (Arslan et al. 2017). Plant hormones affect root and shoot development, architecture, and stress tolerance as a result of interactions of plants with PGPR (Yu et al. 2018; Eichmann et al. 2021). PGPR generally create substances important to plants that facilitate the absorption of nutrients, and they have a role in soil remediation. PGPB work through direct methods, such as the synthesis of plant hormones (such as auxin, cytokinin, and gibberellins) that increase plant growth and the release of compounds that facilitate the uptake of nutrients, solubilization of phosphates, nitrogen fixation, siderophore synthesis, HCN, ammonia, vitamins, whereas indirect mechanisms include protection against plant pathogens, ACC deaminase activity, antibiotic synthesis, modification of plant stress by increasing nutrient uptake, availability of water, and buffering capacity and degradation of contaminants by hydrolytic enzymes before they can negatively impact the plants (Olanrewaju et al. 2017; Aloo et al. 2019; Mahapatra et al. 2019; Asad et al. 2019; Varma et al. 2020). Ethylene production slows plant growth and lowers biomass under stressful conditions, putting the phytoremediation capacity at jeopardy. PGPR is a successful approach for resisting plant stress because it expresses 1 aminocyclopropane-1-carboxylic acid (ACC) deaminase, which hydrolyzes the immediate precursor of ethylene in plants, reducing the rate of ethylene biosynthesis (Glick 2010; Vergani et al. 2017).

PGPR's ability to bioremediate soils as an important environmental cleanup strategy is another important role (Khatoon et al. 2020). PGPB can help in reducing the harmful phytotoxic effects of organic pollutants such as pesticide residues, that lead to the consolidation of these plants in the contaminated soil by improving antioxidant activity such as glutathione, glutathione-*S*-transferase, and superoxide dismutase activities, enhancing plant health, increasing growth, thus improving the biomass of plant shoots and roots, this leads to the consolidation of microbial communities and the degradation of organic pollutants (Singha et al. 2018; Varma et al. 2020; Bhattacharyya et al. 2020; Bakshi et al. 2021). Plant roots can release organic molecules (terpenes, flavonoids, salicylic acid, and phenols) that are structurally similar to some organic pollutants that interact as catalyst for enhancing the dissipation of different pesticides (Arslan et al. 2017). This phenomenon has the potential to enhance the proliferation of rhizospheric bacteria by inducing the expression of degrading genes (Hussain et al. 2018). The existence of catabolic genes and enzymes gives PGPR certain properties that make them suited for cleanup. They are candidates for using organic pesticides as carbon and energy sources because of their unique genes and enzymes (Hussain et al. 2018). Combination of both plants and bacteria with catabolic genes has resulted in the emergence of more than one catabolic enzyme capable of metabolizing and detoxifying xenobiotics as a sole carbon source for their cell functioning and metabolism (Arslan et al. 2017). For example, inoculation of *Clitoria ternatea* by *Bacillus cereus* modified the expression of plant ethylbenzene degradation genes and increased the removal efficiency of ethylbenzene (Daudzai et al. 2018). The plasmid pTOM-Bu61, which encodes degradation enzymes, can spontaneously transfer to numerous plant endophytes and has contributed to effective toluene degradation in poplar trees (Hussain et al. 2018). Besides that, one distinct mechanism of PGPR is the removal of pollutants from the soil by increasing the bioavailability of pollutants in the rhizosphere and plant uptake as a result (Ali et al. 2020; Romeh 2020). This is supported by Chen et al. (2017), who noticed an increase in the amount of pyrene uptaken by the plant as a result of *Scirpus triqueter* inoculation with PGPB. It is found that PGPB may enhance desorption of pollutants from soil by producing biosurfactants, which reacts by emulsifying action, leading to the availability of these pollutants to microorganisms and plants (Varma et al. 2020). The indigenous biosurfactant-producing PGPR S211 could be exploited as a potential material for clean up the environment from pesticide-contaminated agricultural soils. This is due to the low cost of production, emulsification activities, and strong performance in improving the solubility of soil-related pesticide residues (Hassen et al. 2018). *Pseudomonas rhizophila* S211 was found to have remediation abilities by generating dioxygenases, which play a key role in the modification of a variety of resistant pesticides. Producing rhamnolipids can also help pesticides degrade faster by increasing substrate availability or increasing the hydrophobicity of the bacterial cell surface, which makes it easier for hydrophobic substrates to bind to the surface of a bacterial cell (Pacwa-Płociniczak et al. 2014).

Microbial-assisted phytoremediation, termed rhizoremediation, which contains rhizo-microbial population of plants at contaminated site, also known as phytoremediation and bioaugmentation, or phyto-stimulation and rhizo-degradation, has been developed as an effective remedial strategy for cleaning contaminated soil by converting xenobiotics into less dangerous compounds (Gouda et al. 2018; Singh et al. 2019; Song et al. 2020). Due to the presence of compounds secreted by roots such as flavonoids, rhizoremediation occurs naturally, which leads to stimulating the growth and activity of PAH-degrading bacteria. Moreover, soil aeration resulting from root growth and death accelerates the oxidative decomposition of recalcitrant PAHs compounds (Leigh et al. 2006; Bisht et al. 2015). This is done through native plant growth promoting rhizobacteria, colonizing endophytes, bioaugmentation with native or allochthonous bacteria (Gerhardt et al. 2015; Syranidou et al. 2016; Franchi et al. 2016; Song et al. 2020). The success of a plant species in rhizoremediation process depends largely on the ability of its highly distributed root system to establish a large number of bacteria, and interactions with other organisms (Kuiper et al. 2004; Bisht et al. 2015). Rhizospheric microorganisms such as *Azotobacter*, *Bacillus*, *Pseudomonas*, *Arthrobacter*, *Achromobacter*, and *Enterobacter* possess a variety of properties that can improve the desorption process and enhance the solubility of pesticides in the soil. In addition to accelerating phytoremediation by enhancing intrinsic features to promote plant growth such siderophores, phytohormones, and chelators, as well as their ability to biodegrade pollutants and minimizing plant stress in highly contaminated soils (Sun et al. 2018; Song et al. 2020). In this regard, several studies have been mentioned over the past years. The uptake of thiamethoxam was significantly increased in corn seedlings shoots inoculated with *Bacillus subtilis* FZB24 and *Bacillus subtilis* GB03 (Myresiotis et al. 2015). Combination of *Glycine max* and *Pseudomonas fluorescens* increased degradation of the insecticide and the nematicide, fenamiphos to more toxic metabolites, fenamiphos sulfoxide (FSO), sulfone (FSO_2), and phenol (F-phenol), which accumulated in the roots and translocated in the leaves (Romeh and Hendawi 2017). Inoculating insecticide-stressed plants with PGPR increased seed germination (Jaiswal et al. 2019). *Bradyrhizobium* spp. and *Azospirillum brasilense* (Ab-V5 and Ab-V6) inoculated *Glycine max* roots improved the morphological characteristics of the root, such as root length, branch length, and root hair length (Rondina et al. 2020). Cultivation of *Plantago major* beside tomato crops after inoculating them with EM-1 leading to removing imidacloprid from the soil with the most successful method (Romeh 2020). Strain J6 and J8 of *Pseudomonas*

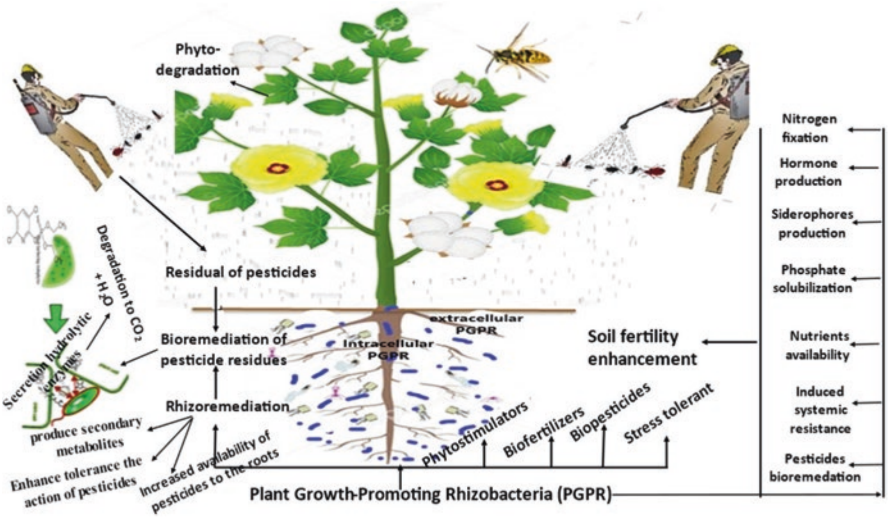

Fig. 14.1 The interactions between plant and PGPR for pesticides-contaminated soil remediation

putida (nitrogen fixers) induced various growth-promoting substances (Indole Acetic Acid, ammonia, protease, HCN, siderophore) in seeds of *Vigna radiata* and biodegradation of chlorpyrifos in soil (Kapta et al. 2020). Gene expression of anti-oxidative defense enzymes (glutathione peroxidase, ascorbate peroxidase, superoxide dismutase, glutathione reductase, and dehydroascorbate reductase) was enhanced in *Brassica juncea* seedlings exposed to chlorpyrifos-induced oxidative stress as a result of the treatment with PGPR, *Pseudomonas aeruginosa* (Ma) and 24-epibrassinolide, EBL (Bakshi et al. 2021). *Bacillus aryabhattai* strain MoB09 could be used to reduce paraquat residue in the soil and mitigation of drought stress as well as increase plant yield in organic agricultural production by enhancing siderophore, indole, 1-aminocyclopropane-1-carboxylic acid deaminase, and phosphate solubilization (Inthama et al. 2021). The understanding of these interactions between plant and PGPR can aid in the development of new sustainable, environmentally friendly, and cost-effective agricultural systems for plant stress modification (Hakim et al. 2021). Data in Fig. 14.1 show the interactions between plant and PGPR for pesticides-contaminated soil remediation.

14.6 Recent Trends in Remedial Potential of Pesticide Residues by PGPR and Future Challenges

Following the Green Revolution, the agroindustry has seen a number of scientific developments that have resulted in increased crop output but with environmental consequences such as chemical fertilizers and pesticides that have become harmful to the soil and the ecosystem. The future scientist hopes to introduce biofertilizers that are highly economical, safe, and the largest alternative to agricultural chemical fertilizers, fungicides, and have an effective role in creating a very economic revolution (Dhayalan and Sudalaimuthu 2021). Therefore, most of the aforementioned issues and disadvantages of contemporary agriculture can also be mitigated by biofertilizers, especially PGPR. Use of PGPB inoculants is an appropriate choice in the management of environmental pollutants. The new eco-friendly PGPR bacteria can be exploited as excellent and effective biotechnological tools and represent promising sustainable solutions to improve plant biomass production, thus contributing to plant health, growth, and development and offering a clean environment free of contaminants such as pesticide residues and alternative to hazardous chemical fertilizers (Umesha et al. 2018; Rani et al. 2019; Liu et al. 2020; Vangronsveld 2020; Basu et al. 2021). Other limitations in PGPR utilization in agriculture due to the existing limited number of PGPR or endophytic strains employed for environmental management which is typically due to inadequate colonization of plant rhizosphere with endophytic bacteria and the lack of a well-understood mechanism of action (Singh et al. 2020; Amaresan et al. 2020). Furthermore, research into genetically modified bacteria and their potential use in environmental management is required. The discovery of genes that are expressed during colonization will aid in our knowledge of the colonization process and the interactions between beneficial microorganisms and plants (Dhayalan and Sudalaimuthu 2021). The biosafety and environmental implications of PGPR following their widespread use in the environment (at least 10^6–10^9 CFU/mL) are rarely considered. As a result, agricultural microbiologists, plant pathologists, and commercial enterprises interested in bioinocula development should use new technologies to obtain enough characterization in an ecosystem while taking safety precautions (Keswani et al. 2019). In addition, advanced biotechnology, microbiology, and genetic engineering can contribute to the provision of rapid progress in the field of pesticide bioremediation through the development of microbial strains powerful and highly adaptable and through improved facilities/processing technologies that already exist. Progress in this field causes higher information knowledge about the biotransformation and bioaccumulation of contaminants together with removal of contaminated biomass and transport of the xenobiotics via plants (Bisht et al. 2015). The new genomics techniques will also allow for the monitoring and selection of catabolic genes in order to increase remediation strategies (Bisht et al. 2015). In order to overcome the various problems remaining in current bioremediation methodologies and to further improve research and development trends as recommended, more collaboration is needed between genetic engineers, biochemists, environmental engineers, and microbiologists (Sharma et al. 2020; Giri et al. 2021; Dhayalan and Sudalaimuthu 2021).

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Chapter 15
Microalgae: A Promising Tool for Pesticide Mitigation in Wastewater

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Abstract In the current scenario, pesticides are widely used as they play a vital role in increasing agricultural yields and ultimately provide economic benefits to farmers. Apart from this positive side, pesticides also have a darker appearance as they became a major threat to soil health and water. The amplified use of pesticides is causing a serious imbalance in the agricultural soil and the aquatic environment. Nowadays, a huge proportion of the pollutants come from pesticides and they have become a serious concern for human health and the natural ecosystem. Researchers

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have applied various methods (physical or chemical) to exterminate the challenges of pesticide accumulation, but still, necessitate extensive research and concrete findings in this area. Currently, pesticide remediation includes chemical, physical, and biological remediation, while some studies support the application of these three methods simultaneously. Most of the tools available to combat pesticide accumulation are inadequate or too expensive. Based on the latest research, bioremediation has become an emerging technique. Bioremediation using microalgae has shown promising prospects since it is an ecological, efficient, and economical method against the accumulation of pesticides. The objective of this chapter is to deliberate the stumbling block of wastewater contamination through pesticide accumulation and to explore the prospective techniques for remediation of pesticides from wastewater.

Keywords Microalgae · Wastewater · Pesticide · Bioremediation · Metabolic mechanism

15.1 Introduction

Different versions of hazardous toxins such as pesticides, insecticides, fungicides, herbicides, rodenticides, plant growth regulators, etc. have been used both commercially and domestically (Rasmussen et al. 2015; Tsaboula et al. 2018). Currently, various pesticides have been occupied a certain place and are being applied in various sectors worldwide such as agricultural fields, industrial areas, and several animal husbandries, to increase yield and economic growth. However, uncontrolled application of pesticides results in rapid intensification and accumulation in the environment, causing severe pesticide toxicity. The worldwide use of pesticides in the form of fumigation/spray produces toxicity in the atmosphere (air, water, and soil). Agricultural runoff increases pollution in water bodies and reservoirs (Bashir et al. 2020; Kumar et al. 2021).

Pesticides contamination in the environment occurs mainly through the sources such as runoff from agricultural fields, previously contaminated agricultural areas, accumulation of volatile pesticides, inappropriate handling during transportation, substandard pesticide storage system, uneven pesticide spraying, the release of untreated wastewater from pesticides industries, etc. (Nie et al. 2020; Jaiswal et al. 2020a; Nanda et al. 2021). The appearance of various pesticides in the environment is related to various complications in the environment and human health since pesticides can alter the development of plants and animals. For example, organochlorine pesticides can alter the growth of animals by affecting the nervous system (Sharma et al. 2020). Pesticides can enter into the food web and accumulate in various trophic strata or sometimes in the human body through biomagnification. Due to exposure to pesticides, various symptoms can appear such as inflammation in the nose and throat, itchy skin, nausea, rash, vomiting, diarrhea, blurred vision, and blisters. However, the acute toxicity level of various pesticides needs much attention for severe medical care in most severe cases (Boudh and Singh 2019).

The discharge of effluents released from the agricultural industry can result in the contamination of water throughout the world, such contamination can appear in the form of pesticides and fertilizers. Different pesticides are reported in various water bodies around the world, which are applied to control insect populations in various agricultural crops (de Souza et al. 2020). In addition, it has been recorded that pesticides cause various harmful impacts in animals and humans, such as hepatotoxicity, genetic disorders, and hormonal alterations. It has been widely noted that pesticides are the major toxicant in water bodies. In addition, bioaccumulation can lead to the deposition of pesticides, which causes the alteration of the food chain and human health. As a tendency to accumulate in the water, pesticides found at higher concentrations can cause toxicity to surround organisms. In several cases, in freshwater and marine fish, the bioaccumulation of pesticides has shown various histological and biochemical alterations that can result in mortality.

Traditional wastewater treatment methods include a combined effort of chemical and physical precipitation, carbon adsorption, microfiltration, and activated sludge technique (Ullah et al. 2020). However, these methods are expensive to apply and may also be insufficient. On the other hand, bioremediation offers a better alternative to eliminate polluting pesticides from the aquatic environment (Dutta et al. 2020; Fatima et al. 2020a,b). Microorganisms such as unicellular photoautotrophs (green microalgae) are widely known to be applied in wastewater remediation processes due to the ability to accumulate harmful pesticides from aquatic effluents. Furthermore, green microalgae have the ability to collectively consume organic carbon and sunlight (Fuentes et al. 2016; Jaiswal and Prasath 2016). Microalgae can act in a synergistic pattern to break down inorganic and organic toxins more efficiently compared to other microorganisms. Various photosynthetic microalgae have shown the ability to convert light into a chemical form of energy. Microalgae have a simple organization at the cellular level and are surrounded by cellular fluids; these fluids provide additional benefits of rapid absorption of nutrients and water (Dolganyuk et al. 2020). Furthermore, microalgae exhibit strong adaptations and can grow through heterotrophic, mixotrophic, and autotrophic modes. Such ability has provided some advantages to survive in an environment (pesticide toxicity) where no other life can survive. As reported by several researchers, microalgae exhibit a strong ability to generate biomass due to the ability to metabolize various toxins in the form of an energy source (Nanda et al. 2019; Chowdhury et al. 2021).

The most promising benefit of bioremediation using microalgae is that it can treat wastewater simultaneously with pH adjustment, reduction in total dissolved solids (TDS), and improvement in chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Furthermore, the remarkable bioremediation capacity of microalgae can be applied in the production of several high-value products. Here, this chapter aims to assess the prospects for microalgae to remove various pesticides. The development of bioremediation approaches has been deliberated through microalgae cultivation for the degradation of pesticides existing in wastewater. In addition, several possibilities of microalgae biomass valorization have been explored

(Jaiswal and Pandey 2014). However, the available research based on microalgae to eliminate pesticides is still at the laboratory level. Currently, recent signs of progress have emphasized the large-scale use of microalgae to treat wastewater.

15.2 Microalgae Cultivation

The growth and cultivation of microalgae can be implemented using different well--recognized methods, such as photoautotrophic, heterotrophic, or mixoautotrophic approaches (Hammed et al. 2016; Naruka et al. 2019; Banerjee et al. 2020). In the photoautotrophic method, three basic components are needed such as CO_2, the carbon source, the light source, and the nutrients. This method uses light to transform CO_2 into chemical energy. On the other hand, heterotrophic algae culture needs water, nutrients, and carbon source (e.g., glucose) (Mohan et al. 2015). The main benefit of this method is that there is no compulsion for light. Microalgae can also be cultivated by mixotrophic culture, in which a combination of photoautotrophs and heterotrophs is applied.

Moreover, microalgae can be screened and identified based on morphological characteristics and molecular identification. During the morphological level, the microalgae are examined for their shape, texture, and cell arrangement. An advanced technique such as scanning electron microscopy is very useful in the characterization of microalgae (Nicolau et al. 2014). As reported by several researchers, morphological characteristics are not sufficient to distinguish microalgae, as microalgae exhibit a variety of sizes and shapes at various stages of the life cycle and this scenario becomes the obstacle to the accurate screening of microalgae. This problem can be solved through the molecular identification process since this method is more efficient and reliable (Tale et al. 2014). Typically, analysis at the molecular level has the following steps such as DNA extraction, PCR amplification, DNA sequencing, and analysis at the phylogenetic level.

15.3 Pesticide Degradation by Microalgae Cultivation and Metabolic Mechanism

Pesticides can be degraded using microalgae through a direct process that requires energy from an external source or through an indirect process that includes a sudden physicochemical interaction with the cell wall structure. Different strains of microalgae require different optimal environmental conditions to grow and survive. Additionally, the function of metabolic activity in microalgae strains depends on environmental factors such as temperature, humidity, pH, etc. At low temperatures, the natural degradation mechanism of pesticides is very slow; however, the rate of metabolic activity increases with increasing temperature to an optimal level. The proliferation of microalgae also depends on the acidity and alkalinity of the

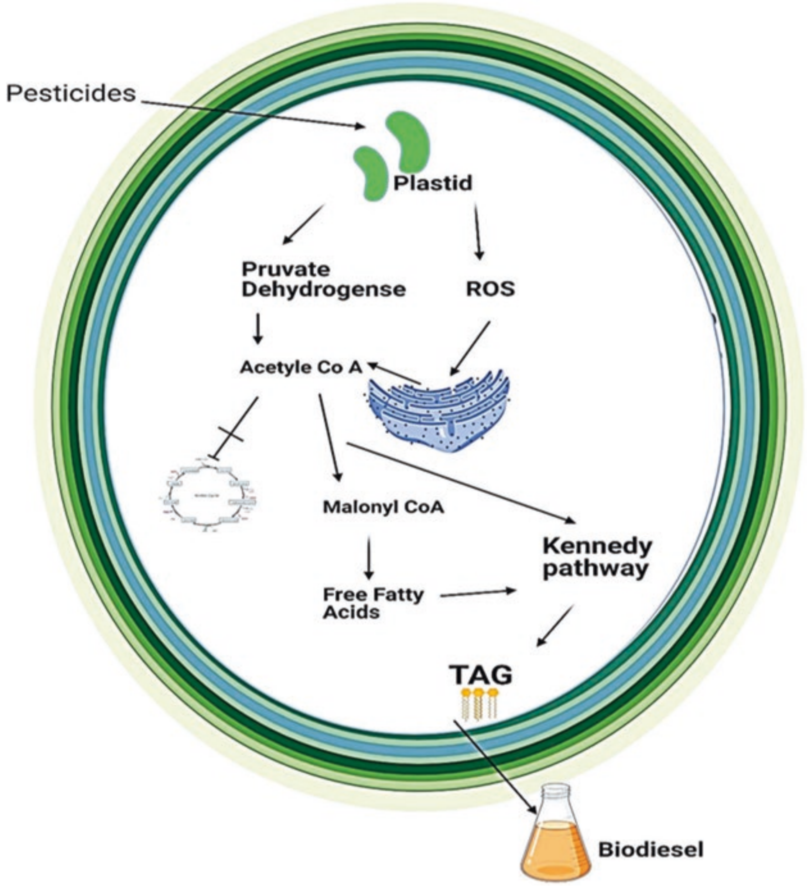

Fig. 15.1 A possible triacylglycerol (TAG) pathway under pesticide stress

environment. Several attempts have been made to study the removal of pesticides through microalgae which have been summarized in (Fig. 15.1 and Table 15.1). Several researchers have reported numerous methods to be applied in the eradication of pesticides through microalgae cultivation with the process of the metabolic mechanism involved bioadsorption, bioaccumulation, and biodegradation.

15.3.1 Bioadsorption

Some biological agents, such as microalgae, have the ability to adsorb pesticides and toxins, including hazardous aromatic compounds (Jaiswal et al. 2021). In some of the latest reports, researchers have observed that 88–97% of the different toxins

Table 15.1 Pesticides degradation using different microalgae

Microalgae	Toxicants	Concentration (mg/L)	Degradation efficiency (%)	Duration (h)	References
Chlamydomonas reinhardtii	Fluroxypyr	0.5	57.0	120	Zhang et al. (2011)
Chlamydomonas reinhardtii	Prometryne	7500	66.0	144	Jin et al. (2012)
Spirulina platensis	Malathion	0.02–100	54.0	480	Ibrahim et al. (2014)
Nostoc muscorum	Malathion	0.02–100	65.0	480	Ibrahim et al. (2014)
Scenedesmus obliquus	Diazinon	20	64.0	288	Kurade et al. (2016)
Chlorella vulgaris	Diazinon	20	94.9	288	Kurade et al. (2016)
Chlorella vulgaris	Pyriproxyfen	0.002	88.2	1.08	Hussein et al. (2017)
Chlorella vulgaris	Carbofuran	0.002	86.3	1.08	Hussein et al. (2017)
Chlorella vulgaris	Atrazine	0.002	89.2	1.08	Hussein et al. (2017)
Chlorella vulgaris	Molinate	0.002	85.6	1.08	Hussein et al. (2017)
Chlorella vulgaris	Propanil	0.002	86.4	1.08	Hussein et al. (2017)

in the aqueous environment have been eliminated through the process of bioadsorption using microalgae (Hussein et al. 2017). The bioadsorption process contains several mechanisms, such as ion exchange, surface complexation, adsorption, and precipitation. However, the effectiveness of pesticide adsorption is greatly affected by the available active groups on the surface of microalgae. Carbohydrates, the intercellular space, and polysaccharides are the main components of the microalgae cell wall; this phenomenon can favor the adsorption of organic toxins (Qiu et al. 2017). Furthermore, microalgae exhibit eradication capabilities against various contaminants. Based on the available literature, it can be stated that the degradation of pesticides depends mostly on the aspects of the favorable environment of the biome for survival abilities, the structure of the pesticide, the factors related to microalgae, pH, salinity, temperature, light intensity, the presence of electron acceptors, and carbon substrates.

15.3.2 Bioaccumulation

The bioaccumulation process has been considered an active process and can be expressed through the bioconcentration factor (BCF), which is responsible for showing the concentration ratio of a particular toxin in any animal concerning the ecosystem. The BCF value is mainly affected by the difference in bioconcentration, physical obstacles, dissolved organic matter, ionization of compounds, and metabolism (Wang et al. 2014). When microalgae get exposed to pesticides, they cause the generation of reactive oxygen species (ROS) from the cell. The ROS released expresses a high oxidative tendency, groups of atoms that cause oxidation of DNA and the lipid membrane, causing disorders in microalgae followed by cell death (Kurade et al. 2016). Any possibility of contamination can induce gene expression within microalgae cells to generate antioxidant enzymes. According to several researchers, microalgae possess the ability to bioaccumulate and biodegrade pesticides. For example, the *Scenedesmus obliquus* has shown the remarkable accumulation of triadimefon, on the other hand, the concentration of the degraded product has been reported, which shows its elimination. The combination of these two processes can rapidly eliminate pesticides using microalgae (Xu and Huang 2017).

15.3.3 Biodegradation

To remove toxins from wastewater, biodegradation is a vital process. Microalgae have the ability to degrade organic toxins existing in wastewater into smaller molecules; these molecules are used as a source of nutrients for the growth and development of microalgae. In the case of malathion biodegradation by various strains of microalgae such as *Spirulina platensis*, and *Nostoc muscorum* exhibited degradation of 55% and 92%, respectively (Ibrahim et al. 2014). According to several researchers, microalgae have shown a remarkable degradation capacity, e.g., *Chlorella* sp. has shown up to 98% removal. Several enzymes such as esterase and transferase have been considered vital for the degradation and detoxification process. Some other enzymes such as oxygenase, oxidoreductase, and phosphotriesterase are widely involved in pesticide removal. However, the process of the degradation mechanism of various pesticides is still needed extensive investigation, as pesticide removal is a very specific scenario.

15.3.3.1 Acclimatization

It has been observed that several strains of microalgae require a different operating procedure, which can be categorized in various steps. The enrichment of a particular strain has been carried out in the presence of different concentrations of substrate. As the environment changes, microorganisms strive to maintain balance in the internal environment with the help of acclimatization, which causes alteration of gene expression. The use of microalgae for environmental stress can cause the biosynthesis of enzymes, which can eliminate toxic substances (Jaiswal et al. 2020b). As reported, *Staphylococcus intermedius* can be acclimatized to maintain lindane toxicity within the range of 6–125 mg/L and obtain a 98% degradation of lindane. The intensity of the light also plays a vital role in the development of microalgae; however, photoacclimatization is considered equally vital (Bernardi et al. 2017). The microalgae co-culture process in bioremediation approaches can be applied in an aseptic environment in the laboratory; however, microalgae cultivation depends mainly on several factors (Fatima and Kumar 2020).

15.3.3.2 Immobilization of Microalgae

The immobilization process has shown promising aspects in the field of bioremediation and has been considered as a suitable approach for the positioning of microalgae by which it can be kept reusable and active. The above said method has the ability to be an alternative to traditional methods such as advanced cell catalyst as well as cell density, separation at a suitable stage, and advanced survival traits in extreme conditions. Generally, established methods for the immobilization of microorganisms can be applied to different strains of microalgae. The limitation to consider is the transmission of light for the immobilization of living microalgae cells. Microalgae generally prefer passive and active immobilization techniques. In passive immobilization, some of the microalgae have a natural tendency to adhere to surfaces and grow, these characteristics support to immobilize the cells of the microalgae in different carriers. This passive immobilization usually has easy reversibility using natural or synthetic adsorbent carriers. However, active immobilization techniques use flocculating agents, chemical interactions, gel entrapment, etc. The most widely used immobilization technique can be categorized into four aspects, i.e., covalent bonding, crosslinking, adsorption, and embedding (Vasilieva et al. 2018). By applying these methods, the adsorption process was found to be the most efficient approach as it is simple to operate. Apart from that, the selection of the carrier (sawdust, perlite, and corn cob) also plays a vital role. In addition, some other aspects have also been monitored when selecting a suitable carrier, such as cost-effectiveness, mechanical strength, and flexibility. As the researchers suggested, inorganic and organic materials can be applied as immobilization vehicles. According to the previous study, *Chlorella vulgaris* was obtained and cultured for 240 h to achieve the necessary microalgae suspension and immobilization on alginate beads. A general representation of the bioreactor with immobilized microalgae for pesticide degradation has been illustrated in Fig. 15.2. The result has been recorded for the degradation of pendimethalin and carbofuran as to be as 95% and 97%, respectively. In addition, various methods can be applied to achieve high degradation and detoxification, e.g., the hybrid microalgae membrane photobioreactor (HMPBR) technique can be used to immobilize microalgae within membrane photobioreactor (Derakhshan et al. 2019).

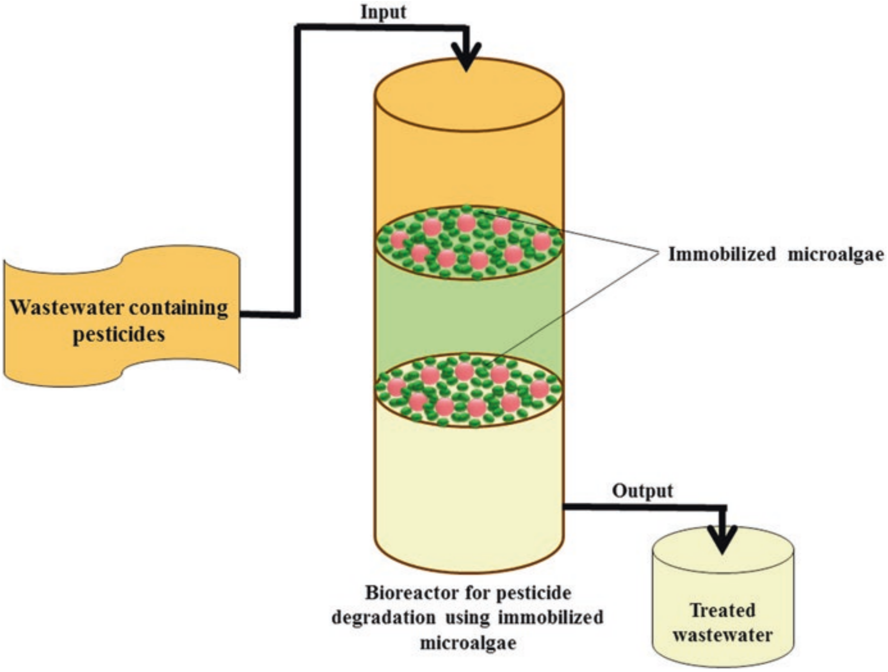

Fig. 15.2 A general representation of the bioreactor with immobilized microalgae for pesticide degradation

15.4 Constraints and Future Perspectives

The degradation of toxic substances by microalgae is still confined to the laboratory level and needs interdisciplinary research investigation to overcome the hindrances:

1. In the current situation, the degradation of pesticides by microalgae is facing to address these commercial related barriers, due to the high cost of production. Recent studies focus on the photobioreactor level to obtain high-value products. During the natural operating environment, microalgae reproduction is altered and controlled by extrinsic factors such as temperature, sunlight, weather conditions, and other life forms. Furthermore, under natural conditions, microalgae face strong threats from bacteria, rotifers, ciliates, and other microorganisms.
2. As microalgae are unicellular organisms, they can be suspended in aqueous conditions and can show negatively charged hydrophilic behavior towards the surface; therefore, sedimentation due to gravitational force is difficult. In biodiesel production, the harvest of microalgae still has to face several challenges, such as a lower operating efficiency, as well as a higher operating cost due to its intensity towards energy. Each harvesting method has some disadvantages and advantages, which depend on the cultivation technique and the variety of microalgae.

Here it can be stated that a single harvesting method may not cover all process requirements and also requires multiple approaches for simultaneous operation.

3. Microalgae use the contaminants as nutrients present in the wastewater to grow and increase their biomass. Also, several particular nutrients can be used to enhance biomass production to a commercial level. However, some pollutants may not be absorbed or degraded. Such a scenario, if not properly addressed, these pollutants can hamper other applications and degrade the entire process.
4. In the area of biodiesel production from microalgae biomass, life cycle assessment studies have been carried out to increase yield, but even so, these attempts have shown certain limitations. This technology has not yet been tested on a large-scale industrial level and so far, any available research is based on data generated by laboratories. Pre-existing evaluations, compared to algae biodiesel and diesel, showed that the latter has performed better in terms of yields and commercially. In addition, the biodiesel from the algae generates reduced greenhouse gases and also generates a lower proportion of net energy.
5. The microalgae genetic modification approach is an advanced perspective to develop a selected gene within the host cell, as well as to eliminate a specific DNA fragment. Such a scenario can avoid the lengthy selection process and the acclimatization process for direct expression of the necessary forms as well as the increase of the cellular metabolic activity. As it can be stated that microalgae strains, those genetically modified for the degradation of pesticides, are still at the initial level and recent updates and data are lacking in this field. The most advanced and efficient research techniques can help to gain the work capacity of microalgae.

15.5 Conclusions

The harmful effect of pesticides in wastewater has become a serious threat to the environment. The bioremediation technique using microalgae offers great prospects for combating pesticide toxicity. The effective uses of microalgae biotechnology in various fields have shown remarkable results in the area of wastewater treatment. The degradation of pesticides in wastewater with the help of microalgae has been considered an environmentally sustainable process. The microalgae biomass, after recycling, can be used for the production of biodiesel and bio-char, etc. considering that the process is environmentally sustainable and profitable. However, the application of microalgae for the degradation of pesticides in wastewater is limited to the laboratory level. Several microalgae strains have prospects for the future. The current attempt focused on enormous research efforts and more on industrial applications so that such technology in the future can be used in the degradation or removal of pesticides. Furthermore, the utility of the latest biotechnological techniques may show the process in a cost-effective and environmentally sustainable application in the near future.

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Part III
Applications and Global Case Studies of Pesticides Bioremediation

Chapter 16

Soils Contaminated with Persistent Organic Pollutants (POPs): Current Situations, Management, and Bioremediation Techniques: A Mexican Case Study

María Luisa Castrejón-Godínez, Alexis Rodríguez, Enrique Sánchez-Salinas, Patricia Mussali-Galante, Efraín Tovar-Sánchez, and Ma. Laura Ortiz-Hernández

Abstract The presence of different Persistent Organic Pollutants (POPs), such as organochlorine pesticides, polybrominated diphenyl ethers, polychlorinated aromatic compounds, polychlorinated dibenzofurans, polychlorinated dibenzo-*p*-dioxins, among others, has been reported in agricultural and industrial areas across different regions worldwide. POPs are highly toxic chemical compounds that cause severe adverse effects on ecosystems and have been related to multiple diseases in humans, including cancer, birth defects, and dysfunction in the immune, nervous, and reproductive systems. The Stockholm Convention is an international strategy for implementing policies to control or eliminate the production and use of these chemicals. In this context, developing strategies for the elimination and remediation of polluted sites by POPs is an urgent requirement. Bioremediation is a process

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whereby dangerous pollutants become less toxic or nontoxic moieties, reducing their concentrations to undetectable levels or eliminating organic pollutants using the physiological capabilities of living organisms. Therefore, bioremediation has been proposed as the most suitable biotechnology for the treatment of polluted environments with POPs. In practically all geographic regions of Mexico, different POPs have been reported in agricultural and urban areas. The main POPs reported include different organochlorine pesticides, such as aldrin, dichlorodiphenyltrichloroethane (DDT), endosulfan, endrin, and hexachlorocyclohexanes (HCHs), in agricultural districts, while in urban areas the most studied POPs were polychlorinated biphenyls and polybrominated diphenyl ethers. In Mexico, the scientific research in POPs bioremediation has been focused on identifying and characterizing microorganisms (bacteria and fungi) capable of biodegrading POPs as a bioprospection strategy for future bioremediation applications. In the present chapter, the chemical characteristics of POPs, their impact on ecosystems and human health, as well as the presence of these compounds in different localities of Mexico and biodegradation studies are reviewed.

Keywords Biodegradation · Dioxins · Environmental pollution; Pesticide · Polychlorinated compounds

16.1 Introduction

There are many organic chemical compounds, with high toxicity, whose generation and release into the environment are related to human activities. Therefore, it is necessary that they should be detected and quantified. Among pollutants, those that have attracted the most attention are those that do not degrade easily and are often the most toxic; these chemicals are recognized as POPs. POPs are a group of compounds of both natural and anthropogenic origins. However, through different industrial processes, human activities constitute the main cause of the intentionally and unintentionally POPs generation (Rottem 2017). POPs are harmful substances that pose a significant environmental and human health risk. POPs are diverse in chemical structure, however they share common characteristics, such as high environmental persistence due to their resistance to the natural biochemical, chemical, and photolytic degradation processes, and high toxicity to living organisms. POPs are semi-volatile compounds with a high capability of long-range transport to other places, such as the polar regions, they also can be bioaccumulated in the fatty tissues of animals, humans included (Rottem 2017; Wahlang 2018; Wang et al. 2019; Kim et al. 2020; Sun et al. 2020; Sheriff et al. 2021). POPs comprise a group of numerous artificial chemicals including dioxins, brominated flame retardants (BFRs), organochlorine pesticides (OCPs), perfluorinated compounds (PFCs), polychlorinated biphenyls (PCBs), and inclusively, polycyclic aromatic hydrocarbons (PAHs) (Wahlang 2018).

With the establishment of the Stockholm Convention in 2001, an international agreement to regulate the production, distribution, use, and disposal of POPs was reached (Sheriff et al. 2021). The first Stockholm Convention list of POPs included 12 priority pollutants: aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, polychlorinated dibenzo-*p*-dioxins (PCDD), and polychlorinated dibenzofurans (PCDFs); these chemicals were known as the "dirty dozen" (Tandon 2021). The production and extensive use of these chemical formulations began shortly after the end of World War II (Jennings and Li 2015). The Stockholm Convention bans these *"first generation"* 12 chemicals because of their toxicity, persistence, bioaccumulation, and long-range transport (Patel et al. 2021). Additionally, the Basel and Rotterdam Conventions contemplate hazardous wastes and other special wastes, such as medical and electronic waste; and provide an information exchange procedure for international trade, such as imports of pesticides and other dangerous substances, in an attempt to reduce the environmental and human health impacts (BRS Conventions 2021).

Many countries signed and ratified Stockholm Convention in 2003 and have subsequently developed their national implementation plans (NIPs). However, some of these countries have proved reluctant to ratify the language of the Convention. Derived from this, the proposal of new compounds and their inclusion in the Convention is complex. Such reluctance increases the production, use, and environmental release of compounds that threaten human health around the world. The signatory parts of the Stockholm Convention must take legislative and administrative actions to prevent the POPs associated environmental impacts, in both inside their territory and at the global level (Sharkey et al. 2020). However, the current knowledge state, environmental management practices, the degree of political and economic controversy in the POPs issue, as well as the importance of this topic in the public opinion and among policymakers, make it challenging to apply (Rottem 2017). Mexico has a robust legal framework that regulates POPs. In addition, numerous evaluations of sites contaminated with POPs have been carried out in different country regions, to establish the quality of the soil and water, highlighting the urgency of developing management alternatives and remediation strategies for these contaminated areas. On the other hand, POPs exposition monitoring studies have been performed in different regions of the Mexican territory to generate a profile on the POPs people exposure. In México, population exposure to DDT, a pesticide used in public health, as well as the exposition to PAHs derived from biomass combustion in indigenous communities has been documented. In addition, communities in industrial and urban areas are exposed to polybrominated diphenyl ethers (PBDEs) and the PCBs present in brick kiln smoke and non-controlled waste disposal sites (Orta-García et al. 2014).

In the present chapter information about the general characteristics of POPs, the sources, pollution, and other environmental impacts are reviewed. It also covers human health threats, POPs environmental biomonitoring and ecotoxicology, the International and Mexican regulation related to POPs, soils polluted by POPs in Mexico, the management alternatives of POPs in Mexico, as well as the bioremediation alternatives.

16.2 Persistent Organic Pollutants (POPs)

16.2.1 What Are POPs

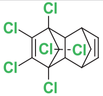
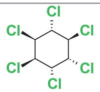
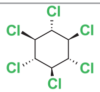
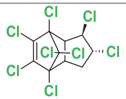
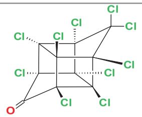
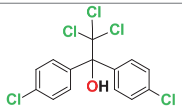
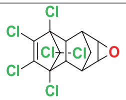
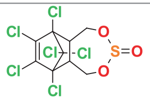
Persistent Organic Pollutants (POPs) are limited water solubility and highly toxic chemical compounds, broadly resistant to most of the physical, chemical, and biological degradation processes in the environment. Due to these characteristics, POPs can persist in nature for a long time in the different environmental strata and be mobilized through the soil, water, and air. In addition, the high lipid solubility of these chemicals lets them be bioaccumulated in animal and human tissues, as well as their biomagnification through the trophic webs (Fu et al. 2003; Klánová et al. 2009). According to their chemical characteristics, POPs are semi-volatile and low water solubility compounds, with molecular weights ranging from 200 to 500 Da (Jacob and Cherian 2013). These chemicals commonly are highly halogenated (Br, Cl, F), being chlorine, the main halogen element present in this group of compounds. The number of carbon–chlorine bonds in a POP compound is directly related to its persistence; the higher the number of these bonds, the more hydrolysis stability and degradation resistance is shown by the compound (Yarto et al. 2003; Weinberg 2009; Venegas and Naranjo 2010; Guo and Kannan 2015; Lorenzo et al. 2018; UNEP 2021).

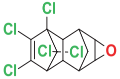
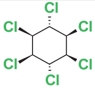
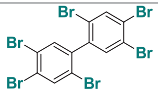
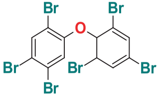
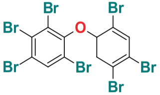
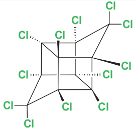
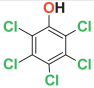
Different studies worldwide have evidenced the adverse environmental and human health impacts of POPs (Fu et al. 2003; Lorenzo et al. 2018). Therefore, the Stockholm Convention on Persistent Organic Pollutants, established in 2001, aims to protect the environment and human health from POPs. This international instrument requires governments to implement measures to eliminate, reduce the production, use, import, export, and environmental release of POPs (Weinberg 2009). In 1995, at the Stockholm Convention, an initial list of POPs that included 12 chemical compounds that were considered as priorities was created. The first included compounds were: aldrin, dieldrin, chlordane, DDT, endrin, heptachlor, hexachlorobenzene, PCBs, PCDD, PCDFs, mirex, and toxaphene (Yarto et al. 2003). In subsequent years, several novel chemicals were included in the Stockholm Convention list of POPs: Chlordecone, HCHs (α-, β-, and γ-isomers), hexabromobiphenyl, tetrabromodiphenyl ether and pentabromodiphenyl ether, hexabromodiphenyl ether and heptabromodiphenyl ether, perfluorooctane sulfonic acid, and perfluorooctanoic acid in the year 2009; endosulfan in 2010; hexabromocyclododecane in 2013; hexachlorobutadiene, pentachlorophenol, its salts and esters, and the polychlorinated naphthalenes in 2015; decabromodiphenyl ether and the short-chain chlorinated paraffins in 2017; and finally, dicofol and pentachlorobenzene in 2019 (UNEP 2011, 2021).

POPs have been classified in three general categories: (1) Pesticides used in agriculture, (2) Industrial chemical products used for diverse applications, and (3) Chemical products generated unintentionally because of incomplete combustion or chemical reactions (Weinberg 2009). Worldwide, pesticides have been employed for multiple activities, including pest control in agriculture, disease vectors control, among others. Once applied, pesticides are volatilized from crop fields to the atmosphere, or are translated to soil, superficial and underground water bodies through runoff and infiltration events. The presence of these pollutants in the environment favors their entrance to the organisms, where pesticides are bioaccumulated in their tissues. The release of pesticides included in the POPs list is implicated in several adverse impacts in the environment, as well as threats to the biodiversity and human health (Gaur et al. 2018). Among the POPs of group two, industrial chemical compounds, PCBs have been reported as highly dangerous to the environment and human health. These chemicals are broadly used for diverse industrial applications due to their unique characteristics of low inflammability, heat resistance, chemical stability, low vapor pressure, high boiling point (320–420 °C), and dielectric properties Due to their intensive use since the 1930s, pollution caused by PCBs has been registered in several regions around the world (Abou-Elwafa 2015; Vukasinovic et al. 2017; Dave et al. 2021).

Currently, 30 POPs are listed in the Stockholm Convention (UNEP 2021). The information related to these compounds is shown in Table 16.1. These POPs are classified in three annexes (A, B, and C). Chemical compounds in Annex A are subject to the prohibition of their production, use, importation, and exportation. The compounds listed in annex B are subject to restrictions in their production and use. However, some of these compounds have exemptions to these restrictions. For example, the use of the pesticide DDT is allowed for the control of disease vectors, such as the mosquitoes of the *Anopheles* genus that are the transmitters of the parasite *Plasmodium* sp. in Malaria, as well as the perfluorooctane sulfonic acid, which is a compound employed in the photographic industry, and the production of semiconductors, plates of metal, certain medical devices, firefighting foam, and insect traps. The compounds listed in Annex C include PCDDs and PCDFs whose unintentional release must be reduced. These compounds are produced and released into the atmosphere due to incomplete combustion and chemical reactions during open waste burning, fossil fuels combustion, and chemicals production processes (UNEP 2011; UNEP 2017; Gaur et al. 2018).

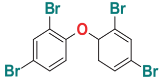
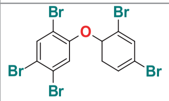
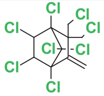
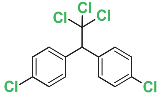
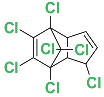
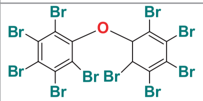
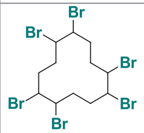
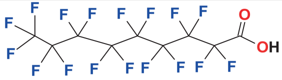
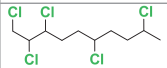
Table 16.1 POPs included in the Stockholm Convention (Fiedler et al. 2013; Jones 2021; UNEP 2021)

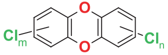
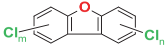
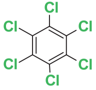
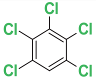
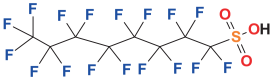
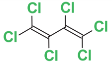
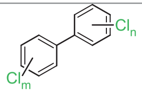
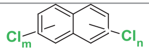
Category	POP name	Acronym	CAS number	Structure	Classification
Pesticide	Aldrin		309-00-2		Elimination
	α-hexachlorocyclohexane	α-HCH	319-84-6		
	β-hexachlorocyclohexane	β-HCH			
	Chlordane		5103-74-2		
	Chlordecone		143-50-0		
	Dicofol		115-32-2		
	Dieldrin		60-57-1		
	Endosulfan		115-29-7		

Category	POP name	Acronym	CAS number	Structure	Classification
	Endrin		72-20-8		
	γ-hexachlorocyclohexane	γ-HCH	58-89-9		
	Hexabromobiphenyl	HBB	36355-01-8		
	Hexabromodiphenyl ether	PBDE	68631-49-2 207122-15-4 446255-22-7		
	Heptabromodiphenyl ether		207122-16-5		
	Mirex		2385-85-5		
	Pentachlorophenol, its salts and esters	PCP	87-86-5 131-52-2 27735-64-4 3772-94-9 1825-21-4		

(continued)

Table 16.1 (continued)

Category	POP name	Acronym	CAS number	Structure	Classification
	Tetrabromodiphenyl ether	BDE	5436-43-1		
	Pentabromodiphenyl ether	PBDE	32534-81-9		
	Toxaphene		8001-35-2		
	Dichlorodiphenyltrichloroethane	DDT	50-29-3		Restriction
	Heptachlor		76-44-8		
Industrial	Decabromodiphenyl ether	Deca-BDE	1163-19-5		Elimination
	Hexabromocyclododecane	HBCD	25637-99-4		
	Perfluorooctanoic acid	PFOA	335-67-1		
	Short-chain chlorinated paraffins	SCCPs	85535-84-8		

Category	POP name	Acronym	CAS number	Structure	Classification
Unintentional production	Polychlorinated dibenzo-*p*-dioxins	PCDDs			Unintentional production
	Polychlorinated dibenzofurans	PCDFs			
Pesticide, industrial, and unintentional production	Hexachlorobenzene	HCB	118-74-1		Elimination and Unintentional production
	Pentachlorobenzene	PeCB	608-93-5		
Pesticide and Industrial	Perfluorooctane sulfonic acid	PFOS	1763-23-1		Restriction
Industrial and unintentional production	Hexachlorobutadiene	HCBD	87-68-3		Elimination and Unintentional production
	Polychlorinated biphenyls	PCBs	11097-69-1		
	Polychlorinated naphthalene	PCN			

16.2.2 Sources, Pollution, and Other Environmental Impacts

POPs as dibenzofurans and dioxins are generated naturally through volcanic activities and forest fires. However, human activities mainly produce these compounds through industrial processes, waste incineration plants, and agricultural activities (Gaur et al. 2018; Thakur and Pathania 2020; Akhtar et al. 2021). The environmental fate of the POPs is the atmosphere, which is the main transport media for these compounds (Fernández and Grimalt 2003). Next, these compounds can reach the water bodies, where they accumulate in the tissues of aquatic organisms (bioaccumulation) increasing their levels through trophic webs (biomagnification), generating adverse secondary effects (Lorenzo et al. 2018). POPs can also be found in soil and river sediments (Ren et al. 2018; Thakur and Pathania 2020).

POPs have generated significant adverse effects over a great diversity of species; their presence has been reported in almost all trophic levels, endangering the biodiversity of the polluted sites (Akhtar et al. 2021). Furthermore, the POPs exposition has been correlated with the reduction in the population levels of several species, due to immunotoxicity, failure in the function of the endocrine, reproductive and immunologic systems, as well as mortality increase in pups, deformations, increase in the incidence of tumors, thinning of the eggs wall, metabolic changes, cancer, changes in their behavior, alterations in the activity of the glutathione-S-transferase enzyme, as well as adult mortality, among others (Yarto et al. 2003; Venegas and Naranjo 2010; García et al. 2012; Alharbi et al. 2018). Likewise, POPs affect environmental factors such as temperature, precipitation, thaw, and biogeochemical cycles such as the carbon cycle, contributing to global warming (Thakur and Pathania 2020).

16.3 Human Health Threats

POPs generate serious problems for human health. Different authors, such as Alharbi et al. (2018), Zacharia (2019), Djangalina et al. (2020), and Thakur and Pathania (2020) point out that different POPs have been found in embryos, fetuses, and people of all ages. Human diseases related to POPs exposition include adverse effects on the endocrine system function, due to their profile as endocrine disruptors, generating hormonal alterations, adversely affecting the reproductive system resulting in birth defects, premature labor, developmental disorders, low birth weight, among others. POPs are also related to the development of cancer, cardiovascular diseases such as hypertension, angina pectoris, cardiac arrhythmias, among others, as well as to obesity, learning disabilities, diabetes, chloracne, porphyria, atherosclerosis, and neuropsychological impairment (Fig. 16.1). According to Tam et al. (2021), the World Health Organization reports 4.9 million deaths directly caused by POPs exposure each year, in addition to millions of people who develop POPs related diseases.

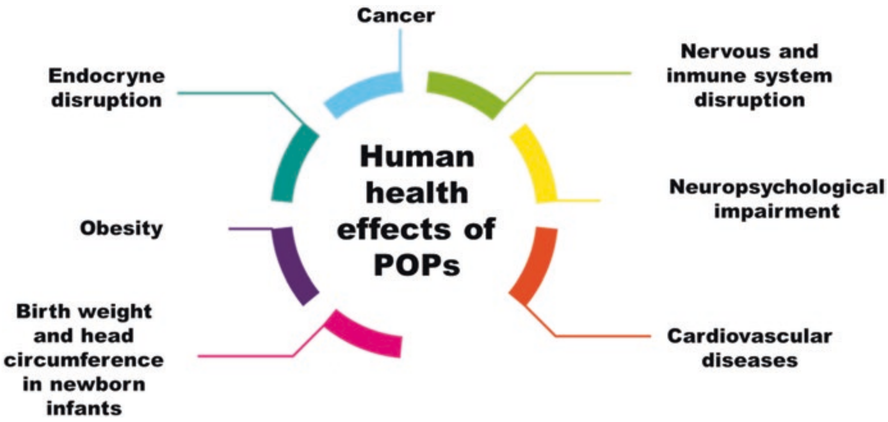


Fig. 16.1 Examples of human health problems related to POPs

16.4 POPs Environmental Biomonitoring and Ecotoxicology

Ecotoxicological studies evaluate the impact of toxic substances on the processes of natural ecosystems, as the flow of matter and energy of ecosystems, the dynamics of communities, the distribution and abundance of populations, and the morphology, physiology, and behavior of individuals (Galloway and Depledge 2001). There are some facts that need to be considered for biomonitoring and assessing ecotoxicological studies regarding the POPs environmental effects. (1) Since POPs bioaccumulate and biomagnificate along the food chain, these effects can be monitored at different levels of biological organization (from molecules to ecosystems). In ecotoxicological studies, biomarkers from the individual to the ecosystem level are used, considering the effects seen at the cellular and subcellular levels (Mussali-Galante et al. 2013). (2) These include a wide range of acute and chronic health effects, including cancer, congenital disabilities, immunosuppression, neurological disorders, and reproductive alterations. POPs are also referred to as endocrine disruptors (Kallenborn 2006; Mitra et al. 2011) being this last toxicity mechanism that is one of the most studied areas to date. (3) As endocrine disruptors, POPs directly compete with several natural hormones displacing them from their respective receptor binding sites, consequently, these pollutants are considered to act as synthetic hormones. The hormonal imbalances caused by pollutant-associated endocrine disruption have proved to be valuable indicators for documenting POPs adverse effects on various organisms (Kallenborn 2006). Hence, ecotoxicological studies and biomonitoring strategies should consider the use of biomarkers for assessing the ecotoxicity of POPs at various levels of the biological organization.

Currently, biomarkers give additional knowledge that cannot be obtained from the analysis of POPs concentrations alone. Also, they may incorporate the effects of chemical mixtures through a long exposure time. It is advisable to use a multibiomarker approach at different levels of the biological organization to evaluate the effects of POPs on the environment, in order to establish a more robust approach to any possible effects that may occur. At polluted sites, the organisms that integrate the top of the food web can bioaccumulate high POPs concentrations in their tissues, pollutant concentrations that exceed the individual toxicity thresholds, trigger several biochemical and physiological alterations in the exposed individuals. Therefore, ecotoxicological studies generate the bases for the prevention and reduction of risk by characterizing and evaluating the possible effects caused by the presence of toxic compounds and substances. In studies at the ecosystem level, it should be considered that toxic pollutants do not occur in isolation but in mixtures, or in combination with physical and biological agents.

Furthermore, in ecotoxicological surveys, the selection of a biomonitor species must be made according to the pollutant of interest and the site that needs to be monitored. The main suggested criteria for selecting them properly are (1) reduced mobility, (2) being in contact with the pollutant; (3) accumulation of high levels of the pollutant; (4) high abundance; (5) wide geographic distribution; (6) high longevity; (7) easy to sample; (8) easy to manipulate; (9) dose–response relationship; (10) long-term presence; (11) simple eating habits; (12) broad environmental stress tolerance; (13) well-defined species taxonomically; (14) extensive knowledge of its life history and biology (Haug et al. 1974; Phillips 1980; Phillips and Rainbow 1994; Rainbow 1995; Tanabe and Subramanian 2003; Luoma and Rainbow 2008; Zhou et al. 2008; Mussali-Galante et al. 2013). Associating molecular change to potential individuals, population, and community, with the aim of establishing links between the different levels of the biological organization is pertinent when considering the impact of POPs, because toxicity appears first in individuals before populations are affected, with subsequent changes at community level.

16.4.1 At the Individual Level

The effect of POPs will depend on the life stage of the exposed species, life history traits, overall health condition, and nutritional status. The main effects of POPs at the individual level are endocrine-disrupting, genotoxicity, ethology changes, reproductive alterations, immune dysfunction, and neurotoxicity.

Endocrine-disrupting. The consequences of these endocrine-disrupting effects can be observed mainly as physiological alterations in reproductive systems, specifically, alteration to sexual organs and hermaphroditism. The hormone-disrupting effects of anthropogenic pollutants have been shown to be valuable indicators for the documentation of pollutant effects on various organisms. For example, the induction of vitellogenin production (a hormone linked to egg production in females) in juvenile or male fish has become one of the most important biomarkers linked to endocrine-disrupting chemical agents. The relationship between POPs exposure and their effects using vitellogenin gene expression has been assessed as a biomarker of effects in fish (Zapata-Perez et al. 2007). For example, Zapata-Perez et al. (2007) studied the hardhead catfish (*Ariopsis felis*) from three ecosystems in the Southern Gulf of Mexico and Yucatan Peninsula. The authors detected that the concentrations of chlordanes, DDTs, HCHs, and PCBs were higher in exposed fish and that vitellogenin gene expression was over-expressed in fish collected from the site registering the highest levels of different POPs. Statistical analysis showed that the vitellogenin gene expression was significantly related to the concentrations of total DDTs and PCBs and negatively related to total Drins (dieldrin, aldrin, endrin).

Genotoxic damage. The genotoxic damage has been reported in different wild species exposed to POPs. González-Mille et al. (2019) found a significant association between total levels of POPs and genotoxic damage in different taxonomic groups, such as invertebrates, fishes, amphibians, and reptiles exposed to POPs mixtures. This is an important finding since genotoxic effects have been linked to ecological effects at higher levels of biological organization (Mussali-Galante et al. 2014).

Ethology changes. It has been documented that exposure to POPs (e.g., DDT) promotes alterations in the central nervous system, manifesting a deficit in learning and memory, and locomotion, as well as ethological alterations (Smith et al. 1976; Topinka et al. 1984; Tilson et al. 1987; Paul et al. 1994; Schantz and Widholm 2001; Mariussen and Fonnum 2006). In general, the main target of POPs (e.g., andrin, α-endosulfan, dieldrin, lindane, aldrin) in the central nervous system is the $GABA_A$ receptor (gamma-aminobutyric acid). Chronic exposure to POPs alters protein numbers, including antioxidant enzymes, receptors, and transporters of certain neurotransmitters, etc. (Slotkin and Seidler 2008, 2009). They also alter metabolic enzymes, including acetylcholinesterase, ion channels such as Mg^{2+}, Na^+/K^+ and Ca^{2+}, and ATPases of the plasma and mitochondrial membrane (Sahoo et al. 1999; Jia and Misra 2007), which contributes to changes in memory and learning. The brain accumulates large amounts of POPs comparable to adipose tissue. Therefore, brains exposed to levels of insecticides are capable of interfering with GABAergic neurotransmission (Vale et al. 2003).

Histopathological effects. As generated by POPs and a good effect biomarker that detects morphological alterations in various tissues by toxic agents. In fish exposed to chlordanes, dieldrin, DDT, and PAHs, histological liver abnormalities have been documented (Stehr et al. 1997).

Cancer. In addition to all the above-described effects at the individual level, many POPs are known or suspected carcinogens. PAHs, PCDD, and PCDFs are perhaps the most obvious examples (Jones and de Voogt 1999). Moreover, in top-predator species, POPs effects also extend to the immune system (Safe 1994; Ross et al. 1995), enhancing their susceptibility to disease and affecting their behavior patterns (De Swart et al. 1994).

Table 16.2 Sites in Mexico polluted with POPs

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
Northwest Region				
ΣCHL	0.38–0.72	Agricultural drain sediments	Mexicali valley, Baja California	Sánchez-Osorio et al. (2017)
ΣDDT	1.5–30			
ΣHCH	0.022–3.4			
ΣCHL	0.055–8.2	Residential soils		
ΣDDT	1.3–152			
ΣHCH	0.034–8.0			
DDD	0.84–12.4	Agricultural soils	Juarez Valley, Chihuahua	Núñez-Gastélum et al. (2019)
DDE	0.28–21.16			
DDT	0.13–171.86			
Endosulfan	0.75–1076			
Isodrin	0.71–17.07			
DDT	ND-336.2	Agricultural soil	Culiacan valley, Sinaloa	García-Hernández et al. (2021)
Endosulfan	1.4–1974.8			
HCH	ND-24.9			
DDT	0.51–21.95	Agricultural drain sediments	Culiacan valley, Sinaloa	García-de la Parra et al. (2012)
Endosulfan	0.5–4.85			
HCH	0.22–8.77			
PCBs	0.05–3.29			
Aldrin	ND-0.6	Agricultural and lagoon sediments	Navachiste-Macapule system, Sinaloa	Montes et al. (2012)
Dieldrin	0.2–2.5			
Endosulfan I	0.2–6.2			
Endosulfan II	0.2–2.5			
Endosulfan sulfate	0.7–9.4			
Endrin	0.3–27.0			
Endrin aldehyde	0.3–1.4			
Endrin ketone	0.3–9.8			
α-HCH	0.3–41.3			
β-HCH	0.3–533.3			
γ-HCH	0.3–7.7			
δ-HCH	0.3–70.2			
Heptachlor	ND–17.9			
Heptachlor epoxide	ND–0.6			
Methoxychlor	0.5–42.1			
p,p′-DDD	ND–0.6			
p,p′-DDE	0.4–2.8			
p,p′-DDT	ND–1.8			
DDT	ND–3131.4	Agricultural soil	Yaqui valley, Sonora	García-Hernández et al. (2021)
Endosulfan	ND–37			

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
CHL	0.009–1.0	Agricultural drain sediments	Yaqui valley, Sonora	Sánchez-Osorio et al. (2017)
DDT	0.21–55			
HCH	0.032–5.6			
CHL	0.062–25	Residential soils		
DDT	0.13–268			
HCH	0.035–3.1			
Aldrin	2.3	Agricultural soil	Caborca, Sonora	Leal et al. (2014)
α-Chlordane	1.2			
γ-Chlordane	2.4			
Dieldrin	3.3			
Endosulfan	8.9			
Endrin	5.6			
HCB	2.9			
α-HCH	2.0			
γ-HCH	1.4			
Heptachlor	2.73			
Isodrin	3.1			
Methoxychlor	2.4			
Mirex	2.2			
p,p′-DDD	3.1			
p,p′-DDE	9.6			
p,p′-DDT	1.3			
Aldrin	2.8	Agricultural soil	Hermosillo, Sonora	
α-Chlordane	2.6			
γ-Chlordane	2.0			
Dieldrin	2.3			
Endosulfan	3.6			
Endrin	7.5			
HCB	ND			
α-HCH	1.4			
γ-HCH	1.7			
Heptachlor	2.5			
Isodrin	8.4			
Methoxychlor	8.9			
Mirex	4.2			
p,p′-DDD	4.0			
p,p′-DDE	7.8			
p,p′-DDT	5.0			

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
Aldrin	2.2	Agricultural soil	Guaymas, Sonora	
α-Chlordane	2.3			
γ-Chlordane	3.8			
Dieldrin	4.3			
Endosulfan	3.9			
Endrin	19.0			
HCB	4.8			
α-HCH	3.7			
γ-HCH	2.0			
Heptachlor	3.4			
Isodrin	1.4			
Methoxychlor	3.1			
Mirex	1.7			
p,p′-DDD	1.8			
p,p′-DDE	45.8			
p,p′-DDT	4.2			
Aldrin	5.4	Agricultural soil	Magdalena, Sonora	
α-Chlordane	1.1			
γ-Chlordane	2.3			
Dieldrin	6.7			
Endosulfan	4.1			
Endrin	24.4			
HCB	0.7			
α-HCH	2.3			
γ-HCH	1.4			
Heptachlor	1.7			
Isodrin	0.4			
Methoxychlor	5.0			
Mirex	2.0			
p,p′-DDD	1.1			
p,p′-DDE	9.0			
p,p′-DDT	3.5			

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
Aldrin	1.0	Agricultural soil	Ures, Sonora	
α-Chlordane	1.7			
γ-Chlordane	1.7			
Dieldrin	0.9			
Endosulfan	1.4			
Endrin	18.8			
HCB	ND			
α-HCH	1.8			
γ-HCH	1.6			
Heptachlor	1.3			
Isodrin	ND			
Methoxychlor	4.2			
Mirex	1.5			
p,p′-DDD	1.1			
p,p′-DDE	1.0			
p,p′-DDT	0.6			
Aldrin	ND–41,000	Agricultural soils	Mayo valley, Sonora	Cantú-Soto et al. (2011)
BHC	ND–127,900			
Lindane	ND–3000			
Methoxychlor	ND–19,900			
p,p′-DDD	ND–23,200			
p,p′-DDE	ND–42,200			
p,p′-DDT	ND–120,400			
Aldrin	ND–74,000	Residential soils		
BHC	ND–938,500			
Endosulfan	ND–35,100			
Endrin	ND–161,400			
Lindane	ND–13,900			
Methoxychlor	ND–20,000			
p,p′-DDD	ND–39,300			
p,p′-DDE	ND–226,300			
p,p′-DDT	ND–301,200			

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
Aldrin	ND–15,900	Agricultural soils	Yaqui valley, Sonora	
BHC	ND–143,100			
Endosulfan	ND–124,000			
Endrin	ND–32,500			
Lindane	ND–2100			
Methoxychlor	ND–71,700			
p,p′-DDD	ND–13,300			
p,p′-DDE	ND–61,600			
p,p′-DDT	ND–110,000			
Aldrin	ND–25,800	Residential soils		
BHC	ND–292,400			
Endosulfan	ND–43,300			
Endrin	ND–377,300			
Methoxychlor	ND–19,700			
p,p′-DDD	ND–197,300			
p,p′-DDE	ND–621,300			
p,p′-DDT	ND–679,700			
Northeast Region				
DDT	25.3–790	Urban soil	Monterrey, Nuevo León	Orta-García et al. (2016)
PBDEs	1.80–127			
PCBs	4.0–65.5			
Western Region				
PBDEs	0.2–2.5	Lake sediments, urban	Chapala lake, Jalisco	Ontiveros-Cuadras et al. (2019)
PCBs	9–27			
PBDEs	0.3–1.5	Lake sediments, rural	El Tule lagoon, Jalisco	Ontiveros-Cuadras et al. (2014)
PCBs	1.7–24.7			
PBDEs	0.4–1.8		Santa Elena lake, Jalisco	
PCBs	1.5–15.4			
East Region				
Aldrin	9.31	Agricultural soil	Tepeaca, Puebla	Islas-García et al. (2015)
Endosulfan I	6.43			
Endosulfan II	1.91			
Endrín aldehyde	2.55			
Heptachlor	13.80			
p,p′-DDE	17.04			
trans-Chlordane	29.70			

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
HCB	0.2–1.5	Agricultural soil	Puebla and State of Mexico	Waliszewski et al. (2008)
α-HCH	0.2–2.2			
γ-HCH	1.0–7.2			
p,p′-DDE	2.0–7.1			
o,p′-DDT	4.9–31			
p,p′-DDT	22.9–99.2			
PCBs	0–88022.1	Agricultural soils	Tlaxcala, Tlaxcala	García-Nieto et al. (2019)
DDT	3.9–208.0			
PCBs	135–93,941	River sediments		
DDT	0.6–137			
PCBs	23.8–77	Lake sediments, urban	Las Matas lagoon, Veracruz	Ruiz-Fernández et al. (2012)
Midwest Region				
PBDEs	5–134	Urban soil	San Luis Potosí, San Luis Potosí	Perez-Vazquez et al. (2015)
PCB	ND–80.5			
DDD	ND–25.6			
DDT	ND–4.9			
Aldrin	0.65–1.35	Agricultural soil	Río Verde, San Luis Potosí	Velasco et al. (2014)
Endosulfan I	1.44–1.45			
Endosulfan II	0.27–48.62			
Endosulfan sulfate	1.96–9.51			
Endrin aldehyde	0.75–4.56			
α-HCH	0.58–0.92			
β-HCH	1.08–5.73			
γ-HCH	0.13–54.68			
δ-HCH	0.08–9.07			
Heptachlor	1.43–11.28			
Heptachlor epoxide	11.18–26.04			
Methoxychlor	1.20–37.70			
p,p′-DDD	1.04–19.32			
p,p′-DDE	0.13–15.01			
p,p′-DDT	14.9–144.10			
PBDEs	2.5–95.0	Urban soil	San Felipe Nuevo Mercurio, Mazapil, Zacatecas	Costilla-Salazar et al. (2011)

(continued)

Table 16.2 (continued)

POP	Concentration (ng/g DW)	Environmental sample	Location	Reference
South Central Region				
PCBs	253	Lake sediments, urban	Espejo de los Lirios, Mexico city	Piazza et al. (2009)
PCBs	621	Lake sediments, urban	Chalco lake, Mexico city	Piazza et al. (2008)
	63.7		Texcoco lake. Mexico city	
PBDEs	115–108,460	Urban soil	Alpuyeca, Xochitepec, Morelos	Perez-Maldonado et al. (2014)
Aldrin	0.1–12.2	Agricultural soil	Tlaltizapán, Morelos	Velasco et al. (2012)
Endosulfan I	0.1–16.2			
Endosulfan II	0.1–35.8			
Endosulfan sulfate	ND–17.9			
Endrin	0.2–18			
Endrin aldehyde	0.2–84			
α-HCH	0.2–129.6			
β-HCH	0.9–12.3			
γ-HCH	0.1–44.2			
δ-HCH	0.2–4.6			
Heptachlor	0.05–36.1			
Heptachlor epoxide	ND–11.1			
Methoxychlor	ND–34.4			
p,p′-DDD	0.2–25.6			
p,p′-DDE	0.1–70.6			
p,p′-DDT	0.2–79.1			
Southeast Region				
PCBs	6–372	Lake sediments, urban	Mecoacán lake, Tabasco	Armenta-Arteaga and Elizalde-González (2003)

DW Dry Weight, *ΣHCH* α-HCH + β-HCH + γ-HCH + δ-HCH (Hexachlorocyclohexanes), *ΣDDT* o,p′-DDE + o,p′-DDD + o,p′-DDT + p,p′-DDE + p,p′-DDD + p,p′-DDT, *ΣCHL* HEPT + HEPX + TC + CC (Chlordanes), *PBDEs* Polybrominated diphenyl ethers, *PCBs* Polychlorinated biphenyls, *ND* Non detected

Table 16.3 Methods applied in bioremediation

Strategies	Description
In situ bioremediation	
Bioaugmentation	Consist in the addition of pure of mixed exogenous microbial cultures to increase the microbial pollutants biodegradation
Bioventing	Consist in the injection of air to contaminated soil to stimulate microbial activity and pollutants biodegradation
Biosparging	Consist in the pressurized air injection below the contaminated water surface, oxygen supply stimulates microbial growth, aerobic biological activity and improve pollutants biodegradation
Biostimulation	Consist in the modification of the characteristics of the polluted environment to stimulate growth and biological activity of the microflora in charge of the bioremediation process; this includes the nutrients availability increase, adding sources of carbon, nitrogen, phosphorous, among others
Microbial assisted phytoremediation	Consist in the use of combination of plants and beneficial microorganisms for degradation and detoxification of pollutants in soil
Natural attenuation	Consist in the natural degradation of the pollutant by the biological action of the autochthonous microorganism from contaminated sites
Phytoremediation	Consist in the use of different higher plants species for soil remediation, plants can extract, stabilize, or biodegrade pollutants
Ex situ bioremediation	
Biofiltering	Consist in the use of a biofilter in which immobilized microorganisms retain or biodegrade pollutants
Biopiling	Consist in a bed of mound of contaminated soil, in which factors as moisture, temperature, nutrients, oxygen, and pH are controlled to enhance microbial pollutants biodegradation
Bioreactors	Consist in the use of a bioreactor system in which microorganism growing biodegrade pollutants. The system controls all parameter for supporting microbial growth and biological activity
Composting	Consist in the mixing of contaminated soil with a bulking agent, the pollutants are biodegraded by aerobic microbial and posterior thermophilic action using static or aerated piles in the treatment
Land farming	Consist in the treatment of contaminated soil, adding it to the superficial layer of the soil or into a treatment cell, polluted material is mixed periodically for biodegradation
Windrows	Consist in forming windrows of polluted soil, polluted material is rotated periodically for microbial-mediated degradation improvement

Sources: Das and Dash (2014); Azubuike et al. (2016); Sharma (2020); Raffa and Chiampo (2021)

16.4.2 At the Population Level

Effects of POPs exposure can be established between molecular and physiological alterations in individuals and changes at population level. These changes include:

Reduction in abundance of the population. It has been documented that wild population exposed to DDT and analogous insecticide rothane caused a reduction in population size. For example, fish-eating in the USA (Hunt and Bischoff 1960), birds of prey in Europe, North America (Hickey and Anderson 1968), and the UK (by a reduction in eggshell weight and thickness) (Ratcliffe 1967). These findings show the lethal effects and toxicity that POPs cause on top species of the food chain. Also, it has been documented that the insecticide dieldrin was responsible for the population crash of sparrowhawks (*Accipiter nisus*) in the UK (Sibly et al. 2000), demonstrating that high bioaccumulation of POPs found in the tissues of this predator species is clear evidence of the lethal effects of these pollutants.

Alteration in sexual organs. This effect can lead to low reproductive success and low fitness rates of the exposed population. Ecotoxicological research on wildlife populations has demonstrated that endocrine-disrupting chemicals profoundly impair animal reproduction and development. It has been documented that tributyltin (TBT) promotes masculinization in female marine mollusks, and this POP may cause a decline or local extinction of the population. For example, Bryan et al. (1986) and Gibbs and Bryan (1986) registered that the Dog whelk (*Nucella lapillus*) exposed to TBT decline its population size in the UK. The observed masculinization in females and the depressed reproductive capacity were explained by the competitive inhibition of TBT with cytochrome P450 dependent aromatase, enzyme responsible for the aromatization of testosterone and its conversion into estradiol (Matthiessen and Gibbs 1998). In many ecotoxicological studies, regional decline in fish, bird, and/or invertebrate populations resulting from exposure to POPs, such as DDT, PCBs, PCDD, and TBT has been related to biochemical, cellular, endocrine, and physiological effects in individuals (Vasseur and Cossu-Leguille 2006). One interesting finding is that organochlorines, notably DDED a metabolic breakdown product of DDT, can affect eggshell thickness in birds of prey (Ratclife 1967; Pearce et al. 1979), resulting in low fitness rates of the exposed population.

16.4.3 At the Community Level

In communities, particularly where contamination may act as a chemical stressor, different indexes and community properties have proved useful for evaluating the extent of environmental pollution. POPs can dissolve in the fatty tissues of organisms reducing their growth, size, fecundity, and fitness, which may eventually influence community structure (Arkoosh et al. 1998; Robinet and Feunteun 2002). However, few studies exist that evaluate changes in wild species assemblages (Clements and Rohr 2009). The little information generated so far at community level generates gaps in the effect of environmental pollutants on community structure, species composition, diversity, and functional groups. At community level, the most employed diversity measure indexes include the species richness, the Shannon–Wiener index (H′), and the Pielou evenness index (J).

In this context, in a study conducted by Neamtu et al. (2009) which characterized POPs in the Bahlui river in Rumania, the communities of phytoplankton and benthic invertebrates were monitored. They observed that water toxicity, related to the presence of POPs, appears to be higher for algae and less for benthic invertebrates, such as *Daphnia magna*, and indicated that primary producers reacted stronger than consumers at the presence of pollutants. The species richness in phytoplankton and macroinvertebrates appears to be negatively influenced by pollution. Also, the Shannon–Wiener diversity index, the Pielou evenness index, and the McNaughton dominant index each indicated that invertebrate communities appear to a have a more stable structure along the river. Johnston and Roberts (2009) documented, in a review and meta-analysis of the effects of contaminants on the richness and evenness of the marine community, that species richness is the most sensitive index for measuring community level effects, evidencing that polluted communities contain fewer species. Also, a near to 40% reduction in species richness was detected, regardless of the type of pollutants. It is important to note that as biological organization levels rise, the complexity of assessing cause-effect relationships between a certain pollutant and their effects also rises. That's why there are very few studies evaluating the ecotoxicological effects of POPs at higher levels of biological organizations, mainly at community level. Therefore, biomonitoring studies of ecological effects exerted by pollutants are urgent and necessary to gain information for more robust biomonitoring and mitigation strategies.

16.5 Soils Polluted by POPs in Mexico

According to Mexican normativity, a polluted site is defined as *"a place, space, soil, waterbody, installation or combination of these kinds of sites that has been in contact with materials or waste, which, due to their concentrations or characteristics, could represent a risk for human health, living organisms or the goods and properties of people*" (LGPGIR 2021). The causes of pollution are diverse. These include the inadequate disposal of different waste categories, leaks of hazardous materials or wastes from tanks, underground containers, tubes and ducts, the lixiviation of hazardous materials from places with production activities, storage sites, landfills, and dumpsites, as well as accidents and spills of chemical substances during transportation operations (SEMARNAT 2021).

The polluted sites can be divided into two main categories: those affected by environmental emergencies and the sites with the presence of environmental passives, the inadequate management of hazardous materials as well as the incidence of accidents that release toxic chemicals causes pollution in all environmental strata (soil, water, and air). The environmental presence and persistence of pollutants are recognized as a serious threat to ecosystems and human health. In Mexico more than 1000 polluted sites are registered. Contamination in these sites is related to different causes, including waste disposal, mining activities, industrial processes, and oil spills and its derivatives (SEMARNAT 2021). As pointed out above, the environmental presence of POPs is recognized as an important contamination concern worldwide. Mexico has committed to reduce POPs generation and encourage scientific research to identify and monitor sites polluted by these kinds of chemicals, as a signatory of the Stockholm Convention. Table 16.2 shows different studies carried out to detect and monitor the presence of POPs in environmental samples around Mexico. The country is divided into eight geographical regions (Northwest, Northeast, West, East, North Central, South Central, Southeast, and Southwest). In almost all regions' sites polluted by POPs have been detected.

Most of the 22 studies shown in Table 16.2 were carried out in the Northwest region, with seven studies carried out in Baja California, Chihuahua, Sinaloa, and Sonora. In these studies, the determination of the presence of different POPs in agricultural drain sediments, agricultural and residential soil, was achieved. The principal POPs monitored include OCPs such as DDT and its degradation products; lindane and other hexachlorocyclohexane isomers; aldrin, dieldrin, endrin, endosulfan, heptachlor, and methoxychlor (Cantú-Soto et al. 2011; García-de la Parra et al. 2012; Montes et al. 2012; Leal et al. 2014; Sánchez-Osorio et al. 2017; Núñez-Gastélum et al. 2019; García-Hernández et al. 2021).

In the South Central region of Mexico four studies have been carried out in lake sediments near urban areas of Mexico City (Piazza et al. 2008; Piazza et al. 2009). In addition, in agricultural and urban soils of the state of Morelos (Velasco et al. 2012; Pérez-Maldonado et al. 2014). POPs evaluated in these studies included polychlorinated biphenyl, PBDEs, and different OCPs.

In the East region, four studies have taken place, two of them evaluating OCPs in agricultural soil samples in the state of Puebla (Waliszewski et al. 2008; Islas-García et al. 2015). The study of García-Nieto et al. (2019) was focused on the evaluation of the presence of DDT and PCBs in agricultural soils and river sediments in the state of Tlaxcala, while in the state of Veracruz, the study carried out identified the presence of PCBs in sediments of the lagoon of Las Matas close to an urban area (Ruiz-Fernández et al. 2012).

In the Midwest region, three studies were identified, two of them for the state of San Luis Potosí. The first study was carried out in soil samples of urban areas to identify the presence of DDT, PBDEs, and PCBs (Perez-Vazquez et al. 2015), and the second evaluated the pollution caused by different OCPs in soil samples of agricultural areas (Velasco et al. 2014). In the same geographic region, Costilla-Salazar et al. (2011) evaluated the presence of PBDEs in soils of urban areas in the mining district of San Felipe Nuevo Mercurio in Mazapil, Zacatecas.

In the Western region, two studies looked at lake sediments of rural and urban areas of Jalisco and evaluated the presence of PBDEs and PCBs. Finally, just two studies were identified for both the Northeast and Southeast regions. Thus, in the city of Monterrey in the state of Nuevo León (Northeast region), the presence of DDT, PBDEs, and PCBs was evaluated in urban soil (Orta-García et al. 2016). While in the state of Tabasco (Southeast region), the presence of PCBs in the sediments of the Mecoacán lake was detected (Armenta-Arteaga and Elizalde-González 2003). For approximately 18 years, and according to the information shown in Table 16.2, several reports of the presence of POPs in agricultural and urban areas around Mexico have been published. Most of the studies have been carried out in soil and water bodies sediments near agricultural areas and urban zones. The presence of POPs evidences the negative impacts of human activities on the environment, especially those related to intensive agricultural and industrial activities.

Therefore, detecting and monitoring POPs studies are essential for establishing soil quality in urban and agricultural areas, highlighting the need for adequate management of these chemicals, and the urgency of developing feasible alternatives for the remediation of these polluted areas.

16.6 International and Mexican Regulation Related to POPs

At the international level different agreements have been signed related to chemical substances and hazardous waste, such as POPs. Among them is the Basel Convention, which covers hazardous waste and other wastes requiring special consideration, including medical waste, household waste, and electronic waste. Since January 1, 2021, it includes additional provisions for curbing the proliferation of plastic waste (BRS Conventions 2021). Furthermore, the Rotterdam Convention provides a structured information exchange procedure based on prior informed consent to international trade (the PIC Procedure), enabling parties to take informed decisions on future imports of hazardous pesticides and industrial chemicals, achieve good management, and lower the risk of harmful impacts on health and the environment. The Convention's implementation contributes to better production, a better environment, better nutrition, and a better life (BRS Conventions 2021).

In addition, the Stockholm Convention covering the elimination and reduction of POPs, such as PCBs and DDT, was adopted 20 years ago. The Convention was agreed in Stockholm, Sweden, in May 2001, and the date of entry into force was May 17, 2004, with 152 signatories (Rottem 2017; Stockholm Convention 2021). The objective of the Stockholm Convention is to protect the environment and human health from compounds recognized as POPs (Alshemmari 2021). The Convention is regulated by the United Nations Environment Program (UNEP) (Fiedler et al. 2019). This international Convention requires governments to follow up on the agreements established as well as the active participation of the organizations that are part of the International Network for the Elimination of POPs. Currently, 184 countries, including Mexico, have ratified the Convention (Sharkey et al. 2020).

The recently published third regional monitoring reports show that the concentrations of POPs in the environment and in human populations continue on a downward trend. The presence of POPs is ubiquitous but if measures are implemented to reduce or eliminate both intentional and unintentional releases, the concentrations measured in humans and in the environment will continue to decrease. The knowledge of the third regional monitoring reports also provides information on the monitoring of POPs and their relationship with changes in biodiversity and the climate change effects on the ecosystems function and structure (BRS Conventions 2021). Since 2005, Norway, Mexico, and the EU have assumed a leading role in nominating new substances for their inclusion in the Stockholm Convention (Rottem 2017). In 2005, five chemicals were proposed for their inclusion in the Convention, two by the EU, and three by Norway, Mexico, and Sweden, one by country. In 2006, five additional chemicals were proposed, three by the EU and two by Mexico. Finally, in 2009, at the fourth meeting of the Conference of the Parties were included nine of these ten nominated chemicals: (1) α-hexachlorocyclohexane, (2) β-hexachlorocyclohexane, (3) chlordecone, (4) hexabromobiphenyl, (5) hexabromodiphenyl ether and heptabromodiphenyl ether, (6) lindane, (7) pentachlorobenzene, (8) perfluorooctane sulfonate, and (9) tetrabromodiphenyl ether and pentabromodiphenyl ether (UNEP 2010a, 2010b; Selin 2010; Rottem 2017).

The three above-mentioned conventions constitute a coordinated life cycle approach to the environmentally good management of chemicals and waste across the world. The legally binding Basel, Rotterdam, and Stockholm (BRS) conventions share the common goal of protecting human health and the environment from the hazards of chemicals and waste, and have almost universal coverage with 188, 164, and 184 parties, respectively (BRS Conventions 2021). Mexico has made the decision to implement this international agreement through a National Implementation Plan (NIP), which was the product of a broad public consultation among authorities, industrial organizations, civil society organizations, and representatives of the private and academic sectors. In compliance with the commitments assumed by Mexico in the Stockholm Convention, the Mexican government has updated its NIP, and presented for registration with the Secretariat of the Convention in its 2016 version (INECC 2017; SEMARNAT 2017).

The legal framework for hazardous chemical substances and their waste provides many legal bases to regulate each step of their life cycle, from their manufacture or production to their final disposal as hazardous waste, which will greatly facilitate measuring the implementation of the Stockholm Convention. The Mexican Government has created numerous laws, regulations, and Official Mexican Standards (NOM) that together regulate every step of the life cycle of hazardous chemical substances and their waste, until their final disposal as hazardous waste (Romero et al. 2009). The instruments that make up the legal and institutional framework of Mexico related to POPs are made up of 17 national laws and 28 NOM, which fall under the responsibility of eight ministries of the 20 that make up the Federal Public Administration. However, the application of the legal provisions is complex due to the large number of legal systems that comprise it and the lack of coordination that has existed between the ministries for their creation, which has generated duplication of competences, regulatory gaps, and obsolescence of some of their instruments (Romero et al. 2009).

16.7 Management Alternatives of POPs in Mexico

In 2003, the General Law for the Prevention and Integral Waste Management (LGPGIR, acronym in Spanish) was issued as part of the Federal Constitution of Mexico to promote sustainable development, by preventing the generation, and promoting the recovery and integral management of waste, as well as preventing soil contamination (DOF 2003; Hernández-Padilla and Angles 2021).

This Law classifies waste as follows (DOF 2003):

(a) **Solid urban waste**. Those generated in homes, which result from the elimination of the materials used in domestic activities; the waste that comes from any other activity within establishments or on public roads that generates waste with domiciliary characteristics, and those resulting from the cleaning of public roads and places.
(b) **Special handling of waste:** These are generated during production processes, with characteristics not considered hazardous or solid urban waste. In addition, those are produced by large urban solid waste generators.
(c) **Hazardous waste:** Those that have any of the characteristics of corrosivity, reactivity, explosivity, toxicity, flammability, or that contain infectious agents, as well as containers, packaging and soils that have been contaminated when transferred to another site.

The LGPGIR established the obligation to formulate and implement management plans for hazardous waste, as well as, used, expired, withdrawn from trade or discarded products. Among them are persistent organic compounds such as PCBs, pesticides, and containers that still contain remnants thereof, which include those subjects to the Stockholm Convention. This law also establishes that hazardous waste generators must present Management Plans every year, which are environmental policy instruments that contribute to the improvement of waste management in Mexico. POPs are considered hazardous waste, so their management is established in the above-mentioned law. In Mexico, most of the products with POPs have been banned since 1994, especially pesticides. For this reason, to comply with the Stockholm Convention, attention is mainly focused on the substitution and elimination of the PCBs contained in electrical transformers and capacitors, as well as on the reduction or elimination of the release of dioxins, furans, and hexachlorobenzene in fixed and diffuse sources. Mexico, with the support of the North American Commission for Environmental Cooperation, and within the framework of the formulation of the National Action Plan, prepared a preliminary diagnosis of POPs. This diagnosis was made to establish the action plan for three groups of POPs: pesticides, industrial POPs, and unintentional POPs.

In the case of PCBs, it is estimated that Mexico imported between 6000 and 20,000 tons in total, which were mainly used in the electrical equipment of parastatal companies (such as the Federal Electricity Commission). For this, the Official Mexican Standard (NOM-133-SEMARNAT-2015, Environmental Protection-Polychlorinated Biphenyls (PCBs) -Management Specifications), was created. "*This Official Mexican Standard establishes the specifications for the environmentally adequate handling and disposal of hazardous waste that contains or is contaminated with PCBs when they are discharged, as well as for the handling and treatment of PCBs equipment*." This Official Mexican Standard, it is established that the handling of PCBs equipment, PCBs hazardous waste and PCBs liquid derived from maintenance activities, or due to removal of the equipment, must be managed through the following stages:

Table 16.4 POPs bioremediation studies in Mexico

POP	Microorganism	Concentration (mg/L)	Result in percentage	Reference
α-Endosulfan	*Bacillus subtilis*	14	76	Casanova et al. (2021)
	Bacillus pseudomycoides		95	
	Peribacillus simplex		95	
	Enterobacter cloacae		95	
	Achromobacter spanius		95	
	Pseudomonas putida		95	
β-Endosulfan	*Bacillus subtilis*	6	86	
	Bacillus pseudomycoides		86	
	Peribacillus simplex		86	
	Enterobacter cloacae		95	
	Achromobacter spanius		95	
	Pseudomonas putida		95	
Endosulfan lactone	*Soil microorganisms and Eisenia fetida*	0.001–0.009	90.1	Vázquez-Villegas et al. (2021)
DDT	*Lysinibacillus fusiformis*	50	41–48	García-de la Parra et al. (2012), Garcia et al. (2021)
	Bacillus mycoides			
	Bacillus pumilus			
	Bacillus cereus			
	Lysinibacillus fusiformis	200	26–31	
	Bacillus mycoides			
	Bacillus pumilus			
	Bacillus cereus			
α-Endosulfan	*Paecilomyces variotii*	17.5	26.4	Hernández-Ramos et al. (2019)
	Paecilomyces lilacinus		10.9	
	Sphingobacterium sp.		14.3	
β-Endosulfan	*Paecilomyces variotii*	7.5	31.4	
	Paecilomyces lilacinus		9.0	
	Sphingobacterium sp.		21.1	
α-Endosulfan	*Enterobacter cloacae* PMM16	1.7	71.3	Jimenez-Torres et al. (2016)
β-Endosulfan			100	
Pentachlorophenol	*Rhizopus oryzae* CDBB-H-1877	0.5	78.6	León-Santiesteban et al. (2016)
		2	90.8	

(continued)

Table 16.4 (continued)

POP	Microorganism	Concentration (mg/L)	Result in percentage	Reference
Lindane	*Streptomyces* sp. A5-M7	1.7	32.6	Fuentes et al. (2011)
	Streptomyces sp. A2-A5-M7-A11		33.1	
	Streptomyces sp. A2-A5-A8		31.4	
Pentachlorophenol	*Pseudomonas fluorescens*	200	77.6	Torres et al. (2010)
		400	94.5	
		600	94.1	
Aldrin	*Pseudomonas fluorescens*	10	94.8	Bandala et al. (2006)
Dieldrin			77.3	
Heptachlor			96.9	
DDT	*Pseudomonas fluorescens*	50	96.8	Santacruz et al. (2005)
		100	87.9	
		150	99.9	
Polychlorinated biphenyls (PCBs)	*Trametes versicolor*	600–3000	29–70	Ruiz-Aguilar et al. (2002)
	Phanerochaete chrysosporium		34–73	
	Lentinus edodes		0–33	
Pentachlorophenol	*Rhizopus nigricans*	12.5	100	Tomasini et al. (2001)
Pentachlorophenol	*Phanerochaete chrysosporium*	100	86	Mendoza-Cantú et al. (2000)

Storage. Hazardous waste of PCBs must be conditioned before being sent to the temporary storage of hazardous waste, considering the prevention of leachate generation and its infiltration into the soils; the dragging by rainwater or by the wind; fires, explosions, and accumulation of toxic vapors, leaks, or spills.

Transport. The transport of PCBs waste can only be carried out by land or sea. The carrier must be trained and have the necessary equipment and materials to contain spills that may occur during the transport of equipment and waste. Transport units that become contaminated by direct contact with PCBs liquids or PCBs hazardous waste must be subjected to cleaning activities, and the generated liquids and solids must be managed as hazardous waste.

Treatment and disposal. This must be carried out, in accordance with the following.

1. Washing of equipment with PCBs, and liquid–liquid extraction.
2. The liquid PCBs that are extracted from the equipment will have to undergo a process of elimination, through incineration, gasification, plasma, pyrolysis, and catalytic chemical.

3. In the case of spills to the soils with liquids containing PCBs, it is necessary to carry out a remediation process, considering the maximum permissible limits of contamination after the remediation. These limits range from 0.5 to 25 mg/kg, considering a subsequent agricultural, residential, and industrial land use, respectively. According to the soil characteristics and the conditions of contamination with PCBs, the biological, physical, or chemical treatments, or a combination of them, can be applied in this remediation process.

Also authorized is the installation of companies that provide transport, repackaging, shipping abroad for treatment (mainly by incineration), equipment decontamination, and chemical dechlorination of liquid waste. About the possibility of existence of generating sources of dioxins, furans, and hexachlorobenzene in Mexico, a diagnosis of the generation was carried out (2012). As a result, the total emission of dioxins and furans from the top ten sources were 9722 g TEQ/year, which include agricultural waste burning, cement kilns, forest fires, industrial waste incineration, medical/hospital waste incineration, metallurgical production, open dump fires, pulp, and paper mills, uncontrolled domestic waste burning, among others (SEMARNAT 2017). For the estimation of dioxin and furan emissions in Mexico, the emission factors provided by the Standard Instrument for the Identification and Quantification of Dioxin and Furan Releases (2005), for waste incineration equipment (hazardous, medical, municipal, etc.), were used (Costner 2005; UNEP 2005).

16.8 Bioremediation Alternatives of POPs

Bioremediation is a process that lets the biological degradation of dangerous pollutants to less toxic or nontoxic moieties, reducing their concentrations to undetectable levels, or eliminating organic pollutants using the physiological capabilities of living organisms (Ramírez-García et al. 2019; Vishwakarma et al. 2020). These organisms include bacteria, fungi, and plants, these the most reported microorganisms, both endogenous of the polluted sites to bioremediate or isolated from different environments and added to the site for the pollution treatment (Zouboulis et al. 2019). In addition, bioremediation has been proposed for the treatment of contamination derived from the presence of different pollutants in water and soil (Bharagava et al. 2020; Singh et al. 2020), including hydrocarbons (Xu et al. 2018; Ławniczak et al. 2020), pesticides (Giri et al. 2021; Sarker et al. 2021), and different persistent organic pollutants (Boudh et al. 2019; Devi 2020; Akhtar et al. 2021). In bioremediation, living organisms are the key factor involved in the biodegradation and elimination of pollutants. Due to this, adequate conditions for their development at the polluted sites are required for successful bioremediation, including adequate moisture, pH, temperature, oxygen, and the availability of nutrients. However, the presence of high-level salinity, metallic ions, and other toxic chemical compounds can reduce the effectiveness of the biological treatments (Khudhaier et al. 2020). These parameters can be controlled through the application of an adequate bioremediation strategy.

The bioremediation strategies are divided into two categories, in situ and ex situ technologies. In the in situ technologies, the polluted material bioremediation process is carried out at the contaminated site, while in the ex situ technologies, the biological treatment of the contaminated material is carried out in specific bioremediation installations (Das and Dash 2014; Azubuike et al. 2016; Sharma 2020; Raffa and Chiampo 2021). Examples of different bioremediation strategies are shown in Table 16.3. Several of these bioremediation strategies have been proposed as effective treatments for soil contamination caused by POPs, in different scientific studies which have been highlighted the potential of plants for POPs phytoremediation (Liu et al. 2018; Misra and Misra 2019; Futughe et al. 2020; Tripathi et al. 2020), as well as different microorganisms (bacteria, fungi, algae), exogenous or isolated from diverse polluted environments, capable of biodegrading POPs (Gaur et al. 2018; Boudh et al. 2019; Zacharia 2019; Mbachu et al. 2020; Sonune 2021).

In Mexico, different studies on POPs bioremediation have been reported in the last 20 years. In these studies, the potential of several microorganisms for application biodegradation and removal of different POPs have been highlighted. Table 16.4 shows 13 studies carried out in Mexico (2000–2021). These reports aimed to evaluate the biodegradation and removal of different POPs employing mainly bacterial and fungi strains. The research in the field of POPs bioremediation in Mexico has focused on the biodegradation of OCPs such as aldrin, DDT, dieldrin, endosulfan, heptachlor, lindane, and pentachlorophenol, with endosulfan being the most evaluated POP. In Table 16.4, just one study evaluates the fungal biodegradation of PCBs. All studies showed in Table 16.4 were carried out at laboratory scale, employing different in vitro approaches. Due to this it is important to evaluate these microorganisms in field studies on sites polluted by POPs. The main bacterial genus reported in the studies were *Bacillus*, *Pseudomonas,* and *Streptomyces*. With respect to the studies employing fungal strains the genus reported include *Lentinus*, *Phanerochaete*, *Trametes*, and *Rhizopus*. In Mexico, significant research efforts have been made to identify microorganisms, fungi, and bacteria, with great potential for applications in bioremediation strategies to eliminate POPs from contaminated sites. However, it is essential to carry out studies that include the evaluation of the biodegradation of other types of POPs, other than OCPs.

16.9 Conclusions and Future Perspectives

The semi-volatile, lipophilic, and high persistence characteristics of POPs were highlighted. These compounds have been detected in different world regions, even in places where they have never been used. Their impacts on the environment and health, on individuals, populations, and communities, have also been discussed, highlighting their toxicity and dangerousness when remaining in the environment. POPs waste can reach the soil, water, and air and remain for long periods. Studies to detect the presence of POPs have been carried out in soils from different regions of Mexico. Knowledge of polluted soils can help plan the restoration of these soils, make clear the need for adequate management, and the urgency of developing feasible alternatives for the remediation of these polluted areas. It has also been stated that Mexico has signed the Stockholm Convention, and to comply with that commitment it has developed internal legislation such as the LGPGIR (DOF 2003), NOM-133-SEMARNAT-2015 (DOF 2016), as well as the development of other instruments such as the Stockholm Convention Implementation, among others. In the LGPGIR, POPs waste is classified as hazardous, so there are standards that must be applied to POPs. For example, domestic legislation establishes how PCBs should be handled, which is why it is an activity monitored by the federal government.

In addition, bioremediation is an environmental-friendly and feasible method for eliminating and detoxifying pollutants, included POPs. Through bioremediation techniques such as phytoremediation and microbial-mediated pollutant degradation, the levels of POPs caused contamination can be reduced. Therefore, these bioremediation processes must be improved to offer a viable alternative for the degradation of POPs or the remediation of soils contaminated with the same compounds. It should be noted that Mexico is a country that has assumed the commitment to address the problem related to POPs, since it has established normative instruments for their management and treatment. In addition, economic resources have been allocated for the diagnosis of POPs in Mexico, for the analysis of soils, water, and air contaminated with POPs, as well as for the remediation of contaminated sites. However, much remains to be done. Greater investment is necessary for the development of technologies for its effective treatment, and for remediating sites contaminated with POPs. In this way, Mexico could have the necessary capacity to positively impact on the elimination of POPs.

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Chapter 17
Integrated Application of Green Nanotechnology, Bioremediation, and Solubility Enhancing Chemicals for Improving Phytoremediation Efficiency: A Case Study in Egypt

Ahmed Ali Ali Romeh

Abstract Soil is the essential region for accumulating heavy metals and persistent organic pollutants, on this way, the cleanup of soil is largely significant. In addition, with the fast growth in industrialization, business liquid waste poses threats to the environment and human health, so it has become a major concern to clean up the environment from these unsafe wastes for the sustainable improvement of human society. In soils polluted with highly hydrophobic pollutants with the logarithm of the octanol–water partitioning coefficients (log K_{ow}) higher than three, those compounds are highly adsorbent in the soil and their degradation is slow. Phytoremediation of these compounds is not an appropriate solution, because of the fact plants are not able to degrade those organic pollutants in rhizosphere area or uptake in the upper tissues. Phytoremediation with different technology can already provide a sustainable and less expensive alternative to soils and sites moderately contaminated over large surfaces. Plants and different technology which include biosurfactants excreted through microorganisms or plants, nanomaterials which include green-nZVI technology and chemicals which enhancing bioavailability in the soil are combined in phytoremediation, may also enhance the desorption of such persist organic pollutants in soils through enhancing their bioavailability, accumulate and translocate through plants, or microbial degradation leading to improving the capability of phytoremediation. A combination of green nanotechnology, adsorption, advanced oxidation process, and phytoremediation process can reduce the drawbacks of individual process. The complement of a strong oxidant, which include H_2O_2 to NZVI, results in the formation of ·OH radicals that can efficaciously oxidize most of the organic matter to CO_2, H_2O, and salts. Joint action between plant-associated microorganisms, especially the rhizosphere zone, which stimulate plant growth or

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biosurfactants proved to increase plant growth biomass production and improve the phytoremediation process through effect on the availability, accumulation, degradation of xenobiotics in soil and plants. Genetic engineering has additionally contributed to the improvement of genetically modified plants and their related bacteria to enhance the remediation performance through plants for pollutants. Also, integration among strategies, which include chemical improving agents (ethanol, SiO_2, hydroxypropyl-ß-cyclodextrin (HPßCD), natural humic acid) and surfactants such as Tween 80 with phytoremediation capability, mainly, in the existence of green nanoparticles. The research performed in Egypt on phytoremediation of xenobiotics is constrained, and maximum research focused on remediation of heavy metals by plants. Research in the field of eliminating pollutants and the use of the contemporary technology in environmental remediation in Egypt still requires government support and cooperation for a clean environment free of pollutants.

Keywords Soil · Water · Phytoremediation · Green nanotechnology · Plant-associated microorganisms · Chemical enhancing agents

17.1 Introduction

Soil is the important region to accumulate metals and persist organic pollutants, so soil management and remediation are essential. Pesticides are commonly utilized worldwide; this widespread prevalence is the cause of major problems in sustainable agriculture in addition to soil and water pollution because of its persistence in soil or leaching to groundwater causing serious risks to ecosystem, mainly community health and environment. Furthermore, with the huge of industrialization, disposal of industrial liquid wastes is necessary because it reasons a threat to the environment and will become the most important situation for reaching sustainable improvement of human society. In addition, compounds of organic origin causing pollution which include trichloroethylene, explosives, hydrocarbons, and fossil fuels are the leading polluting agents (Hakeem et al. 2014; Ali et al. 2019; Varma et al. 2020; Pecina et al. 2021; Kumar et al. 2021). Wastewater reclamation and recycling are essential priorities for protecting the worldwide and enhancing environmental sustainability (Rasalingam et al. 2014). New cost-effective and safe remediation strategies are urgently needed for the alleviation or detoxing of organic pollutants in soils and water. Scientists and engineers in the field of remediation need successful treatment methods for soil and groundwater polluted with toxic organic compounds. Therefore, over the decades soil remediation approaches consist of physical, chemical, and biological, along with soil excavation, incineration or thermal degradation (thermal desorption), extraction of soil through vapor, soil washing/flushing, photocatalytic strategies using TiO_2, soil washing, metal-catalyzed reactions, electroremediation, bioremediation, and phytoremediation (Hakeem et al. 2014; El-Temsah et al. 2016; Wu et al. 2017; Jiang et al. 2018; Romeh 2021; Zakria et al. 2021). Moreover, many approaches have been used to remove the pollutants from contaminated water sources, along with progressed oxidation techniques (Wet chemical oxidation, biochemical oxidation, ozone oxidation, Fenton process), membrane techniques and adsorption a number of the presently to be had strategies for eliminating the pesticides from wastewater. However, these strategies are not preferred as there are some disadvantages such as high cost, long response time, and low degradation performance, and are at risk of relatively costly, time consuming, and secondary emissions (Rasalingam et al. 2014; Bao et al. 2019). Therefore, in current decades, new technology for the elimination of contaminants has been built to lessen costs. More recently, to enhance the elimination of xenobiotics in soil and water, scientists have attempted to search for numerous strategies and consistency among them. Of those attempts, researchers used phytoremediation incorporation with green nanotechnology, green nanotechnology assisted through adsorbent materials (which include raw clay minerals to enhance adsorption and reduction process), oxidation process (strong oxidant which include H_2O_2, persulfate, and permanganate) plus nano zerovalent iron (nZVI), microbial activity, surfactants and improved agents result in enhancing solubility and desorption of pollutants from soil and uptakes through plants to increase the performance of phytoremediation.

17.2 Enhancing Phytoremediation Technology

Phytoremediation is a process utilized by plants capable of storing heavy metals or degrading or eliminating persistent organic contaminants, for example, polyaromatic hydrocarbons (PAHs), explosives, pesticides, petroleum hydrocarbons, chlorinated solvents, radionucleosides, and surfactants to mitigate pollutant concentrations in polluted soils, water, or air (Chatterjee et al. 2013; Ali et al. 2012; Newete et al. 2016; Ali et al. 2020), in association with the indigenous soil microorganisms. In assessment to traditional physicochemical strategies, phytoremediation may also now offer a safe and less costly alternative to soils and sites reasonably contaminated on large surfaces (Schwitzguébel 2017). The process consists of the accumulation of contaminants through roots, and body tissues, decomposition, and transformation into much less dangerous kinds of pollution. Phytoremediation technology is an evolving technology that is rapidly gaining popularity and promises effective, quick, powerful, compatible, environmentally friendly, low-cost cleaning of polluted hazardous waste sites and is one of the key components of green technology (Xia et al. 2003; Xia and Ma 2006; Ansari et al. 2020). Many common grasses in addition to maize, wheat, soybean, peas, beans, and numerous tree species (extensive and fibrous roots) can stimulate the degradation of organic molecules in the rhizosphere (Glick 2003; Yan et al. 2020; Antoniadis et al. 2021). Phytoremediation, however, gives best a partial method to remediate soil contaminated with organic contaminants, mainly highly persistent organic pollutants with a high distribution coefficient ($\log K_{ow} > 3.0$) or hydrophobic properties. Phytoremediation of certain long-lasting pollutants which include PAHs, which might be poorly bioavailable (9–24%) in the soil, will also be ineffective (Parrish et al. 2004). Organic compounds regulated by the hydrophobicity of those organic pollutants are taken up through plants. Organic pollutants which have a log K_{ow} between 0.5 and 3.0 easily have a tendency to be accumulated through plant roots. Adequately lipophilic organic pollutants with a log K_{ow} range between 0.5 and- 3.0 can accumulate or degrade by roots of plant and enter the stream of xylem for translocation by plant shoots (Chakraborty and Das 2016). In soils polluted with highly hydrophobic pollutants (poor water solubility) with a log K_{ow} higher than 3.0, these compounds are highly adsorbent in the soil and their degradation is slow. In this case, phytoremediation is not considered a suitable solution for these persistent organic compounds, this is often due to the plant's inability to degrade these persistent organic substances in the rhizosphere or translocate them into the shoot tissues (Arslan et al. 2017; Shekhar et al. 2015). Furthermore, the remediation process by plants is also a long process, and the site may not be completely remediated, and the consumption of contaminated plants through wildlife is also a remarkable concern (Sophia and Kodialbail 2020). Many technologies such as the presence of biosurfactants released by micro-organisms or plants, nanomaterials, bio-nZVI technology, and chemicals that enhance soil bioavailability are being combined in the process of phytoremediation to address these problems can encourage the removal of persist organic pollutants in soils through enhancing their bioavailability, accumulation and translocation by plant or degradation process by microbial organisms, and as a result improve the capacity of phytoremediation in situ (Shekhar et al. 2015; Kong and Glick 2017; Feng et al. 2017; Romeh 2021) as shown in (Fig. 17.1).

17.2.1 Green Nanotechnology for Enhancing Phytoremediation

Technology of nano has spread through all science and innovation fields in current years, along with engineering, medicine, pharmaceuticals, agriculture, the environment, and many more. In the environmental field (environmental nanotechnology), using nanomaterials (NMs) is one of the many general applications of nanotechnology which leads to accelerate in the overall effectiveness of remediation methods (Cao et al. 2005; Ghasemzadeh et al. 2014; Patil et al. 2016). Recently, the trend has increased to clean the environment with a new and powerful method via nano-treatment, which has performed an important role in pollution alleviation or decontamination (Rajan 2011; Zakria et al. 2021). Due to the large surface area and small particle size, using Zero Valent Iron (Fe^0) nanoparticles suggests excessive elimination performance of maximum contaminants and reactivity (Bao et al. 2019; Romeh and Saber 2020). NZVI can only remove/degrade those pollutants through the adsorption and dissipation process. However, for multiple non-degradable pollutants, this method by myself can't be efficiently applied and need to be efficiently tackled. These remediation techniques are often costly, and their products may also

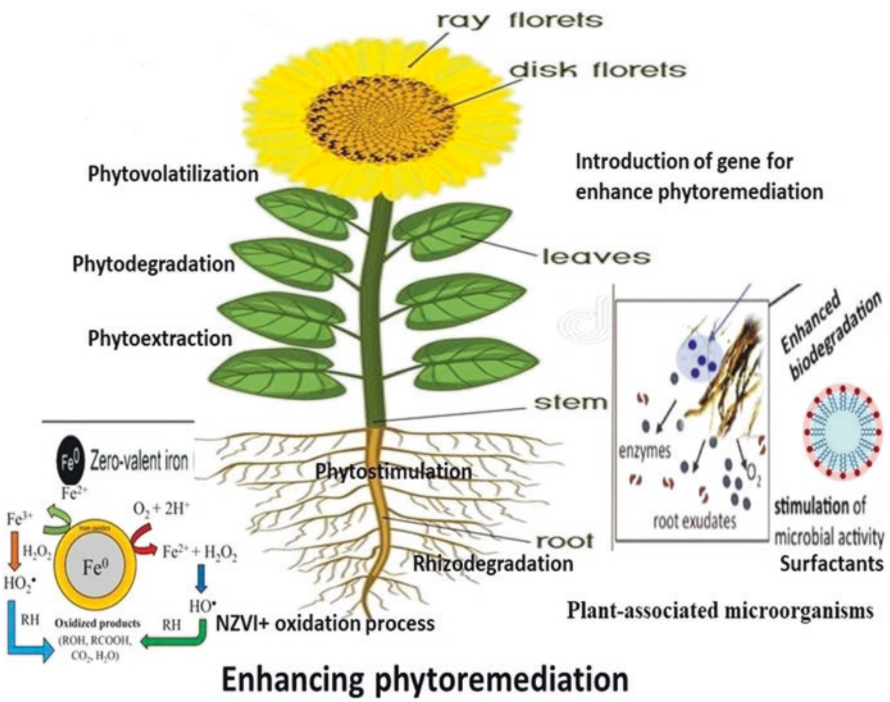

Fig. 17.1 Cleared different methods which enhanced phytoremediation

pose an environmental danger (He and Zhao 2005). Physical and chemical techniques, for instance, are commonly used for the processing of nanoparticles of metal and metal oxides. These strategies, however, are commonly costly and require unique equipment, excessive energy and consist of poisonous, corrosive, and flammable chemical substances which include sodium borohydride and hydrazine hydrate or organic solvents as reducing agents that cause unnecessary adverse environmental impacts. In addition, if not properly coated, nanoparticles appear to aggregate leading to reduction of the reactivity and decreeing stability of these nanoparticles (Shahwan et al. 2011; Bardos et al. 2011; O'Carroll et al. 2013). Researchers are continuing to work on developing simple, efficient, and reliable green chemistry processes to develop nanomaterials to solve this problem. To produce low-cost, safe, eco-friendly, energy-efficient, and non-poisonous environmentally friendly metal nanoparticles, biological tools such as algae, microorganism, fungi, actinomycetes, and plants had been applied (Mandal et al. 2006; Jebali et al. 2011; Machado et al. 2013; Romeh and Saber 2020). Many researchers have stated that different plant extracts (leaf, stem, seed, and root) which are containing a higher content of polyphenol directly related to a higher content of antioxidant can utilize in synthesis of safety nanoparticles (Phumying et al. 2013; Mystrioti 2014; Romeh and Saber 2020). The antioxidant polyphenol from plant extract which include green tea, black tea, bran, grape, coffee, lemon, balm plays a main role in the transformation of the ferrous or ferric to Fe^0 in green nanoparticles through acting as reducing and capping agents (Huo et al. 2017; Tyagi et al. 2021; Balciunaitiene et al. 2021). To date green synthesized nZVI has proven its success in removing organic pollutants, especially polychlorinated biphenyl, trichloroethene, pesticide, and nitrate by the reductive process (Smuleac et al. 2011; Olson et al. 2014; Abdel-Aziz et al. 2019) or oxidation of cationic and anionic pollutants as a fenton catalyst (Shahwan et al. 2011). This approach is one of the technologies that has received great interest as it is a simple, cost-effective, and reproducible trend without any environmental pollution, non-toxic nature. It is one of the easy-to-produce, environmentally friendly alternative methods for synthesizing nanoparticles, and improving remediation efficiency. Therefore, green nZVI is a remediation strategy suitable with clean and green highly sustainable technologies for remediating the contaminated soil (Shahwan et al. 2011; Kumar et al. 2013; Xu et al. 2012; Wang et al. 2014; Huo et al. 2017; Romeh and Saber 2020). Little research focuses on water and soil remediation technologies through the combined application of green nanotechnology and phytoremediation. It is worth noting that the combination between nanotechnology and phytoremediation (nano-phytoremediation) is a promising cleaning technology of contaminated environments, with different pollutants (Gong et al. 2017; Jiang et al. 2018; Song et al. 2019). In addition, plants exposed to nZVI have various effects, such as which include seed germination stimulation and development, biomass and chlorophyll increases (Xie et al. 2016; Libralato et al. 2016).

A combination of green nanotechnology, adsorption, advanced oxidation process and phytoremediation process can reduce the drawbacks of individual process, and is environmentally, economically, and significantly technical for cleaning water polluted with organics (Romeh 2018a, b; Anjum et al. 2019; Romeh and Saber 2020). Some examples of nanomaterial-assisted phytoremediation have shown that nano-phytoremediation has proven to be more efficacious as a technique of degrading and removing TNT-contaminated soils (Jiamjitrpanich et al. 2012). Phytoremediation of the soil contaminated with endosulfan through Fe^0 combined with *Alpinia calcarata, Ocimum sanctum, and Cymbopogon citratus* plants increased from 81.2 to 100%, from 20.76 to 76.28%, and from 65.08% to 86.16%, respectively. Owing to the reduction of endosulfan dichlorination, small quantities of endosulfan have accumulated in the plants (Pillai and Kottekottil 2016). Silver nano-catalysts (Ag^0) synthesized by green nanotechnology using *Mussaenda erythrophylla* leaves extract (as reducing and catalytic agents) have been used for the dissipation of the azo dye and methyl orange (Varadavenkatesan et al. 2016). The combined use among Ag^0 and *Plantago major* effectively led to remediation of fipronil-contaminated water and flooded soil through the accumulation of large amounts of the polar metabolite, fipronil amide as a phytoremediation (Romeh 2018a, b). The use of green nanotechnology which includes iron nanoparticles from ficus plant (F-Fe^0), silver nanoparticles from ipomoea (Ip-Ag^0), and silver nanoparticles from brassica (Br-Ag^0) and phytoremediation such as *P. major* has played a principal role in the cleanup of soil and water polluted with chlorfenapyr (Romeh and Saber 2020). The green nano synthesis showed different shapes, in the case of F-Fe^0, the circular shape appeared with sizes ranging from 2.46–11.49 nm, while in the case of Ip-Ag^0 and Br-Ag^0, the circular, cubical, hexagonal, triangular, and rod-like in shape appeared with sizes ranging from (6.27–21.23 nm) and (6.05–15.02 nm), respectively. Additionally, Mohammadi et al. (2020) display that Fe^0 nanoparticles can increase the efficiency of sunflower plants leading to alleviating the Cr toxicity and increasing detoxification enzyme activity (SOD, CAT, POX, and APX) in cells. Furthermore, Fe^0 nanoparticles can improve phytoremediation efficiency at lower doses, at the same time beneficial rhizosphere microorganisms can reduce nZVI stress in plants make them less prone to stress even under high dose conditions (Mokarram-Kashtiban et al. 2019). The positive impact of a low nZVI dose can be because of the entry into the soil of iron, which is a significant nutrient in stimulating the growth of plant and for microorganisms in the soil (Souza et al. 2015). Important beneficial effect on plant photosynthesis has been observed by the combined use of nZVI and PGPR. Co-utility of nZVI and PGPR could minimize the amount of nZVI required for effective phytoremediation of contaminated metalloid soils (Zand et al. 2020). The combined action of nanotechnology and species of plants, which include *Alpinia calcarata*, *Ocimum sanctum*, and *Cymbopogon citratus* confirmed excessive performance in eliminating endosulfan and different contaminants under natural environmental conditions (Jesitha and Harikumar 2018). By straightforwardly acting on the contaminants and plants, nanomaterials can enhance phytoremediation. It can also play a role in the interactions among contaminants and plants, indirectly influencing the final efficiency of the remediation (Zand et al. 2020). Researchers confirmed that NZVI supported on clay minerals, e.g., palygorskite, kaolinite, zeolite, bentonite, and diatomite, activated charcoal, pillared clay, rectorite, clinoptilolite, and organo-bentonite enhanced the adsorption and dissipation of contaminants in the wastewater (Shahwan et al. 2011; Zhang et al. 2011; Li et al. 2013; Qu et al. 2013; Lin et al. 2014; Nairat et al. 2015; Sun et al. 2016; Yuan et al. 2016; Altuntas et al. 2017; Bao et al. 2019; Romeh and Saber 2020). Ficus-Fe^0-supported on wheat bran (WB) and *P. major* caused complete dissipation of chlorpyrifos from the water with a huge decrease in the metabolite TCP (Romeh 2021). Also, *P. major* plus Marjoram-prepared Fe^0 (Mar- F-Fe^0) and Moringa-prepared F-Fe^0 (Mor- F-Fe^0) supported on activated charcoal (Ach), bentonite (Bent) plays a high role in the decontamination of flonicamid-contaminated water (Rady et al. 2019). For nZVI-reduced graphene oxide (rGO), the removal rate and adsorption capability had been discovered to be the most, which makes this adsorbent a possible futuristic adsorbent for explosive removal (Khurana et al. 2018).

17.2.2 Enhance the Performance of nZVI Strategy

Physical, chemical, and biological methods had been utilized by researchers to enhance the activity of the nZVI approach (Sun et al. 2007; Lemaire et al. 2013; Gomes et al. 2014; Stefaniuk et al. 2016; Danish et al. 2016; Jiang et al. 2018; Romeh and Saber 2020; Romeh 2021). NZVI has the maximum potential for the treatment of waste water by combining its reduction property with the advanced oxidation process (AOP). The addition of effective oxidant to NZVI, which include H_2O_2, contributes to the formation of radicals of ·OH. The generation of Fe^{2+} ions from NZVI interacts with H_2O_2 to generate Fe^{3+} and ·OH radicals that could efficiently oxidize most organic matter to CO_2, H_2O, and salts (Xi et al. 2014; Pullin et al. 2017; Clarizia et al. 2017; Liu et al. 2018; Zhang et al. 2020; Bao et al. 2019). With the addition of 0.01 g/L nZVI, recalcitrant PAHs which include anthracene and benzoapyrene had been as much as 90%, in comparison to 10.7% with un-activated persulfate (Pardo et al. 2016; Lv et al. 2016), since $S_2O_8^{-2}$ is catalyzed through the Fe^{2+} source to SO_4·—via the direct transfer of electrons from nZVI to $S_2O_8^{-2}$ (Pardo et al. 2016). Moreover, surfactants can increase the solubility of organic pollutants in soils (Gharibzadeh et al. 2016), and the supplement of surfactant (1%) to the commercial suspension of F^0, leading to removing 83% of PCBs (Gomes et al. 2015). In addition, PAHs improved dissipation through the addition of sodium dodecyl sulfate (SDS), because of the oxidation process (Peluffo et al. 2016). Additionally, research has proven that Tween- 80 also leading to increasing the bioavailability of pollutants (Binh et al. 2016). The integration of nZVI nanoparticles and the phytoremediation indicated in the bio-nZVI technology gives great attention to cleaning the soils contaminated with organic and inorganic compounds. Combination of *Helianthus annuus* and *Panicum maximum* plants with nZVI caused successful remediation of TNT polluted soil (Jiamjitrpanich et al. 2012).

17.2.3 Plant-Associated Microorganisms for Enhancing Phytoremediation Efficiency

Phytoremediation is a cost-effective, safe, and promising process, using plants and their related microorganisms to dispose of soil pollutants (Arslan et al. 2017; Sharma 2021; Han et al. 2021; Supreeth 2021). Based on the joint action between plant-associated microorganisms, studies have proven that phytoremediation processes are less expensive and more environmentally friendly methods of soil pollutant remediation than traditional soil phytoremediation (Zhang et al. 2010; San Miguel et al. 2013; Arslan et al. 2017; Gupta et al. 2019; Yang et al. 2020). By various detoxification and bio-transformation techniques, along with sorption in plant parts, bacteria specializing in breakdown can be utilized enzymatically to transform and dissipate organic pollutants into other degradation products less toxic by a greater variety of organisms (Glick 2010; Tahir and Chen 2016). In addition, using endophytic and rhizospheric bacteria, which stimulate plant growth has been shown to increase plant growth biomass production and increase plant phytoremediation capability through affecting the availability, accumulation, pollutant degradation in soil and plants, and reduced metal stress in plants (Afzal et al. 2014; Ali et al. 2020; Romeh 2020). Rhizospheric and endophytic bacteria caused rhizoremediation of PAHs using *Populus sp.* in soil (Bisht et al. 2014, 2015; Ruley et al. 2020). Phytoremediation with endophytic plants played a significant role in soil decontamination (Afzal et al. 2014). PGPR has been proven to improve phytoremediation of petroleum and different contaminants, primarily species of *Bacillus* and *Pseudomonas* (Almaghrabi et al. 2013; Dong et al. 2014; Gkorezis et al. 2016; Fatima et al. 2017; Yu et al. 2020). *Azospirillum lipoferum* (Beijerinck) supported on peat moss and inoculated to the soil samples leading to chlorpyrifos and cyanophos degradation more than different treatments (Romeh and Hendawi 2014). In addition, mycorrhizal fungi associated with plant roots have played a useful role in phytoremediation through excretion of organic acid, followed by the reduction of soil pH, siderophore improvement, amino acids, phytochelatins, and 1-Aminocyclopropane-1-carboxylate (ACC) deaminase improvement (Bisht et al. 2015; Coninx et al. 2017; Jambon et al. 2018). Both of *Glycine max* plant inoculated with *Pseudomonas fluorescens* become more effective than *G. Max* alone or *G. max* inoculated with *Serratia marcescens* in dissipating fenamiphos to the metabolites fenamiphos sulfoxide, sulfone, and phenol, which accumulated in the roots and the leaves (Romeh and Hendawi 2017). Studied by Romeh (2020) confirmed that cultivation of *Plantago major* beside tomato crops after inoculating them with EM-1 leading to eliminating imidacloprid from the soil with the most successful approach. Studies demonstrated that the combination of both plants and microorganisms using *Saccharibacteria* and *Alcanivorax* increased significantly in the low and medium contamination of crude oil with *Suaeda salsa* (L.), at the same time as *Saccharibacteria* and *Desulfuromonas* were predominant in the high contamination of crude oil (Yu et al. 2020). Additionally, the interactions through bacterial-fungal or yeast-bacteria can increase phytoremediation process for organic pollutants through the interaction of degrading microorganisms with pollutants. Bacteria, yeast, and fungi can supplement each other in the dissipation pathway of pollutants, leading to complete pollutant degradation via co-metabolic degradation of organic pollutants (Furuno et al. 2010; Ma et al. 2012, 2015). Chen et al. (2015) studied the ability of bacteria and yeast to participate in cleaning up polychlorinated biphenyl (PCB) polluted environments. Enhance the efficiency of the phytoremediation by introducing main biodegradation genes into bacteria that are natural plant symbionts were studied. Important studies by Eapen et al. (2007) show that genes involved in xenobiotic pollutant degradation can be separated from bacteria/fungi/animals/plants and inserted into selected plants using gene transfer methods mediated through agrobacterium or direct DNA. Transgenic plants (tobacco, rockcress, mustard, poplar, rice, and potato) had been confirmed so that you can enhance phytoremediation (phytoextraction, phytovolatilization, and phytodegradation) for organic contaminants which include polychlorinated biphenyls, explosives, PAHs, chlorinated solvents, various herbicides, and atrazine (Eapen et al. 2007; Rylott and Bruce 2009; Panz and Miksch 2012; Truu et al. 2015). Genetically engineered plants and related microorganism had been evolved to enhance phytoremediation performances of every class of organic pollutants (Van Aken et al. 2009; Van Aken 2011). With genetically modified rice and rice plants expressing human cytochrome P-450 2E1 (CYP2E1), scientists had been capable of inducing a metabolism of TCE and chlorinated herbicides, along with atrazine and chlorotoluene, more rapidly through the oxidative processes of wild plants (Zhang et al. 2011; French et al. 1999;

Kawahigashi 2009). A promising advance in transgenic technology is the introduction of multiple genes which include cytochrome P450, glutathione S-transferase, compound glutathione (Mishra et al. 2020).

Phytoremediation processes in aquatic plants are important components in pollutant control within aqueous environments. Because of its abundance and limited movement in addition to their capability to take up and photodegrade the contaminants, watery plants in particular have a high potential for removing water pollutants similar to in situ biofilters (Anudechakul et al. 2015; Mercado-Borrayo et al. 2015). This approach is used effectively to clean up water pollution and has received serious support from scientists, government, and non-governmental organizations. The effectiveness of aquatic plants in removing pesticides which include organophosphorus pesticides from water has been studied in several studies (Xia and Ma 2006; Olette et al. 2009). However, for environmental cleanup of various organic and inorganic contaminants, plants and their associated microbial rhizospheres are used. The successful use of plants utilizing plant-related bacteria has played a useful role in the elimination, detoxification, or immobilization of environmental pollutants (UNEP (Undated) 2019; Shahid et al. 2020). Synergistic action of *Enterobacter crassipes* and *Acinetobacter sp*., root-associated bacteria for chlorpyrifos degradation become elucidated through bioaugmentation (Anudechakul et al. 2015). Furthermore, *E. crassipes* played a role in petroleum hydrocarbon phytoremediation (Ochekwu and Madagwa 2013). In general, the mechanism of bioremediation is not a single step process, however multiple techniques are interrelated and rely on plant physiological techniques powered through sun energy, rhizosphere techniques, and other available precursors to carry out the cleanup process in an environmentally friendly way. In the root region, organics are degraded depending on plant properties or taken up, observed through sequestration, degradation, or volatilization (Dutta et al. 2014; Hussain et al. 2019; Skinder et al. 2020; Ansari et al. 2020). The excretion of organic carbon by the roots stimulates microorganisms in the rhizosphere, which leads to an increased dissipation of complex organic compounds (Paris et al. 1981). To enhance plant growth, bacteria additionally release indole acetic acid (IAA) (Golubev et al. 2009). Microorganisms, i.e., fungi and bacteria, might be closely associated with the roots, i.e., rhizosphere, it plays a vital role in eliminating organic pollutants (Vangronsveld et al. 2009). Metal accumulation and increased biomass of subsurface plant led to bioaugmentation of endogenous rhizobacteria of *Spartina maritima* (Mesa et al. 2015). It is the direct addition of pre-grown microorganisms that could break down and accelerate the degradation of contaminants as pre-grown microbial cultures increase microbial communities at a site to improve clean up of pollutants and minimize cleanup time and expense (Azubuike et al. 2016). Inoculation of copper eliminating rhizospheric bacteria, strain CU-1 with or without oxytetracycline into water hyacinth culture leading to improving copper accumulation in the plant roots and the strain CU-1 colonized the area of plant roots (So et al. 2003).

17.2.4 Enhancing Phytoremediation of Organic Pollutants by Biosurfactants

The solubility of petroleum hydrocarbons (PHs) results in low availability of PHs for bacterial cells and as a result, there may be minimal cleanup of soil contaminated with those compounds (Johnsen et al. 2005). The surfactants are those low toxicity and rapid biodegradability, making them "environmentally friendly" (Deshpande et al. 2000; Supreeth 2021; Mulligan 2021). The vital role of biosurfactants is to improve contact surfaces between bacteria and pollutants. It is worth noting that the use of endophytic inoculants leading to generating biosurfactants, which play an essential role in pollutants desorption from the soil to facilitate the dissipation of organic-contaminated soils through phytoremediation or endophytic bacteria or with the assist of each other, depending on the bioavailability of contaminants and the solubility of root-microbial modifications (Wenzel 2009; Feng et al. 2017; Ptaszek et al. 2020). The use of biosurfactants (either microbial or plant-derived) as mediators can improve the bioavailability and solubility of hydrophobic organic pollutants, which include PHs, via desorption process from soil particles, leading to increasing bioremediation efficiency (Silva et al. 2014; Liduino et al. 2018). It can also affect the surface of cells and control their transport (Zhang et al. 2014; Kukla et al. 2014). This approach is achieved via through good emulsification operation, excellent surface-active properties, and high stability, making it suitable for the bioremediation of polluted soils (Pathak and Keharia 2014) and promoting the degradation of organic xenobiotics in plant tissues. Additionally, indirect effect suggests that endophytic bacteria that dissipate PAH may also significantly minimize the accumulation of lipophilic PAHs in the tissues of plant (Liu et al. 2014; Sun et al. 2015). By growing pseudo solubility through partitioning into micelles, biosurfactants may also promote bacterial growth on PHs, resulting in improved bioavailability of pollutants to degrading bacteria (Mulligan 2009; Pacwa- Plociniczak et al. 2011; Ławniczak et al. 2013; Gkorezis et al. 2016). Biosurfactants are also amphiphilic molecules formed through species of *Pseudomonas* that can minimize the interfacial tension between the aqueous phase and PHs and form a microemulsion by solubilizing hydrocarbons in water (Pacwa-Płociniczak et al. 2014; Varjani and Upasani 2017a, b). Several research of endophytic microbes such as *Bacillus, Pseudomonas, Acinetobacter, Kocuria, Microbacterium,* and *Rhodococcus* had been evaluated for the improvement and possibility applications of biosurfactants and bioemulsifiers in phytoremediation (Kukla et al. 2014; Pathak and Keharia 2014; Karlapudi et al. 2018). Studies showed that sunflower cultivation is a practical and efficient technique to treat soils containing organic hydrocarbons and heavy metals with the addition of biosurfactant (rhamnolipids) glycolipids (Liduino et al. 2018). Rhamnolipids are very effective surface-active molecules resulted by *Pseudomonas aeruginosa* strains resulting from wetting, emulsifying, solubilizing, detergency, foaming, metal sequestering, and phase dispersion properties (Franzetti et al. 2010; Lovaglio et al. 2015; Ptaszek et al. 2020).

17.2.5 Enhancing Phytoremediation of Pollutants in Soil Chemically

The solubility of hydrophobic contaminants, which include PAHs, PCBs, PHs, radio nucleosides, a few pesticides and explosives, results in low plant availability because of phytoremediation, thus limiting the removal of soil contaminated with these compounds (Otero-Diaz 2017; Jing et al. 2018). As referred to earlier than through Arslan et al. (2017), it is confirmed that highly hydrophobic pollutants (log $K_{ow} > 3.0$) are adsorbed rapidly and slowly degraded to the soil, consequently phytoremediation of these compounds is not an appropriate solution, it is often due to the plant's inability to break down these persistent organic toxic compounds in the soil in the rhizosphere zones or translocate them into the shoot tissues. Studies performed through Parrish et al. (2004) have indicated that 9–24% of some long-lasting contaminants which include PAHs inefficient and poorly bioavailable through phytoremediation. Adequately lipophilic organic pollutants with a log K_{ow} range between 0.5 and 3.0 can accumulate or degrade through roots of plant and enter the stream of xylem for translocation by plant shoots (Arslan et al. 2017). An effective strategy improves desorption and availability of pollutants for plants through the use of solubility improving materials. In the existence of ethanol, aqueous solubility of pesticides was increased, therefore the partitioning behavior between the organic liquid phase (such as gasoline and iso-octane) and the water of these compounds will change. This study showed that ethanol shows a high preference for the aqueous phase in a water/ethanol/organic liquid system (Otero-Diaz et al. 2017). Biofuels which include E85 (85 percent ethanol and 15 percent volume of gasoline) also are fully mixable in water. The excessive ethanol concentration led to an improved concentration of organochlorine pesticides in the aqueous phase, leading to a 4.83, 2.03, and 4.82 magnitude decrease in the log K_{ow} for dieldrin, lindane, and chlorpyrifos, respectively, due to the using pressure produced through the increase in the aqueous phase solubilization potential (Toso and Higgins 2012). The ability of water-miscible organic solvents, which include short-chain alcohols utilized in oxygenated fuels which include M85 (85% methanol and 15% gasoline) or E85 (85% ethanol and 15% gasoline), substantially increases the aqueous solubility of several organic hydrophobic compounds (HOCs), like PAHs (Chen et al. 2005), polychlorinated biphenyls (PCBs) (Schwarzenbach et al. 2003), and the BTEX compounds (Lee and Peters 2004). In addition, Smith and others (2004) discovered that the quantity of p, p′-DDT desorbed from the soil improved in the aqueous process by methanol, ethanol, 1-propanol, and 2-propanol. Previous studies by Chiou and others (1986) have proven that dissolved organic matter (DOM) can enhance HOCs' aqueous solubility, along with PAHs, (Cho et al. 2002; Zhao et al. 2020), PCBs (Chiou et al. 1986), and pesticides (Ma et al. 2012; Carpio et al. 2021). For example, Chiou and others (1986) observed that when 100 mg/L of humic acid become present, DDT's aqueous solubility increased by a factor of eight. These studies indicate that the increase in aqueous solubility will increase linearly with the concentration of DOM. Fulvic acid is soluble in acid, insoluble in alkali, fully soluble in aqueous solution and able to form water-soluble complexes with organic compounds, maybe due to carboxylic and phenolic hydroxyl functional groups (Schnitzer 1986). Also, Otero-Diaz et al. (2017) cleared that, the solubility relationship is heavily influenced through cosolvent–solvent interactions, for example, solubility of dieldrin and lindane were increased 7.5 and 3.3 orders of magnitude resulting to increasing ethanol mass fraction, ωc, from 0.0 to 1.0. In the same trend, Paan et al. (2006) show that through increasing the number of straight-chained carbon atoms in the co-solvent leading to increasing toxaphene aqueous solubility, at the same time as the branched cosolvents leading to lowering solubility of toxaphene. Cosolvency forces had been expected to be 3.43 for methanol, 3.64 for ethanol, 3.51 for isopropanol, and 3.91 for propanol, respectively. The ethyl lactate/water system confirmed a better efficiently to desorb highly hydrophobic pollutants than the ethanol/water system (Yap et al. 2012). Diphenoxylate become preferentially solved through organic solvents for intermediate and organic composition mixtures of acetonitrile: water, ethanol: water, methanol: water and isopropanol: water at the ratio of (1:2) (Li et al. 2020). The integrated chemical reagent delivery approach using surfactants/cosolvents with oxidants, either simultaneously or sequentially, promises to increase the depletion of dense nonaqueous liquid in situ mass, DNAPL (Dugan et al. 2010). Surfactants can improve the solubility and mobility of hydrophobic organic xenobiotics (Gharibzadeh et al. 2016; Binh et al. 2016). Increased solubility is caused by the liquid phase of the hydrophilic headgroup, while the hydrophobic tail appears to be associated with hydrophobic organic contaminants (Wang et al. 2019). In recent years, use both AES-D-OA as surfactant and toluene achieved best results for raw oil elimination, where the efficiency of the overcoming adsorption performance of crude oil was increased by 97% than the other systems (methanol and acetone), possibly because of their similar constitutes and structures in terms of chemical properties (Wang et al. 2019). Some amendments (e.g., methylated-β-cyclodextrins, Tween 80, oxalic or citric acids, and biochar) have been successfully supplemented to promote the phytoremediation of soil contaminated with organic compounds, in order to increase the bioavailability of organic xenobiotics in soils (Beesley et al. 2010; Shen et al. 2009; Mitton et al. 2012). In addition, an integrated approach to chemical enhancers such as ethanol, SiO_2, hydroxypropyl-cyclodextrin (HP-CD), natural humic acid (HA), and surfactants such as Tween 80 has increased the solubility of pesticides in contaminated soil and increased the potential of phytoremediation, especially in the existence of green nanoparticles. For example, the remediation capability of *Plantago major* L. was increased more by liquid SiO_2 than the other systems, leading to dissipating of substantial amounts of cyanophos from soil. The use of solubilizing agents (surfactants, hydroxypropyl -ß- -cyclodextrin (HP ß CD), humic acid (HA), and Tween 80) approximately caused 60% removal for cyanophos insecticide from polluted soil (Romeh 2015). Other studies by Romeh and Hendawi (2017) in batch experiment showed that the efficiency of the desorption performance of fenamiphos become improved through the addition of SiO_2 more than other treatments. Romeh and Saber (2020) showed that *P. major* improved with SiO_2 plus F-Fe^0 and *P. major* improved with 1% ethanol plus F-Fe^0 led to the removal of chlorfenapyr (log K_{ow} = 4.83) from the water, while the addition of

P. major improved with 1% ethanol, SiO_2, and argal leading to removing 54.92%, 49.92%, and 41.36% in flooded soil. The combined use of SiO_2 plus *P. major* has achieved great success in reducing the amount of cypermethrin contaminated soil than 2-hydroxypropyl-beta-cyclodextrin (HPBCD) at 1%, humic acid, HA at 10 mg L^{-1}, and Tween 80 at 9.2 mg L^{-1} (Aioub et al. 2019).

17.3 Applicability in Egypt: A Case Study

Egypt is situated in the northeastern most corner of Africa, occupying an area of almost one million square kilometers. It borders the coast of the Mediterranean Sea to the north, and the coast of the Red Sea to the east. Egypt reached the largest population in Africa of over 100 million in 2020 (Abd Ellah 2020). The Nile Delta is one of the oldest and most heavily populated cultivated regions on earth (Zeydan 2005). Four sources of trace element pollution occur in the soil of Egypt's Middle Nile Delta. Fe, Co, Cr, Ni, and V pollution results from geogenic, which slightly improved through anthropogenic input, whereas As, Pb, Zn Cu, Ba, and P are from manufacturing activities. Furthermore, Ba, Pb, Zn, and Cu are from traffic emissions, while P, As, and Cu are from using pesticides and agricultural fertilizers and irrigation of drain water (Abu Khatita et al. 2020; Shokr et al. 2016). Additionally, said et al. (2019) explained that vehicle traffic and industrial activities are the principal sources of pollution with heavy elements in the El Tebbin region, Egypt. On the other hand, organic chemicals which include phthalate, DDD, DDE, and dieldrin insecticides had been detected in all seasons, while chlorpyrifos-methyl residues were founded only in the water canal of El-Mahmoudia, El-Beheira Governorate, Egypt, for the duration of the summer and autumn seasons (Radwan et al. 2019). These techniques result in water and fish pollution and health risks to communities in Egypt. The research performed in Egypt on phytoremediation of organic compounds is limited, and most studies focused on phytoremediation of heavy metals, for example, in 2019, an Egyptian case study investigated the effect of plant types on the performance of constructed wetlands treating real municipal wastewater for reuse. Study showed that the order of the eliminate efficiency of biochemical and chemical oxygen demand in the three basins was *Phragmites australis* (88.6%and 89.1%) > *Cyperus papyrus* (86.9% and 87.5%) > *Canna flaccida* (83.4 and 83.5%*).* The higher removal effectively of nitrogen (N) and phosphorus (P) was achieved dissentingly by *C. papyrus, P. australis, C. flaccida* plant species, respectively (Abou-Elela et al. 2019). *P. australis* and *Cyperus alopecuroides* are promising organisms for phytoremediation of Fe, Mn, Zn, Cu, Pb, and Cd from wastewater and soil (Moussa 2015). The most successful approach for degrading imidacloprid from the soil in the field become studied by Romeh (2020) who discovered that cultivation of *Plantago major* beside tomato crops after inoculating them with EM-1 leading to eliminating imidacloprid from the soil. Field experiments showed that *P. major* reduced azoxystrobin concentration from 10.44 to 0.00 µg/g next to tomato crops inoculated with EM1, recording 47.82–100.00% elimination over 2 h to

10 days of exposure (Ramadan et al. 2019). Regarding the remediation of heavy metals in Egypt, two forms of natural plants on the banks of the River Nile in Egypt known as *Echinochloa pyramidalis* and *Ludwigia stolonifera* were evaluated in 2020 for the green remediation of pollutants, in particular heavy metals from secondary treated wastewater. In combination, the planting of these two plants confirmed the very best elimination of Cd and Pb, at the same time as the complete removal of Ni was demonstrated through *L.* stolonifera (Abd-Elaal et al. 2020). The accumulation of heavy metal ions was recorded by *Typha domingensis* as a rhizofiltration in wastewater ponds at El-Sadat city, Egypt rather than sediment (Hegazy et al. 2011). The area of Sahl El Husseiniya, the government of Alsharqia, is primarily irrigated through the Bahr El-Baqar drain wastewater. In the study field, two forms of higher accumulator plants consisting of kenaf (*Hibiscus cannabinus* L.) and flax (*Linum usitatissimum* L.) had been successively cultivated. Data showed that *H. cannabinus* had a more beneficial impact on the remedial of Cr, Co, and Cd, while *L. usitatissimum* was higher in the remedial of Mn (Shehata et al. 2019). To alleviate pollution of the water in the Egyptian wetlands, the efficiency of *Pistia stratiotes* for heavy metals removal has been investigated through the bioaccumulation and rhizofiltration processes. Heavy metals' rhizofiltration potential (RP) was greater than 1000 for Fe, and 100 for Cr, Pb, and Cu (Galal et al. 2018). In Egypt, research in the field of removing pollutants and the use of the latest technology in environmental remediation still require the support and cooperation of governments for a clean environment free of pollutants.

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Chapter 18
Environmental Bioremediation as an Eco-sustainable Approach for Pesticides: A Case Study of MENA Region

Alaa El Din Mahmoud, Manal Fawzy, Heba Khairy, and Ahmed Sorour

Abstract Pesticides possess a role in controlling pests and insects that are attacking on crops. Various types of pesticides have been used to protect crops for centuries. However, the used chemical pesticides have a significant negative impact on the environmental components. This chapter summarizes the types of pesticides with their functions and their classifications to show the variety of available pesticides. With excessive usage of pesticides, their status in MENA (the Middle East and North Africa) region is highlighted. This chapter discusses also various pesticide bioremediation techniques because there is a necessity for eco-friendly and sustainable solutions for pesticides contamination. Herein, microbial remediation for pesticides is discussed with examples including bacteria, cyanobacteria, and fungi. Furthermore, the potential of bioremediation challenges has been highlighted.

Keywords Remediation · Pesticides · Organophosphorus · Organochlorines · Carbamates · Microbes · Bacteria · Fungi · Health effect · Challenges

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18.1 Introduction

Food production and security are vital for every country so there are a lot of social and economic pressures that triggered many environmental issues when using more synthesized agrochemicals (Sawicka et al. 2021). In worldwide, more than 60,000 chemicals are used as pesticides, fertilizers, food additives, industrial solvents, and drugs (Das and Dash 2014). The production of pesticides are ~2 million tonnes which used worldwide every year according to Rajmohan et al. (2020).

Herein, we focus on pesticides that describe all substances used to control any organism that threaten the human beings or their interests. They include a wide spectrum of substances including insecticides, herbicides, fungicides, plant growth hormones needed in agriculture to protect the plant from pests, weeds and enhance the quality of the food products (Mahmoud and Fawzy 2021). According to the United States Environmental Protection Agency (UNEPA), the various types of pesticides are in Table 18.1. The global consumption of insecticides, herbicides, and fungicides are ~29.5%, 47.5%, and 17.5%, respectively. The rest types account for 5.5% (Aktar et al. 2009).

The categorizations of pesticides are on the basis of chemical composition as organophosphates, organochlorines, carbamates, and substituted urea (Bhat et al. 2020). Table 18.2 highlights their classifications with chemical structures. In addition, they can be classified depending on their toxicity and the functionality.

Organochlorines and persistent organic pollutants (POPs) are the most hazardous because they have risks to the environment and officially determined in many countries (Alvarez et al. 2017; Bhat et al. 2020). Nowadays, more pesticides are formulated and synthesized to ensure food security. The inconsistent use of these pesticides affects the ecosystem components and the whole ecological structure.

Pesticides contain both active and inert ingredients. An active ingredient is the chemical which prevents, destroys, or repels pests, whereas the inert ingredients are combined during the manufacturing of a pesticide product. The term inert does not mean non-toxic and it must be approved by the environmental protection agencies. Persistent organic pollutants are chlorinated compounds, and they are used as pesticides' ingredients (Hajjar 2012; Ziarati et al. 2019). Chlorinated pesticides, polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), hexachlorobenzene (HCB), polychlorinated dibenzodioxins (PCDD), and polychlorinated dibenzofurans (PCDF) have both health and environmental hazardous effects (Crinnion 2009).

Health hazardous effects are occurred due to acute or chronic exposure to the pesticides. Acute exposure is the exposure of human to a large amount or high concentration of pesticides for a short time (2–8 h), whereas chronic exposure is the exposure of human to a small amount or low concentration of pesticides for a short time. Table 18.3 summarizes the toxicity effects of using certain types of organophosphates and carbamates based on (Table 18.2). Environmental hazardous effects of pesticides as general are also summarized in (Table 18.4).

Microorganisms including bacteria, cyanobacteria, and fungi are applicable in remediating pesticides and other pollutants as bioremediators. The evaluation of the

Table 18.1 Types of pesticides and their functions according to United States Environmental Protection Agency (UNEPA)

Types of pesticide	Function
Algicides	Kill algae
Antifoulants	Kill or prevent organisms that found on underwater surfaces
Antimicrobials	Kill microbes such as bacteria
Attractants	Tempt pests into a trap
Biopesticides	Derived from living organisms
Biocides	Kill microorganisms
Defoliants	Cause shedding of leaves to facilitate harvesting
Desiccants	Cause dehydration of living tissues
Disinfectants and sanitizers	Inactivate or destroy microorganisms
Fungicides	Destroy fungi
Fumigants	Kill pests by producing fumes or gases
Herbicides	Kill unwanted plants or weeds
Insect growth regulators	Disrupt the developmental stages of insect life cycle
Insecticides	Insect killers
Acaricides	Kill parasitic mites on plants and animals
Microbial pesticides	Microorganisms that inhibit other microbes or pests
Nematicides	Kill nematodes feeding on plant roots
Ovicides	Destroy eggs of mites and insects
Molluscicides	Kill molluscs such as snails
Plant growth regulators	Affect plant developmental stage such as flowering
Plant incorporated protectants	Produced through manipulation of the plant genetic materials
Pheromones	Disrupt the behavior of insects sexual mating
Repellents	Fight off pests such as insects
Rodenticides	Control rodents such as mice

Table 18.2 Pesticides classification based on the chemical composition

Pesticide type	Common name	Chemical formula
Organophosphates	Parathion	$C_{10}H_{14}NO_5PS$
	Basudin/Diazide	$C_{12}H_{21}N_2O_3PS$
	Malathion/Carbofos/Maldison/Mercaptothion	$C_{10}H_{19}O_6PS_2$
	Chlorpyrifos	$C_9H_{11}C_{l3}NO_3PS$
Organochlorines	Dichloro-Diphenyl-Trichloroethane (DDT)	$C_{14}H_9Cl_5$
	Methoxychlor Methoxide Dimethoxy-DDT Methoxy-DDT	$C_{16}H_{15}Cl_3O_2$
	Lindane	$C_6H_6Cl_6$
	Aldrin	$C_{12}H_8Cl_6$
	Endosulfan/Benzoepin/Endocel/Parrysulfan	$C_9H_6Cl_6O_3S$
Carbamates	Benomyl	$C_{14}H_{18}N_4O_3$

Table 18.3 Toxicity effects of using certain types of organophosphates and carbamates

Pesticides	Toxicity effects	References
Chlorpyrifos	• Significant damage in brain and kidney of rat • Leukemia and brain cancers • Linked to neurological effects • Linked to persistent developmental disorders	Lee et al. (2004); Mulla et al. (2020)
Parathion	• Headaches • Sleeplessness • Diarrhea • Breathing problem • Substantial variations in the enzymatic profiles in *Catla catla*	Abhijith et al. (2016); Mulla et al. (2020)
Malathion	• Effect on blood cells through clotting time prolongation • Pulmonary distress • Hepatotoxicity and nephrotoxicity	Ramadan et al. (2017); Badr (2020)
Benomyl	• Brain malformations • Inducing neuronal cell death at nanomolar concentrations	Kara et al. (2020)

Table 18.4 Toxicity effects of pesticides on environmental components

Environmental threat	Toxicity effects	References
Aquatic biodiversity	• Drastically low O_2 levels because of killing aquatic plants (provide 80% of dissolved oxygen). • Excessive use of pesticides led to decline in fish. • Changing the composition and abundance of plankton. • Developing ovaries in male frogs within their testes. • Biomagnification and bioaccumulation in the food chain	Scholz et al. (2012); Mahmood et al. (2016); Badr et al. (2020); Mahmoud (2020); Mahmoud et al. (2020)
Terrestrial biodiversity	• killing non-target plants. • Reducing the seed quality. • Affect wildlife (bird populations have declined ~20–25% since pre-agricultural times). • Disrupting nitrification and denitrification process in soil when chlorothalonil and dinitrophenyl fungicides are used. • Toxicity to earthworms *Eudrilus eugeniae* via redox-related mechanisms.	Fletcher et al. (1993); Lang and Cai (2009); Mahmood et al. (2016)

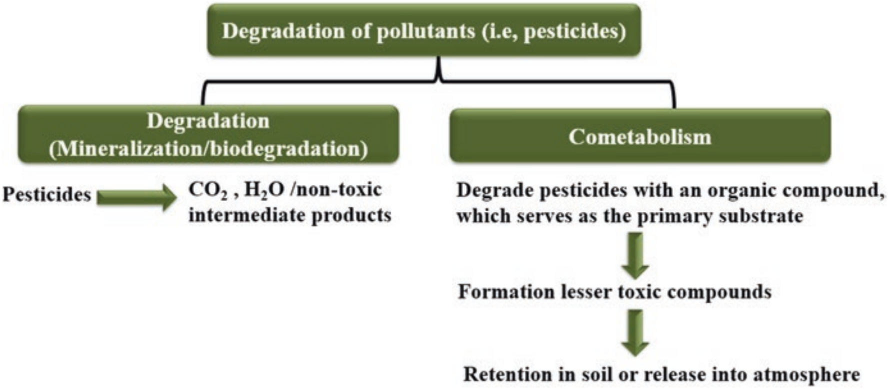

Fig. 18.1 Bioremediation principles with microorganisms through transformations of pollutants (i.e., pesticides) in environment

microbial remediation is depending on significant factors (Das and Dash 2014). For instance,

- The toxicity magnitude of the contaminated sites should be investigated as well as the mobility of the contaminants that depends on the geology of the site.
- The contaminants degradabilities in the environment; depending on molecular weight (high molecular weight compounds degrade slower than low molecular weight compounds).
- The ability to monitor the contaminated sites due to the heterogenies of the contaminated matrix.

Generally, microorganisms produce various metabolic enzymes that can be utilized for the degradation of various pollutants to a safer or lesser toxic intermediate by different mechanisms. Figure 18.1 summarizes those principal mechanisms.

In this chapter, we have an insight into pesticides used in the Middle East and North Africa (MENA) region and the possible bioremediation strategies with varied microorganisms.

18.2 Status of Pesticides Used in MENA Region

The second major category of pesticides are organophosphates. Organophosphorus insecticides are increasingly used in Eastern Mediterranean region, such as chloropyriphos, malathion, dimethoate, and fenitrothion (Naughton and Terry 2018). Fungicides used in Egypt are mostly inorganic compounds which include 593.7 and 9118.8 tonnes of Cu oxychloride and sulfur, respectively. However, the amount of total organic compounds used as fungicides was 1786.1 tonnes (Pülschen et al. 1994). Atrazine, bromoxynil, glyphosate, and furon are commonly used as herbicides to control weeds (Badawy 1998).

High residues of DDT were detected in soil samples collected from different regions in Egypt (Dogheim et al. 1996). Recently, Rohlman et al. (2019) studied the exposure of organophosphorus pesticides such as chlorpyrifos to the pesticide applicators and compared to non-applicators in the age range of 12–21 years old. They concluded that the symptoms of attention deficit hyperactivity disorder (ADHD) are more prominent in pesticide applicators than non-applicators with one fourth. It is worth mentioning that ADHD rates are 3–9% among children in worldwide (Froehlich et al. 2007). Organochlorin insecticides were detected in both water and soil collected from Damascus in Syria and 15 regions in Saudi Arabia (Hajjar 2001; Al-Wabel et al. 2011). Aldrin, dieldrin, endrin, heptachlor, and hexachlorobenzene (HCB) have been detected in 233 dairy products samples collected from Jordan market (Nida'M et al. 2009). Tunisia registered 215 active ingredients of pesticides and distributed them on the national market under 493 commercial brand names. Highly hazardous pesticides active ingredients among the national registered pesticides in Tunisia are listed in Table 18.5 (Ipen 2020).

Environmental bioremediation is a sustainable, promising, and cost-effective technique for cleaning the environment. It involves the utilization of plants and microorganisms for the degradation/transformation and removal of various contaminants into less toxic compounds (Bhat et al. 2020; Rajmohan et al. 2020). Bioremediation is a cleanup phenomenon in which the organism is used in a biological system to maintain or restore contaminated areas (Kensa 2011). Successfully

Table 18.5 Registered pesticides in Tunisia

Abamectin	Ethoprophos	lambda-Cyhalothrin	Pirimiphos-methyl
Acrinathrin	Fenazaquin	Linuron	Propiconazole
Amisulbrom	Fenoxycarb	Lufenuron	Propineb
Borax	Fenpyroximate	Magnesium phosphide	Pymetrozine
Brodifacoum	Fluazifop-P-Butyl	Malathion	Pyridalyl
Chlorantraniliprole	Flufenoxuron	Mancozeb	Spinetoram
Chlorothalonil	Folpel	Manebe	Spinosad
Chlorpyrifos-methyl	Gamma-cyhalothrin	Metaflumizone	Spirodiclofen
Copper hydroxide	Glufosinate	Metam potassium	Sulfoxaflor
Cypermethrin	Glyphosate	Metam sodium	Tefluthrin
DDVP	Haloxyfop-R	Methiocarb	Tepraloxydim
Deltamethrin	Hexythiazox	Methomyl	Thiacloprid
Diafenthiuron	Imidacloprid	Metirame of zinc	Thiamethoxam
Difenacoum	Indoxacarb	Metribuzin	Thiophanate-methyl
Diméthoate	Iprodione	Milbemectin	Triadimenol
Dimoxystrobin	Flufenoxuron	Mineral oil	Trifluralin
Meptyl dinocap	Folpel	Oxamyl	Zeta cypermethrin
Diquat	Gamma-cyhalothrin	Oxyfluorfene	ZIRAM
Emamectin benzoate	Glufosinate	Paraffin oils	
Epoxiconazole	Iprovalicarb	Pendimethalin	
Esfenvalerate	Kresoxim-methyl	Phosmet	

environmental restoration is consistently reported by indigenous microbes which could oxidize, immobilize, or transform the contaminants such as the use of different bacterial strains to oxidize petroleum oil as a first step in its degradation. Thus, microbes are able to reduce pollutant levels up to undetectable, non-toxic, or acceptable levels (Xu et al. 2018). Therefore, the aim of the next section is to discuss the history of bioremediation. Moreover, we state the application concerning pesticides remediation in MENA region.

18.3 Bioremediation Strategies

18.3.1 History and Application

Environmental biotechnology including composting, wastewater treatments, petroleum oil remediation, and several xenobiotic bioremediations is attracting every day more and more concern. Notable accomplishments in MENA region including the clean up of polluted water and agricultural areas contaminated with different types of pesticides are on the first goal for sustainable development. Bioremediation is defined as the controlled process in which different xenobiotic compounds could be degraded by the action of microorganism or its enzymatic product (Mueller et al. 1996; Kensa 2011).

The cleaning up of Sun Oil pipeline spill at Ambler, Pennsylvania in 1972 was first use of bioremediation process on a large scale (Kumar et al. 2018). George M. Robinson was the first to identify bioremediation concept with sewage and oil treatment experiments on laboratory-scale. After that, new emerging words like phytoremediation in which plants are used in the degradation process and rhizoremediation where the whole rhizosphere is considered as the bioremediator organism are getting attention (Kuiper et al. 2004). Additionally, each strategy of bioremediation should be named appropriately regarding the organism used. For example, using algae and fungi as bioremediators, the remediation word adapted to be phycoremediation and mycoremediation, respectively (Velázquez-Fernández et al. 2012). The concepts of biodegradation, biotransformation, and mineralization are always in extensive overlap. Nevertheless, there are difference between synonyms of bioremediation. Hence, biodegradation comprises the biological reactions that alter toxic chemical compound to less toxic ones. In contrast, biotransformation is defined as the modification or translocation process aiming to reduce the pollutant concentration. However, biotransformation end by either decreasing/increasing the undesirable effects of the transferred compound (Mishra et al. 2022). Biological detoxification systems are considered to be a synonym to biotransformation concept (Parkinson et al. 2011). The key concept of bioremediation strategies is to eradicate undesirable effects of pollutants to organisms through biotransformation and bioremediation (Mahmoud et al. 2021a, b). On the other hand, mineralization is leading to the biologically assimilated compounds such as CO_2 or NH_3 as an end product (Alexander 1999).

A great attention of scientific community is given to the indiscriminate use of pesticides for pest and vector control all over the world as effect of their multifaceted toxicity, persistence, and recalcitrance of several pesticides. Thus, the choice of an eco-friendly, cost-effective, and efficacious nature process such as bioremediation is the best option for protecting the environment (Varshney 2019; Mahmoud et al. 2021c).

18.3.2 Bioremediation Techniques

Two bioremediation strategies are well identified: (a) in situ and (b) ex situ bioremediation.

18.3.2.1 In Situ Bioremediation

It is the treatment of waste at polluted locations without excavation or transportation of contaminants, obviating the requirement to excavate contaminated water or soil for remediation.

In situ remediation strategy is suitable for the sustainable cleaning up of groundwater and soil with pesticide contaminate (Sawicka et al. 2021). This type of bioremediation gives the cones of reducing shipping costs and utilizing native microorganisms to remove chemical contaminants. (Hara and Uchiyama 2013). These microorganisms showed a high chemotactic affinity toward contaminants are able to use it as a sole carbon source. However, time-consuming, seasonal variation in the microbial activity, and uncontrollable environmental factors are the main disadvantage of the in situ bioremediation strategy (Sawicka et al. 2021). According to literature, in situ bioremediation are sub-divided into the subsequent categories:

Bioventing

Used to decompose any degradable substance under aerobic circumstances, in which oxygen (supplied via low air flow rate) is fed into the contaminated site as nutrient, and nitrogen and phosphorus are injected into the contaminated site as nutrient (Rockne and Reddy 2003). This technique is used to clean up soil, however, the concentration of nutrient and oxygen depends upon the soil texture. It is mostly used to remove gasoline, petroleum oil, insecticides, and other chemicals. Because of differences in soil texture and xenobiotic chemical composition, the rate of removal of these substances varies from one location to another (Rockne and Reddy 2003).

Biosparging

In order to boost the concentration of oxygen for the indigenous bacteria, biosparging entails injecting air under pressure into the groundwater. This technique increases the aerobic degradation and volatilization (Lambert et al. 2009). In order to prevent the transmission of volatile substances into the environment, pressure control while injecting oxygen at the polluted site is crucial. Soil texture and soil permeability should be taken into consideration before injecting the oxygen, beside lowering the injection area will reduce the cost (Singh and Garima 2014).

Bioaugmentation

Is a technique that involves introducing laboratory-cultivated microorganisms with specialized metabolic capabilities to a contaminated location in order to improve waste breakdown (Niu et al. 2009; Singh and Garima 2014). For example, the use consortium of microalgae and cyanobacteria isolated from Burullus lake in the north of the Egyptian delta and cultivated in lab and controlled cultivation conditions in order to remediate an organophosphate pesticide called malathion (Abdel-Razek et al. 2019).

18.3.2.2 Ex Situ Bioremediation

It is the excavation or removal of contaminated soil. It is divided into several categories:

Land Farming

Is termed as sandwich layer technique in which contaminated excavated contaminated soil is layered between a clean soil and a clay containing indigenous microbes. The main aim is to activate indigenous biodegradative microorganisms in clean soil and make it easier for them to degrade pollutants aerobically. It is, however, limited to treating the top 10–35 cm of soil. Land forming is the useful most used technique for pesticides degradation (Singh and Garima 2014).

Compositing

A process in which microorganisms degrade the waste at temperatures between 55- and 65-degrees results in a soil-like substance. This technique entails mixing polluted soil with non-hazardous organic amendments like manure or agricultural wastes, during which microbes emit heat, resulting in increased waste solubility and metabolic activity in composts (Antizar-Ladislao et al. 2007).

Biopiling

Referred to the hybrid form of land farming and composting. It comprises a treatment bed with controlled moisture, heat oxygen and pH, an aeration system, indigenous microbes, and an irrigation/nutrient system. Biopiles provide a favorable environment for both native aerobic and anaerobic bacteria (Niu et al. 2009).

18.3.3 Methods for Pesticide Bioremediation

The high level of pesticide toxicity leads to the great need to be degraded. Certainly, in situ bioremediation in which the benefits of microbes that are already present in polluted ecosystems are taken into consideration may be not sufficient in some cases (Gauthier 2006). Furthermore, ex situ bioremediation takes the advantage of pesticides degradation over in situ bioremediation. As up to 99.8% degradation efficiency are recorded in ex situ bioremediation in soil, sludge, groundwater, and sediments (Shanahan 2004; Niu et al. 2009).

18.4 Microbial Remediation for Pesticides

Pesticides are common hazard persisted chemicals, these chemicals are used to control agricultural pets, however, it is leaching into soils, different water streams such as groundwater, sea water, drinking and surface water so having health concerns in many communities specially developing societies. Therefore, the removal and detoxification of this xenobiotic pesticides are taking more concern due to its persistence nature. From a microbiological point of view, the most effective way of reducing the toxicity or the contamination of pesticides is through using microbes and/or plants in eco-friendly bioremediation processes (Malik and Grohmann 2011).

Microbial bioremediation takes place when microorganisms use pesticides as carbon and energy. As reported by (Metting 1993), one gram of soil may contain more than 100 million bacterial species (expressing about 5000–7000 different species) and more than 10,000 fungal species with different metabolic potential (Kensa 2011). Such indigenous microorganisms can detoxification those contaminants in the environment in a process called natural attenuation (Siddique et al. 2003; Kumar et al. 2018). In this section, we proved examples of microbial remediation (bacteria, cyanobacteria, and fungi) for pesticides.

18.4.1 Bacteria

Bacteria is the most extensively used organism for bioremediation purposes this is due to the fast growth rate, and low-cost medium in addition to the ease handling. However, pathogenicity, bioactivation, and the disposal of bacterial biomass are among the cons of using bacteria. More than one microorganism is participating in pesticide degradation occurs, as each microorganism degrade a reaction on pesticides as the mineralization doesn't takes place by a single strain. Thus, these microorganisms' consortia mainly belong to basidiomycetes or to groups of gamma-proteobacteria (*Pseudomonas*, *Aerobacter*, *Acinetobacter*, *Moraxella*, *Plesiomonas*), alpha-proteobacteria (*Sphingomonas*), beta-proteobacteria (*Burkholderia*, *Neisseria*), flavobacteria (*Flavobacterium*), and actinobacteria (Micrococcus) (Velázquez-Fernández et al. 2012).

As bacteria are omnipresent; only a small fraction of bacteria (<10% from soil) is culturable in laboratory conditions (Cycoń and Piotrowska-Seget 2009). Langenhoff et al. 2002 stated that the degradation process could be either under anaerobic or aerobic conditions with participation of different enzymes. However, dechlorination of pesticide is more adequate under anaerobic metabolism (Barragán-Huerta et al. 2007; Baczynski et al. 2010). In aerobic metabolism, cleavage in aromatic or aliphatic cyclic metabolites takes place. Consequently, aerobic conditions are better for biodegrading hydrocarbon metabolites (Qureshi et al. 2009). Several actinomycetes species and bacteria belonging to *Acinetobacter, Neisseria, Pseudomonas, Moraxella* are able to degrade nearly completely DDT (Carrillo-Pérez et al. 2004). *Enterobacter* sp. isolated from Egyptian soil showed degradation ability to malathion (organophosphorus insecticide), Granstar (sulfonylurea herbicide), and Topik (aryloxyphenoxypropionate herbicide) through high esterase activity (Ibrahim et al. 2015). Additionally, *Bacillus, Staphylococcus* isolates and *Pseudomonas* isolated from soil in Mansoura city showed a high degradation ration of both diazinone and malathion (Ramadan et al. 2017).

18.4.2 Cyanobacteria

On the other hand, less studies on algae and cyanobacterial (blue green algae) abilities bioremediate pesticides in water all over the world and not only in MENA region. Moreover, as take place by aquatic plants, the biomass overproduction of algae could be a serious disadvantage of bioremediation in waterbodies when using algae (Velázquez-Fernández et al. 2012). Additionally, Ibrahim et al. 2014 could have isolated strains of cyanobacterial (*Anabaena oryzae, Nostoc muscorum*, and *Spirulina platensis*) in the collected water samples from Al-Fayoum Governorate, Egypt that were found to biodegrade and use organophosphorus pesticide malathion as a source of phosphorus up to 90% in a MENA region case study.

18.4.3 Fungi

White rot fungus such as the *Phanerochaete chrysosporium* can decompose wide range of persistent/toxic environmental pollutants including pesticides (Kensa 2011). Ligninolytic fungi are reported as a good mycoremediators. Unfortunately, some species of fungi require a certain nutrition, humidity, and pH requirements which represent a big hindrance for its use. Fungal peroxidases, dioxygenases, and oxidases showed a biodegradation ability to several types of pesticides (Velázquez-Fernández et al. 2012). It was reported that *P. chrysosporium* can biodegrade endosulfan (Kullman and Matsumura 1996). The ligninolytic fungus such as *Ganoderma australe*, isolated from the stone pine (*Pinus pinea*), showed an ability to degrade lindane (Rigas et al. 2007). It was reported that the mycoremediation showed a glyphosate disappearance after 16 days especially by using *Aspergillus flavus* WDCz2 (99.6%). Therefore, WDCZ2 and *Penicillium spiculisporus* ASP5 are advised as effective fungal strains and environmentally sustainable tools to degrade the herbicide glyphosate (Eman et al. 2013).

18.5 Challenges of Bioremediation

Bioremediation is a sustainable strategy to solve several environmental man-made problems and remove organic xenobiotic pollutants either from contaminated soils or wastewater. Furthermore, bioremediation has traditionally been less expensive than other strategies for removing harmful chemicals. As a result, bioremediation is a potential alternative to the more common use of physicochemical decontamination methods, which are not always cost effective. On the other hand, a variety of conditions, such as the presence of a certain microbial community, contaminants' bioavailability, and several environmental factors influence the bioremediation process. Moreover, pesticides are common hazard around the world, posing health concerns in many societies especially in MENA region especially with the outbreak of COVID-19 (Mousazadeh et al. 2021; Khan et al. 2021a, b). Thus, its bioremediation faces number of challenges concerning the type of used pesticide its toxicity level on bioremediators and condition influencing its complete or even partial detoxification (Malik and Grohmann 2011).

18.6 Conclusions

Although most harmful pesticides are restricted to be produced or utilized in agriculture, many of them are still produced and utilized in low- and middle-income countries. The appropriate use and application of pesticides should be announced and clarified to the users so we can conserve the environmental quality and the citizens' health and safety. Furthermore, the investigation of occupational and environmental exposures to pesticides is required to be monitored regularly through the authorities. In future pesticides applications, biopesticides can be used which result in elimination of target pests and insects.

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Chapter 19
Progress in Pesticides Bioremediation from South Asian Countries: Challenges and Way Forward

Bimal K. Chetri and Deki Choden

Abstract Extensive and frequent use of synthetic agricultural fertilizers for pest control have resulted in pesticide pollution of water, soil, food, and air around the globe particularly in developing nations. Higher persistency and bioaccumulative nature of various pesticides pose a challenge to the evolution of biodiversity by accumulating toxicity in all living organisms eventually reaching humans. While the traditional remediation approaches for pesticide removal are often expensive and contaminant specific, bioremediation technique is widely used in most countries to reduce pesticide exposure to living organisms. The technique employs microbes and plants to treat pesticide-polluted environments with minimal environmental impact and residual contamination. The chapter considers various bioremediation strategies for the clean up of pesticide-contaminated sites which includes bacterial bioremediation, phytoremediation, microbial-assisted phytoremediation, myco-and phycoremediation. The chapter goes on to present the pesticide scenario of South Asian countries, current researches, and advances in pesticide bioremediation. The discussion concludes with challenges and a way forward to effective pesticide bioremediation.

Keywords Pesticides · Contamination · Bioremediation · South Asian Countries · Future prospects

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19.1 Introduction

The use of agricultural pesticides is widespread in South Asia. In terms of pesticide output, India is placed second in Asia (after China) and twelfth globally (Devi 2020). Findings have shown that pesticide residues remain in the top soil as a result, causing toxicity in the soil-water system. Since agriculture employs the vast majority of Indian population, they are exposed to pesticides used in agriculture (Boricha et al. 2009). Pesticide residues in the soil-water cycle are a major contributor to negative biota effects and, as a result, entering the food chain (Gaur et al. 2018). Over time, residues from animal products and other foods accumulate in the human body, affecting blood, adipose tissue, and lymphoid organs. Pesticide residues in the air are a major cause of sickness and mortality (Jaiswal et al. 2019). Pesticides may induce acquired immunodeficiency, autoimmunity, and hypersensitivity reactions in animals and humans, including eczema, dermatitis, and allergic respiratory disorders, and they may also cause chronic infections (Kalia and Gosal 2011). Many pesticides have been linked to gene changes in humans and animals, which may have a role in lung and liver cancer. They are mutagenic and teratogenic, causing liver damage, neuropathy, nephropathy, and reproductive problems (Chaudhry et al. 2002). Bioremediation, a method that uses biological diversity to reduce emissions, has been made possible owing to advances in science and technology (Mani and Kumar 2014; Kaushal et al. 2020). This technique attempts to minimize harmful contaminants from the environment or convert toxic materials into harmless substances using microbes and plants. Table 19.1 lists the major pesticide groups,

Table 19.1 Major group of pesticides, pesticides persistence (Jayaraj et al. 2016), and bacterial remediation

Pesticides group	Examples	Persistence	Bacteria	Reference
Organochlorides	Dichlorodiphenyl trichloroethane (DDT), hexachlorocyclohexane (HCH), dieldrin, toxaphene, chlordane, lindane, endosulfan, aldrin, heptachlor	High	*Pseudomonas* sp.	Eevers et al. (2017), Mishra et al. (2012), Robinson et al. (2019), Rajmohan et al. (2020)
Organophosphates	Parathion, malathion, acephate, phorate, chlorpyrifos	Medium	*Pseudomonas* sp., *Paenibacillus* sp.	Latifi et al. (2012), Chen et al. (2015a, b)
Carbamates	Carbaryl, methomyl, aldicarb, carbofuran	Low	*Pseudomonas putida*	Chanika et al. (2011)
Pyrethroids	Permethrin, bifenthrin, esfenvalerate, decamethrin	Low	*Pseudomonas fulva*, *Sphingobium* sp.	Grant et al. (2002), Guo et al. (2009), Yang et al. (2018)

ranging from high to low persistence, as well as the microbes that degrade them. Decontamination of soil, sediments, surface water, groundwater, and air is now being done using bioremediation (Rani et al. 2020). Due to comparatively low-cost capital, least disruptive methodologies, and eco-friendly, this technology has become an intriguing alternative to traditional physicochemical approaches (Salicrup and Fedorková 2006). This chapter will focus on some of the most recent developments in the field of pesticide bioremediation in South Asian countries.

19.2 Strategies for Pesticide Remediation: Progress Made in Bioremediation from South Asian countries

Phytoremediation and microbial remediation are the most common methods used in bioremediation (Fig. 19.1). Living plants are used in phytoremediation procedures to clean up soil, air, and water that have been contaminated with dangerous chemicals. Green plant and related microbes, as well as proper soil amendments and agronomic practices, are used to either contain, eradicate, or render hazardous environmental contaminants harmless (Sudharshan et al. 2012). Despite its low cost, phytoremediation has yet to be shown to address any major environmental issue to the point where polluted land can be reclaimed. Microorganisms break down contaminants by utilizing them as a food source or metabolizing them with a food source in microbial remediation.

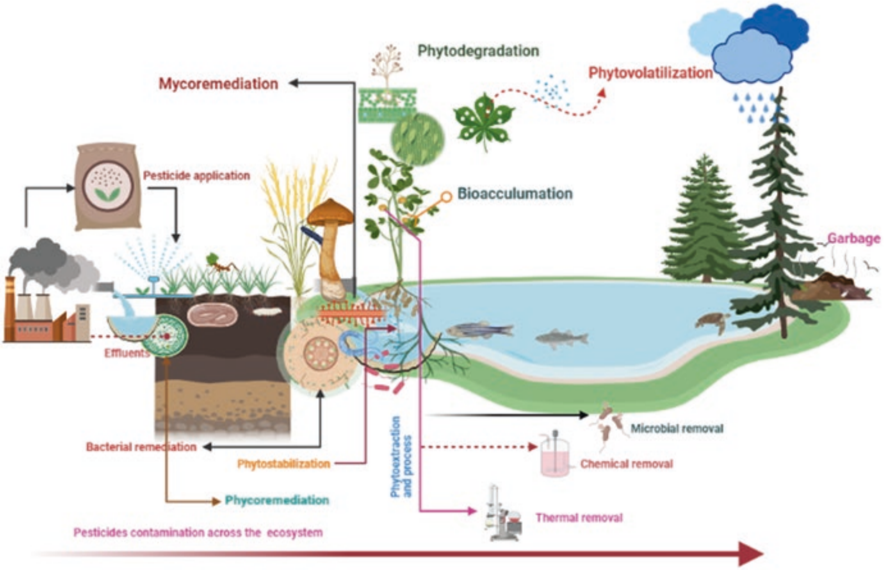

Fig. 19.1 Role of plants, fungi, bacteria, and algae in bioremediation (Created with BioRender.com)

19.3 Bacterial Bioremediation

Since the mid-twentieth-century green revolution, developing countries all over the world have relied heavily on pesticides. Because of different regulations and restrictions, the study indicates that the pattern of pesticide use varies greatly across developed and developing countries (Odukkathil and Vasudevan 2013). Many pesticides banned or prohibited (such as carbofuran, endosulfan, monocrotophos, among others) by the USEPA (United States Environmental Protection Agency) are often used in many developing nations.

The extensive and frequent use of synthetic agricultural fertilizers for pest and disease control in agricultural land has been reported to have negative effects on the environment, non-targeted organisms, and human health (Igbedioh 1991). Pesticide residues have been found in groundwater and drinking water worldwide as a result of subsurface runoff from agricultural fields containing a variety of pesticides, as well as various pesticide residues discharged by industries that generally flow into local rivers (Chopra et al. 2011). Pesticide diffusion and retention in the land ecosystem are determined by its solubility in water, adsorption by soil particles, and persistence, which determines its bioavailability and degradation (Becerra-Castro et al. 2013). Notably, traces of pesticides have been detected in areas other than the area of use as a result of atmospheric redistribution (Shegunova et al. 2007). Pesticide pollution of water, soil, food, and air has resulted from the persistent and bioaccumulative nature of various pesticides. The solubilization-limited bioavailability of hydrophobic organic compounds is one of the key reasons for their long-term persistence in the environment (Pieper and Reineke 2000). As illustrated in (Fig. 19.1), pesticide fate in the environment is determined by a variety of factors, including the rate of microbial, physical, and chemical degradability, as well as adsorption to soil and sediments. Conventional remediation techniques are quite often costly, contaminant specific, and can have a negative impact on the soil's physicochemical properties (Chirakkara et al. 2016). Bioremediation appears to be an efficient and cost-effective strategy for the complete degradation of organic pollutants in situ and ex situ with minimal environmental impact and residual contamination (Timmis and Pieper 1999). The production of innocuous end products (CO_2 and water) from biological pesticide degradation via oxidation of original compounds reduces environmental impact. According to Singh et al. (2006), local environmental conditions, soil water content, redox conditions, temperature, pH, and organic matter content all influence bioremediation efficiency. Soil moisture content, both limited and excessive, can have an impact on redox conditions and biochemical degradation reactions. While a high soil water content can result in anoxic conditions, a low soil moisture content can affect the availability of water to soil microorganisms, altering microbial activity (Phillips et al. 2006; Schroll et al. 2006). An interesting study by Phillips et al. (2006) and Wu et al. (2014) reported that anoxic conditions can improve pesticide (HCH) and DDT degradation. Temperature and pH also have an impact on the rate of pesticide biodegradation (Arshad et al. 2008). The optimal temperature for pesticide degradation ranges between 150 and

400 °C for fenitrothion (Hong et al. 2007) and fenamiphos (Singh et al. 2006). Soil pH influences the enzymatic activity of bacteria. Hussain et al. (2009) reported that between 6.5 and 7.5 most bacteria achieve optimal function. According to Ferrell et al. (2003), soil pH can affect abiotic adsorption and desorption processes in pesticide-contaminated soils. Reducing soil pH can improve bioavailability and, as a result, bioremediation efficiency by increasing desorption from soil particles.

In the environment, pesticide biotransformation happens through metabolic and co-metabolic processes. Pesticides are biotransformed in different pathways, including oxidative, reductive, hydrolytic, and conjugation. Depending on the pesticide, ambient conditions, and microbe species, pesticide biodegradation takes multiple paths (Odukkathil and Vasudevan 2013). Pesticide degradation can be divided into three stages. In phase 1, parent compounds are converted into more water soluble and less toxic compounds via oxidation, reduction, or hydrolysis. In phase II, a pesticide or pesticide metabolite is conjugated to glutathione, a sugar, or an amino acid, which increases water solubility while lowering toxicity as compared to the original chemical. The metabolites from phase II are further converted into non-toxic secondary conjugates in the third phase (Hatzios 1991; Palanisami et al. 2009).

Pesticide bioremediation includes three strategies: bioaugmentation, biostimulation, and enzymatic bioremediation. While biostimulation promotes the growth of already existing pesticide-degrading microorganisms in polluted soil by incorporating several nutrients into the media to improve microbial strain degradation ability (Wang et al. 2017), bioaugmentation employs live non-indigenous inocula of pesticide-degrading bacteria. Both require a favorable soil environment for microbial growth. Enzymatic bioremediation uses the catalytic properties of purified or partially purified enzymes to catalytically detoxify contaminants (Alcalde et al. 2006; Jørgensen 2007; Sutherland et al. 2004). Attempts to demonstrate pesticide bioremediation potential have resulted in the identification of several microorganisms for the restoration of pesticide-contaminated land. Different microorganism strains have been tested for their ability to degrade pesticides, such as *Sphingobium japonicum* for chlorinated pesticides (Liu et al. 2007), *Pseudomonas putida* and *P. mendocina* permethrin for cypermethrin pesticide degradation (Mendoza et al. 2011), *Bacillus* and L-proteobacteria for organophosphate pesticide degradation (Sabdono and Radjasa 2008), and *Sphingomonas* for DDT degradation (Shunpeng and Mingxing 2006). For pesticide bioremediation, majority of the bacterial species are from the genera *Arthrobacter*, *Azotobacter*, *Burkholderia*, *Flavobacterium,* and *Pseudomonas*. A study on the isolation and characterization of Arthrobacter sp. AK-YN10 (Sagarkar et al. 2016) confirmed degradation of atrazine by the species within 24 h, converting it to cyanuric acid, which has a low level of toxicity and poses no serious health concerns in low concentrations. Endosulfan, an organochlorine pesticide, has been reported to be degraded by an *Arthrobacter* strain after 6 weeks of incubation, with 73% biodegradation of a-endosulfan and 75% biodegradation of b-endosulfan (Kumar et al. 2008). According to reports, *Pseudomonas* sp. and *Klebsiella pneumoniae* have hydrolytic enzymes which can help break down s-triazine herbicides such as atrazine. Mulbry and Kearney (1991) discovered that a variety of enzymes found in *Pseudomonas* and *Alcaligenes* sp., including oxygenases, hydroxylases, hydrolases, and isomerases, can degrade herbicide 2, 4-D and organochlorine pesticides. Cyanobacteria have numerous advantages over other microbes as bioremediators, according to Sorkhoh et al. (1992), due to their photoautotrophic nature and nitrogen fixation capacity, which allows for better survival in polluted environments. *Anacystis nidulans*, *Microcystis aeruginosa*, and *Synechococcus elongatus* have all been shown to be effective organophosphorus and organochlorine insecticide degraders (Subramaniyan et al. 2012). Cáceres et al. (2008) observed *Nostoc* sp. MM1, *Nostoc* sp. MM2, *N. muscorum*, and *Anabaena* sp., could degrade fenamiphos and convert it to its primary oxidation product, fenamiphos sulfoxide (FSO).

Studies have also shown that microbial consortia are more appropriate than single cultures for the complete mineralization of pesticides because they can have better biodegradation performance due to their increased metabolic capabilities and synergistic activity than individual species. Through the shared collaboration of two or more microorganisms for better waste degradation and abatement, the mixed bacterial consortium has the most advantages (Liu et al. 2019). Mixed populations are more resistant to environmental fluctuations and foster cohesion in times of stress (Brenner et al. 2008). *Proteus vulgaris*, *Serratia ficaria*, *Serratia* spp., *Stenotrophomonas maltophilia*, *Vibrio metschnikovii,* and *Yersinia enterocolitica* a bacterial consortium made up of six bacterial strains from agricultural soil were found to have tetrachlorvinphos and organophosphate pesticide degradation capacity (Ortiz-Hernández et al. 2010). Myresiotis et al. (2012) reported that the use of multiple *Bacillus strains* to remediate soil polluted with various pesticides (acibenzolar-S-methyl, metribuzin, napropamide, propamocarb hydrochloride, and thiamethoxam) was found to be beneficial. When members of an engineered microbial consortia have diverse metabolic modes, they can perform better in changing environments (Kato et al. 2008).

The development of recombinant DNA and genetic engineering technologies has significantly improved the efficiency of contaminant degradation (Tropel and Van Der Meer 2004). The discovery of genes and degradation pathways in bacteria, as well as the elucidation of degradation mechanisms, has resulted in the development of genetically engineered strains for accelerating the degradation rate of various environmental contaminants (Zhao et al. 2017). In comparison, genetically engineered bacteria have demonstrated a greater adaptability to a wider range of environmental conditions (Yuanfan et al. 2010). Neumann et al. (2004) observed that atrazine chlorohydrolase, encoded by the gene atzA, has higher degradation activity towards atrazine. Another research found that utilizing recombinant Escherichia coli with atrazine chlorohydrolase resulted in successful atrazine polluted soil bioremediation on a field scale (Strong et al. 2000). Overexpression of the organochlorines-degradation gene (linA) and the organophosphates-degradation gene (mpd) in *E. coli* resulted in simultaneous organochlorine and organophosphate degradation (Yang et al. 2012).

Furthermore, there is mounting evidence that biosurfactants can improve xenobiotic compound bioavailability by increasing the surface area of hydrophobic, water-insoluble growth substrates. This is accomplished by increasing their apparent solubility or desorbing them from surfaces, as well as regulating microorganism attachment and detachment from surfaces (Rosenberg and Ron 1999). Previous research has shown that both synthetic surfactants and biosurfactants can increase pesticide water solubility, thereby enhancing pesticide degradation. *P. aeruginosa*, *Corynebacterium*, *Nocardia*, and *Rhodococcus* spp., *Bacillus subtilis* (surfactin), *Bacillus licheniformis*, and *Arthrobacter paraffineus* are among the bacteria that produce biosurfactants (Lang 2002). Awasthi et al. (1999) used a biosurfactant synthesized by MTCC 14 *Bacillus subtilis* to improve endosulfan biodegradation in soil. In the presence of biosurfactant generating bacteria, Odukkathil and Vasudevan (2013) reported increased biodegradation of endosulfan isomers and their main metabolite endosulfan. Investigations into the use of immobilized microbial cells for bioremediation purposes have revealed improved performance with increased degradative enzyme production, increased tolerance to high concentrations of toxic compounds, no cell washout, and a longer biochemical or biotransformation reaction time. Vancov et al. (2005) observed that *Rhodococcus erythropolis* NI86/21-encapsulated cells can reduce atrazine residues in both aquatic and terrestrial environments. In addition, genetically engineered bacteria have been used to degrade pesticides (Cui et al. 2012).

19.4 Phytoremediation (Phytodegradation and Phytoextraction)

Phytoremediation is a passive in situ cleanup technology that uses vegetation to decontaminate soil without interfering with its biological activity or fertility (Marmiroli et al. 2006). Bourgeois et al. (2015) demonstrated that plant development in polluted soils can help regenerate the soil microbial population, stimulate diversity, and increase organic matter content. Furthermore, plants render toxic substances harmless by stabilizing, immobilizing, and mineralizing soil contaminants, thereby reducing their potential risk. It is a potentially clean, effective, and low-cost technology. Phytoaccumulation, rhizofiltration, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization are the main phytotechnologies (Fig. 19.2). When grown in contaminated areas, phytoaccumulation or phytoextraction uses hyperaccumulators to accumulate a massive amount of contaminants in their harvestable tissues (shoot). Following the transfer of contaminants to the shoot, the plants are harvested, treated, and safely discarded (Reddy and Mathew 2001). Rhizofiltration takes place in the plant root zone where adsorption and precipitation and concentration of contaminants that are in solution occur (Lee et al. 1995). Metal tolerant plants are utilized for phytostabilization to immobilize and reduce the mobility and bioavailability of pollutants through adsorption by roots or precipitation in the root zone (Gomes et al. 2014). Phytodegradation/phytotransformation utilizes the plant metabolic activities to break down any organic compounds

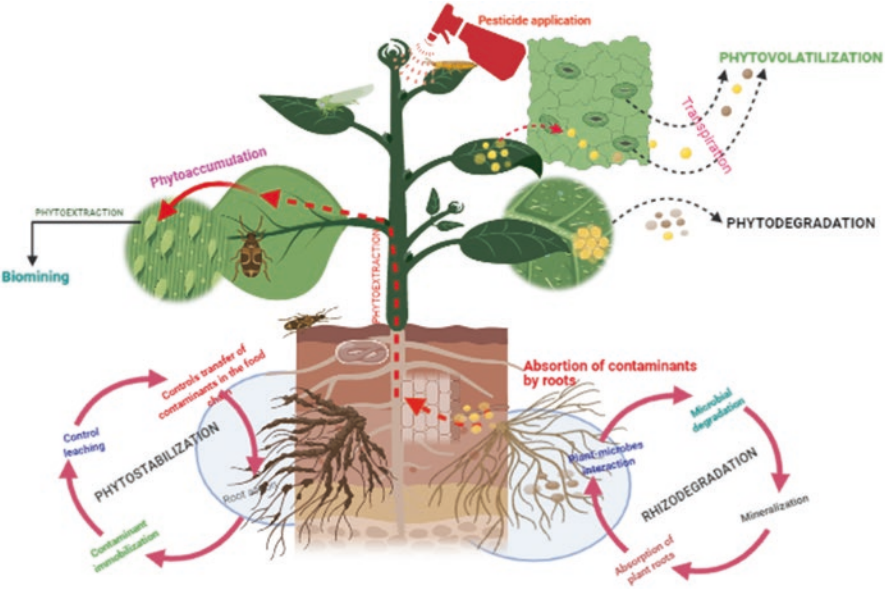

Fig. 19.2 Schematic representation of phytoremediation strategies (Created with BioRender.com)

absorbed by plants. Secretion of external enzymes brings about contaminant degradation (Lee 2013). During rhizodegradation, contamination is transformed in the rhizosphere through plant excretion of root exudates and enzymes, which stimulate bacterial and fungal activity and help in the degradation of organic pollutants (Arthur et al. 2005). Plants that can ingest volatile organics in soil and groundwater and emit the gaseous form of the pollutants through stomata in the leaves are involved in the phytovolatilization process. Enzymatic activity is used in both phytodegradation and rhizodegradation. The rate of chemical uptake for a given phytoremediation scheme is determined by the rate of transpiration of the plant. When considering uptake efficiency, the concentration of the chemical in soil water and the physical-chemical properties of the contaminant are also important factors to consider (Schnoor et al. 1995).

Various researches have unrevealed the pesticide phytoremediation potential in plants. Suresh et al. (2005) demonstrated the ability of *Cichorium intybus* and *Brassica juncea* to degrade DDT. The hairy root cultures of both plants were found to be responsible for the increased pesticide uptake and phytodegradation. Evidence suggests that *Eichhornia crassipes* can be used as a cost-effective and biological alternative for pesticide phytodegradation in water bodies (Li et al. 2011). Dosnon-Olette et al. (2010) observed that *Lemna minor* and *Spirodela polyrhiza* remove dimethomorph from water in their study. The sensitivity of *L. minor* towards dimethomorph was correlated with their ability to remove it from aquatic ecosystems. According to reports, it also decontaminates heavy metals and organic pollutants such as pesticides through rhizofiltration (Sasmaz et al. 2018). *Acorus* *gramineus* has been shown to have exceptional phytoremediation potential in terms of removing organophosphate and organochlorine pesticides from water, including diazinon, fenitrothion, malathion, parathion, dieldrin, and hexachlorobenzene (Chuluun et al. 2009). *Plantago major* L. has been shown to be a potential candidate for phytoremediation of cyanophos insecticide-polluted water bodies. Its roots and leaves can both absorb cyanophos from water (Romeh 2014). Findings have shown that DDT can be removed from the soil and transported into several different plants such as zucchini, pumpkin, alfalfa, ryegrass, and tall fescue (White and Kottler 2002; Lunney et al. 2004; White and Zeeb 2007). At a field scale, a phytoremediation efficiency as high as 98.1% was achieved by *Eucalyptus dunnii* trees for the remediation of soil contaminated with hexachlorocyclohexane. Results showed that the removal of HCH from soil was via phytoextraction and incorporation into tree tissues (leaves and stem wood) (Gotelli et al. 2020).

Pesticide-tolerant plant species identified in Kazakhstan's historic storehouses revealed that these species can accumulate organochlorine pesticides and their metabolites such as 4,4-DDE, 2,4-DDD, 4,4- DDT, -HCH, -HCH, and -HCH. The rate of accumulation depends on plant species and degree of soil contamination. *Artemisia annua*, *Ambrosia artemisiifolia*, *Erigeron canadensis*, *Kochia sieversiana*, *Kochia scoparia*, and *Xanthium strumarium* exceeded Kazakhstan's maximum allowable concentration (MAC) for plant tissue by 90–400 times for four accumulated DDT metabolites and isomers of HCH in plant tissue (Nurzhanova et al. 2013).

Numerous soil and plant characteristics influence pesticide availability in soil and, as a result, plant uptake. The amount of moisture in the soil, the amount of organic carbon, and the amount of clay in the soil can all have an impact on plant availability and transport (Koskinen et al. 2006). Pesticide removal in soil is also affected by plant type. Bouldin et al. (2006) observed higher atrazine uptake in *Juncus effusus* and higher λ-cyhalothrin uptake in *Ludwigia peploides* under hydroponic conditions. While atrazine was translocated to upper plant biomass in macrophytes, lambda-cyhalothrin was sequestered in roots in *L. peploides*, with 25.4% translocated to upper plant biomass. Certain pesticide properties have been found to favor pesticide uptake by the majority of plant species. Lipophilic compounds can quickly cross biomembranes and sorb to the roots, whereas extremely polar compounds have difficulty crossing biomembranes and thus have limited uptake (Burken and Schnoor 1996; Trapp 2000, 2004). Pesticides undergo chemical or biological transformations in the soil and water environment, forming metabolites that are easily absorbed by plants (Trapp 2000). Heavy metals, it has been reported, can influence the rate of pesticide uptake by plants in a mixed contaminated environment (Fig. 19.3). According to Su et al. (2005), the combination of cadmium and atrazine in rice seedlings lowered individual toxicities. Adding equimolar quantities of Cd^{2+} and atrazine to a solution also raised the bioconcentration factor (BCF) of atrazine in rice seedling roots and shoots. The addition of soil amendments such as manure, enzymes, biosolids, and compost to pesticide-contaminated soils can speed up biodegradation and reduce toxicity in vegetated soils (Pidlisnyuk et al. 2014). Plants and microorganisms frequently contain several similar enzymes for the

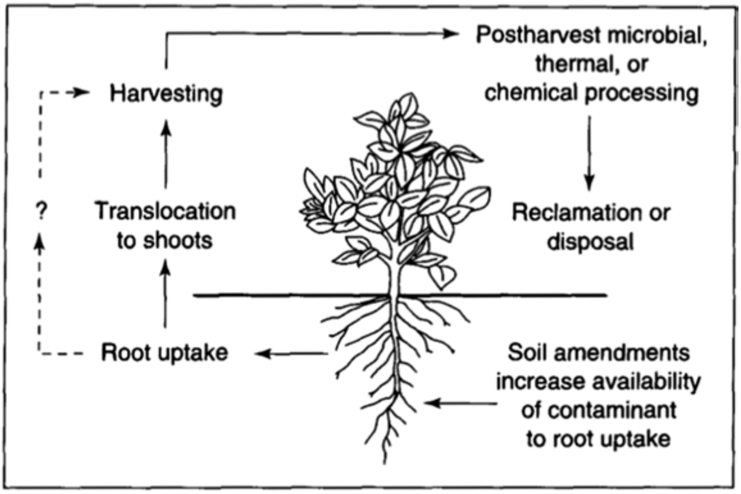

Fig. 19.3 Processes involved in the phytoextraction of contaminants from soils (Adapted from Cunningham et al. 1995)

transformation and detoxification of contaminants; however, microbes are more likely to mineralize or use the contaminant as a nitrogen source (Assaf and Turco 1994; Hoagland et al. 2001). The activity of oxidative enzymes in plants results in hydroxylated metabolites of aromatic rings during the phase I transformation. Glutathione-S-transferase can then conjugate these metabolites to sugars, amino acids, or glutathione. These are commonly referred to as phase II transformations. Herbicide detoxification in plants is attributed to GST-catalyzed conjugation with glutathione. To protect crop species from herbicide damage, glutathione conjugation and detoxification can be assisted by raising glutathione levels or increasing GST activity. Finally, in phase III, further conjugations, sequestration, and compartmentation of the metabolite in organelles, or incorporation into plant tissues can occur (Manahan 1992). In barley cell cultures, the transport of glutathione conjugates into the vacuole has been observed. The degradation of atrazine, a non-acidic pesticide involves hydrolases, ureases, dehalogenases, and cytochrome P450s encoded by atz ABCDEF, trzND, and psbA1 (Hussain et al. 2009). The breakdown of atrazine by transgenic plants has been evaluated (Dhankher et al. 2012). Bioremediation on the rhizosphere and the plant are both necessary for effective pesticide degradation by plants. Endophytic bacteria with biodegradation potential have been genetically modified to help plants with phytoremediation (Behera 2014; Eevers et al. 2017).

Horizontal gene transfer of degradative genes from foreign bacteria to indigenous soil bacteria has been confirmed to improve the degradation ability of the indigenous population. In the natural environment, Miyazaki et al. (2006) observed horizontal transfer of linB genes for HCH degradation. Zhang et al. (2006) and Desaint et al. (2003) showed horizontal transfer of organophosphorus pesticide hydrolase gene cluster and methylcarbamate-degrading mcd gene in soil microbial population, respectively. Often during rhizoremediation of soils contaminated with pesticides, the root growth of plants can be inhibited due to the production of endogenous ethylene production in soil and plant tissues. Arshad et al. (2008) proposed using hyperaccumulators in combination with bacteria harboring 1-aminocyclopropane-1-carboxylate (ACC) deaminase or transgenic plants expressing ACC deaminase genes to overcome ethylene-induced stressors in plants and minimize biomass loss.

Several authors have also documented the use of transgenic plants for improved pesticide-polluted soil decontamination. According to Karavangeli et al. (2005), transgenic plants have significantly higher tolerance and increased phytoremediation of alachlor-polluted agricultural fields (herbicide). Sonoki et al. (2005) observed that adding the laccase of *Coriolus versicolor*, an extracellular fungus enzyme, into tobacco plants increased pentachlorophenol elimination considerably. The transgenic plant's production and secretion of laccase into the rhizosphere improved pesticide removal efficiency. After 14 days of growth, a transgenic plant (tobacco) with the introduction of bacterial organophosphorus hydrolase (OPH) achieved a 99% degradation rate of methyl parathion (Wang et al. 2007). It has been reported that plant enzymes required for plant defense mechanisms are overexpressed. It was confirmed in one of the studies conducted under greenhouse conditions by (Peuke and Rennenberg 2005) that the use of transgenic poplars with enhanced GSH synthesis increased the uptake and detoxification of heavy metals and pesticides. Nonetheless, given the potential impacts of GM plants on the environment, biodiversity, and human landscape, using transgenic plants for soil remediation may pose a number of challenges. Some of the risks associated with using GM plants in phytoremediation include the emergence of resistant biotypes and superweeds, gene flow and horizontal gene transfer among wild types, and disruptions in the genetic makeup of biodiversity.

19.5 Microbial-assisted phytoremediation

Phytoremediation-assisted microbial inoculants can increase microbial breakdown, plant uptake and accumulation, phytovolatilization, and phytodegradation of organic pollutants (Kang 2014). Plants and microorganisms can work together to optimize the contaminant degradation process. Plant roots, according to reports, produce organic acids, amino acids, enzymes, and complex carbohydrates that serve as nutrients for rhizosphere bacteria. In exchange, the bacteria convert mineral nutrients in the soil into plant-available forms. Microorganisms can also synthesize plant hormones, such as auxins, cytokinins, and gibberellins, which protect plants from pathogenic microbes and promote faster growth in the rhizosphere (Anderson and Coats 1995; Tanimoto 2005; Abhilash et al. 2013). The release of root exudates stimulates microbial activity, creating an environment in the rhizosphere conducive to contaminant degradation (Dzantor 2007). Figure 19.4 depicts a comparison of

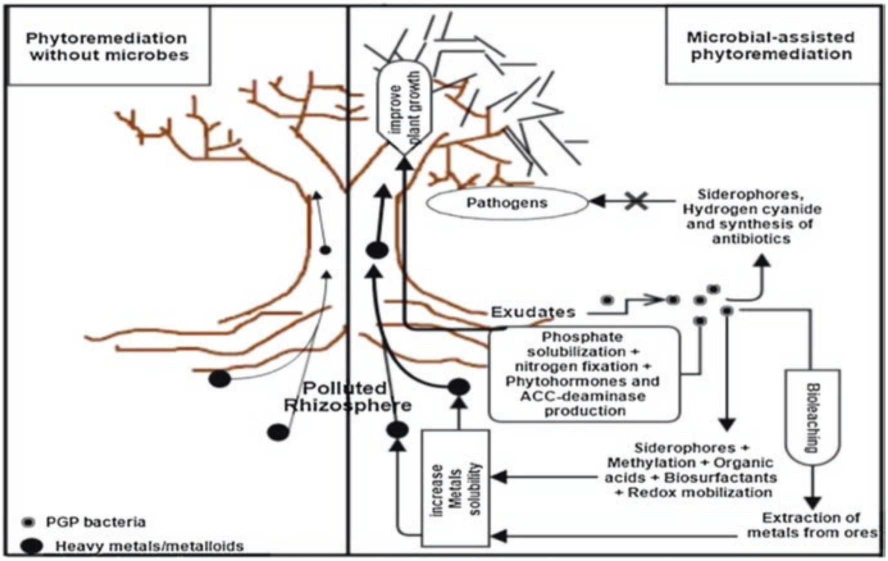

Fig. 19.4 Comparison of plant growth promotion performance with and without PGP (Ullah et al. 2015)

heavy metal removal efficiency by inoculated and uninoculated plants. Furthermore, the plant root system has the ability to enrich the soil, disperse bacteria through the soil, and penetrate impermeable soil layers, while also attracting soluble forms of contaminants in the soil water to the plant and microbes.

Organic contaminants in the rhizosphere are either degraded to simple organic molecules by root exudates or by microorganism activity. Organic compounds degrade into non-toxic constituents like carbon dioxide, nitrate, chloride, and ammonia (Dhankhar et al. 2012). The enzymatic transformation of organic contaminants into simple molecules can result in phytodegradation of organic contaminants in plants. The physical and chemical properties of the contaminants and their interactions with the environment have a significant impact on phytoremediation efficiency. Aside from the availability of degrading bacteria, studies have shown that the solubility and bioavailability of pollutants affect the effectiveness of the remediation method. Furthermore, direct absorption of organics by plants has been shown to be an effective removal mechanism for moderately hydrophobic organic chemicals (Dettenmaier et al. 2009; Chang et al. 2013). Strongly hydrophobic chemicals, on the other hand, are difficult to transport to aerial tissues. Because of the negative effect on plant development, phytoremediation efficiency decreases as contamination concentration rises. For instance, Cai et al. (2010) found that the degradation rate of petroleum hydrocarbons (PHCs) by *Impatiens balsamina* in soils containing 5000 mg kg^1 was three times higher than in soils containing 40,000 mg kg. Similarly, Chinese cabbage (*Brassica pekinensis* L.) had a substantially higher Pb translocation factor in soils with an initial Pb concentration of

500 mg kg^1 than in soils with an initial Pb concentration of 1500 mg kg^1 (Liu et al. 2010). According to Alori and Fawole (2017), the efficiency of microbial-assisted phytoremediation can be affected by the abiotic factors such as temperature, aeration, soil pH, cation exchange ability (CEC), soil organic matter quality, soil sorptive capacity, and redox potential. Temperature in the range of 5–30 °C and pH in the range of 5–8 have been found to affect microbial-assisted phytoremediation (Diels and Lookman 2007; Grundmann et al. 2007). In a study conducted by Goux et al. (2003), the phytoremediation efficiency of two microbial consortia on atrazine was significantly affected by pH and soil organic matter content. It was found that atrazine was effectively degraded by the consortia at pH >7. However, only one consortium degraded atrazine at pH 6.1. The microbial inoculants were ineffective at pH 5.7 due to its interaction with organic matter. An appropriate plant–bacteria partnership is the key to successful remediation of polluted soils (Khan et al. 2013).

Plants used in the remediation process must be contaminant-tolerant, fast-growing, and produce a lot of biomass. They should also be easy to harvest. Essentially, for the establishment of rhizosphere microorganisms, plants recruited for the remediation must have extensive tap root systems with a good ability to accumulate contaminants and must be able to thrive in new locations with a wide range of climatic conditions (Seth 2012). Choden et al. (2020) reported that growing *Ocimum gratissimum* alongside *Pseudomonas putida* in co-contaminated soil would result in simultaneous phytostabilization of Zn and TPH removal under natural environmental conditions. Studies have shown that microorganisms can render tolerance to plants from contaminant toxicity and enhance the degradation of organic compounds in co-contaminated soils (Zhang et al. 2009). Several plant species have been described and experimentally confirmed for the restoration of land polluted with heavy metals, radionuclides, bombs, and pesticides (Kennen and Kirkwood 2015). Many plant species have been found to be capable of accumulating and translocating high levels of DDT and its metabolites. White et al. (2003) reported that some species of the genus *Cucurbita* can absorb 4.4 0-DDE metabolites in their root system and transfer into the shoot via its unique mechanism. While some plant species can accumulate high levels of DDT metabolites in their roots, others move them to their shoots (Mitra and Raghu 1989; White and Kottler 2002; Nwoko 2010; Nurzhanova et al. 2013). Bacterial strains of *Rhodococcus* have been found to be capable of degrading organochlorine and organophosphorus pesticides (Cycoń et al. 2017). More than 90% of 4.40-DDE was used by *Bacillus vallismortis* after 21 days of inoculation in liquid medium (Satsuma and Masuda 2012). Abhilash et al. demonstrated that inoculation improves phytoremediation efficacy (Abhilash et al. 2011a, b). The presence of *Staphylococcus cohnii* subspecies ureolyticus in lindane-spiked soil (20 mg kg^1) improved rhizoremediation ability in *Withania somnifera*. Switchgrass-treated soil with *Burkholderia xenovorans* strain LB400 performed better than switchgrass-treated soil alone for complete polychlorinated biphenyl elimination (Liang et al. 2014). Plants inoculated with an active and tolerant microbial population can boost growth and speed up the process of cleaning pesticide-polluted soils. The interaction of phytoremediators with plant growth-promoting rhizobacteria (PGPR), primarily *Bacillus* and *Pseudomonas* species, can promote plant growth and contaminant bioavailability. Plant biomass has been reported to increase following *Bacillus* (Babu et al. 2013), *Pseudomonas* (Agnello et al. 2016), and *Serratia* (Dong et al. 2014) inoculation with the production of 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase. This is due to the fact that ACC deaminase can reduce the production of ethylene, which inhibits plant growth (Chang et al. 2014). In pot experiments, *Azospirillum brasilense* inoculation accelerated the tolerance and growth of plant roots of *Festuca arundinacea* in soils contaminated by PAH (Huang et al. 2004). Previous research has shown that tobacco (transgenic plant) degrades methyl parathion at a rate of 99% after 14 days of growth. It was reported that a bacterial organophosphorus hydrolase (OPH) gene was expressed in tobacco plants to decontaminate organophosphorus pesticides. Plant enzymes such as peroxidase, peroxygenases, glutathione-S- transferases, cytochrome P450, carboxylesterases, O- and N- malonyl transferase, and O- and N- glycosyltransferases are involved in the phytotransformation of xenobiotics in plant cells (Karavangeli et al. 2005). Transgenic plants have also been investigated for the remediation of herbicide-polluted soils. It has been successful in developing herbicide-tolerant transgenic plants, such as rice plants augmented with cytochrome P450 (CYP) for atrazine removal. An effective removal of alachlor in poplar by introduced g-glutathione synthetase gene has been demonstrated. Introduction of bacterial genes such as atrazine chlorohydrolase can increase root mass through production of bacterial 1- aminocyclopropane-1-carboxylate deaminase (Abdel-Shafy and Mansour 2018).

19.6 Myco- and Phycoremediators

Microorganisms play a significant role in the bioremediation of degraded land. To eliminate undesirable effects of pesticides from the environment, bioremediation using microorganisms has been applied extensively. Rapid multiplication and efficient enzymatic pathways enable them to eliminate and modify various environmental pollutants (Antizar-Ladislao et al. 2008). Biostimulation and bioaugmentation can further enhance the bioremediation potential of microorganisms. Factors alter the growth and metabolism of the bioremediators and hence the biodegradation efficiency includes temperature, pH, water potential, oxygen and substrate availability as shown in (Fig. 19.5). Bioremediation using fungi and algae is termed myco- and phycoremediators. Myco-remediation plays a key role in the degradation of xenobiotic compounds like petroleum hydrocarbons, polychlorinated biphenyls, and pesticides (Goyal and Basniwal 2017). Fungi possess robust morphology, diverse metabolic capacity, and powerful enzymatic system for the detoxification of various toxic pollutants (Deshmukh et al. 2016). As evidenced by Kurnaz et al. (2009) significant quantities of organic pollutants can be removed by fungal biomass from aqueous solution by adsorption.

Mycelium in fungi is said to help them penetrate deep into the substrate and colonize quickly (Reddy and Mathew 2001; Fragoeiro and Magan 2008). They can use

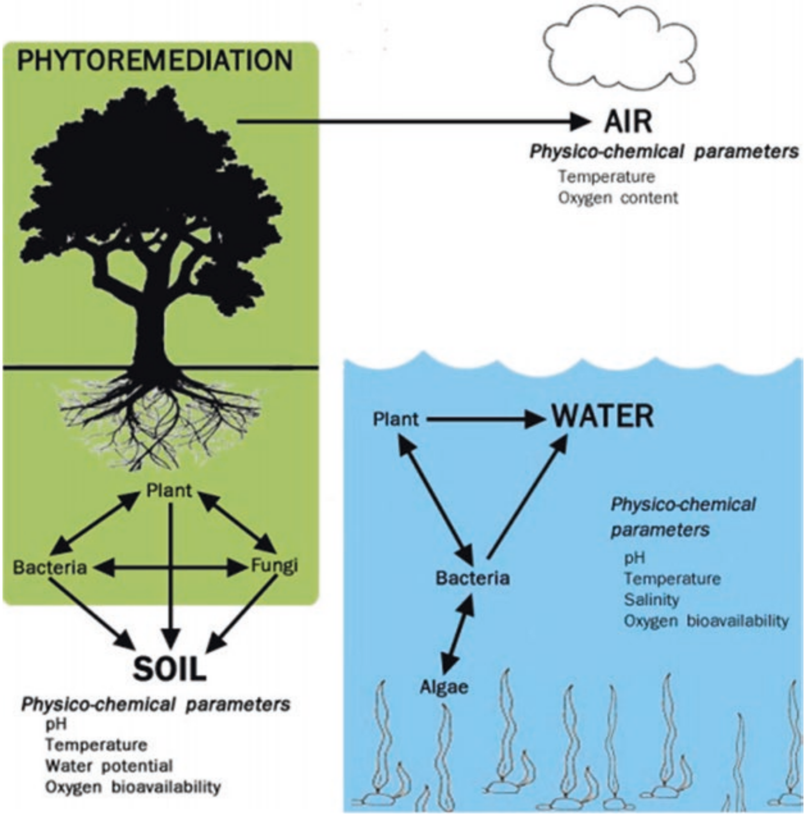

Fig. 19.5 Factors affecting biodegradation and bioremediation in soil, water, or air (adapted from Velázquez-Fernández et al. 2012)

organic compounds as a growth substrate because of the extended hyphae network (Harms et al. 2011; Chen et al. 2012). Fungi are preferred for pesticide remediation because their hyphae make pesticide molecules easily accessible through micropores, increasing the rate of degradation and enhancing nutrient and water availability to the plant (Huang et al. 2008) (Fig. 19.6).

This increases its physical, mechanical, and enzymatic contact with the environment. Fungi can thrive under extreme environmental conditions such as extremes of temperature, pH, and moisture levels (Gadd and Gadd 2001). Despite being less studied, findings show that fungi secrete enzymes such as peroxidases, dioxygenases, and oxidases for pesticide degradation in soil rather than cytochrome P450 (Aust 1995). Pentachlorophenol biodegradation is mediated by fungal peroxidases and dioxygenases (Rüttimann-Johnson and Lamar 1996; Sun et al. 2011). Adequate biodegradation of endosulfan by *Phanerochaete chrysosporium* and *Fusarium ventricosum* has been reported by Kullman and Matsumura (1996); Siddique et al. (2003), respectively. *P. chrysosporium* and *F. ventricosum* are members of soil

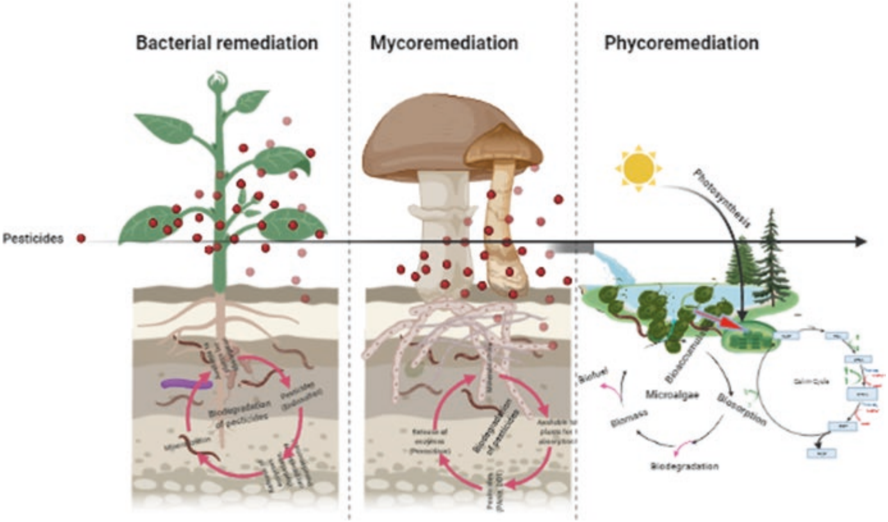

Fig. 19.6 Role of plants, bacteria, fungi, and algae in bioremediation (Created with BioRender.com)

microbial communities. Some examples of biotransformation enzymes produced by fungi like *P. chrysosporium*, *Pleurotus ostreatus*, *Ganoderma australe,* and *F. ventricosum* include lignin peroxidase, laccase, and dichlorohydroquinone dioxygenase. In another study with straw cultures, within 14 days of incubation, *P. chrysosporium* could degrade 91% of the herbicides (Pointing et al. 2000**;** Alves et al. 2004) combination of plant *Saccharum* and yeast *Candida* VITJzN04 resulted in fast and efficient remediation of lindane (100 mg/kg) in a soil microcosm experiment. Notably, *Candida* sp. demonstrated plant growth-promoting effect due to its ability to solubilize insoluble phosphates in soil and via production of growth hormones which had positive influence on the growth of the experimental plant (Salam et al. 2017).

Saprotrophic fungi, followed by white rot fungi, soft rot fungi, and brown-rot fungus, have showed enzymatic transformation of recalcitrant substances (Wu et al. 2015). *P. chrysosporium*, *Trametes hirsutus*, *Phanerochaete sordida*, *P. ostreatus*, *Pleurotus*, and *Cyathus bulleri* have all been found to breakdown lindane, diuron, and other resistant pesticides (Jauregui et al. 2003; Sagar and Singh 2011). Commonly, during pesticide degradation, fungi introduce structural changes by attacking on functional groups. Badawi et al. (2009) reported that certain fungi such as Ascomycetes, Basidiomycetes, and Zygomycetes use processes like polar hydroxylation, demethylation and dehydrogenation, deoxygenation, and esterification, for pesticide degradation (Pinto et al. 2012; Deng et al. 2015). A mixed population/consortia of different fungi can degrade different pesticides faster than a monoculture and improve survival in a hostile environment (Maqbool et al. 2016).

In contrast, various species of algae have been studied in the aquatic environment for pesticide remediation. Phycoremediation is the use of macro/microalgae to remove contaminants from the environment (Goyal and Basniwal 2017). The ability of microalgae to remove pollutants has been demonstrated for the treatment of wastewater (Rawat et al. 2011) and brewery effluents (Mata et al. 2012). When compared to conventional treatment methods, phycoremediation has been shown to be one of the most effective and ecologically friendly wastewater treatment technologies (Clarens et al. 2010; Wijffels and Barbosa 2010). Algae, whether free or immobilized, can be used for bioremediation of organic and inorganic compound-polluted wastewater. Microalgae have been successfully used in treatment technologies to remove nitrogen, phosphorus, and chemical oxygen demand from industrial effluents, either as single species (Voltolina et al. 2005) or in consortia (Bhakta et al. 2015; Tarlan et al. 2002). Dwivedi (2012) demonstrated that microalgae can remove heavy metals from contaminated wastewater. *Chlamydomonas* sp., *Chlorococcum* sp., *Chroococcus* sp., *Desmococcus* sp. and *Dactylococcopsis* sp. are among the algal species identified for xenobiotic compound degradation (Sivasubramanian et al. 2010). Comparatively, microalgae have higher potential (40–50%) for CO_2 sequestration (Chisti 2007; Ng et al. 2017) than terrestrial plants due to its higher photosynthetic efficiency (Chen et al. 2015a, b).

Furthermore, Mata et al. (2010) concluded that microalgae can adapt to hostile environmental conditions and grow efficiently in stress conditions. Oxygen production by microalgae can assist bacterial growth and improve pesticide degradation in contaminated ecosystems (Munoz and Guieysse 2006) via bioaccumulation and biosorption (Chojnacka 2010). Biosorption, unlike bioaccumulation, does not involve energy from the living system to absorb contaminants from the surroundings (Velásquez and Dussan 2009). It uses both dead and living species to remove toxins from polluted ecosystems (Aksu 2005). Microalgae can bioaccumulate pesticides and turn them into non-toxic compounds in a pesticide-degraded climate, according to studies (Rath 2012). Biosorption by blue green algae seems to have a distinct benefit over other types of environmental restoration, according to the findings. According to Parameswari et al. (2010), they are cost effective, selective, and simple to operate when treating large amounts of wastewater. Thies et al. (1996) reported that the unicellular green alga *Chlorella fusca* var. *vacuolata* could biotransform the herbicide Metfluorazon via a CYP. To learn more about algae's capacity as bioremediators, Jin et al. (2012) confirmed bioaccumulation and biodegradation of herbicide prometryne by alga *Chlamydomonas reinhardtii*. Microalgal metabolism is influenced by biotic factors such as microbial load, including competing pathogens, as well as abiotic factors such as nutrients, pH, and CO_2. Furthermore, when using algae as bioremediators, biomass overproduction can be a limiting factor (Velázquez-Fernández et al. 2012).

19.7 Pesticide Scenario of South Asian Countries

Pesticides are generally acknowledged as one of the most powerful and protective methods for preventing crop loss and disease in humans. When used properly, many pesticides are safe and effective, but they must be used with caution. A number of pesticides are effective in eradicating pests in agriculture. However, the disadvantages often outweigh the benefits. The use of pesticides is a cause of concern for environmental health and global peace. According to the World Health Organization, pesticides infect 3,000,000 people each year, resulting in up to 220,000 deaths, mostly in developed countries (Dixit et al. 2019). Humans, especially infants and children, are at high risk of pesticide-related harm due to pesticides' non-specific nature and poor implementation. Pesticide contamination is a concern for approximately 2.2 million people, the majority of whom live in developing countries. Pesticides have a wide range of health effects on humans, affecting any organ and system in the body. Ingestion, inhalation, and skin exposure are all ways pesticides penetrate the human body, but the majority of humans are affected by pesticide-contaminated food (Dixit et al. 2019). Increased pesticide inputs clearly have a negligible impact on overall farm production. Pesticide use, on the other hand, causes three million poisonings, 220,000 deaths, and 750 thousand chronic diseases worldwide each year. The vast majority of these incidents occurred in developed countries. Furthermore, it is estimated that these developed countries use only one-fifth of the pesticides used globally, and the number of pesticide-related deaths is further underestimated because many cases go unreported. The chemical affects a large number of farmers, millions of other people living in agrarian communities, and an uncountable number of consumers. Pesticide usage in South Asian countries and other countries is compared by inhaling contaminated air, drinking contaminated water, and consuming contaminated food (Atreya et al. 2011). One aspect of risk management is the isolation and characterization of resistant mutations in model organisms or target pathogens. With the benefit of hindsight, it is fascinating to consider how such experiments could have aided in predicting the likelihood of major fungicide findings. Pathogens like *Sphaerotheca fuliginea* (Schlecht.) Pollacci and *B. cinerea* developed resistance to benzimidazoles in a matter of years. Prior to the commercialization of new fungicides, it is now standard practice to determine the number of sensitivities found in essential pathogen species. Insecticides, especially those with narrow spectra of activity or activity directed on pests with a history of resistance issues, are increasingly subjected to similar practices. Laboratory trials, such as the identification of target sites and metabolic degradation pathways, mutagenesis, computational models, and cross-resistance tests, as well as field research, such as physiological sensitivities and anti-resistance strategy evaluation, all play a role in such assessments (Jutsum et al. 1998).

19.8 Current Research and Advances in Pesticide Bioremediation in the Region

The remediation for the clean up of pesticide-contaminated sites such as land and groundwater is vital to ensure good public health, healthy productive soils, and safe drinking water. Rodrigo et al. (2014) provided a comprehensive overview of electrochemically assisted pesticide remediation, the electro-fenton process, which produces hydrogen peroxide electrochemically in situ. One of the benefits of using the Fenton process to oxidize pesticides is that the oxidation is completed with few toxic intermediates in the processed product.

Thailand, North India, Pakistan, and Vietnam are among the Asian countries that use pesticide remediation techniques. Composting wastes is a quick procedure that can be carried out anywhere in the world. One issue with pesticide composting is the degree to which the pesticide degrades during the composting process. The product's toxicity after composting should be assessed. There is some beneficial dilution of pesticides in soil as manure and other wastes are added to the compost. Another method is land farming of soils containing pesticides which requires spreading of amendments in upper soil zone that is designed for bioremediation of the pesticide. The development of in situ bioremediation for pesticides has made considerable progress. Phytoremediation, bioremediation by indigenous plants, and bioaugmentation are the three broad categories of these techniques. Table 19.2 lists a few research projects from the countries of South Asia. In several areas, using plants has been proven helpful in the remediation of pesticides polluted sites. Where there is vegetation in the polluted soil, substrates from the roots promote pesticide degradation near the roots, enhancing microbial growth and the size of the active microbial population. Beneficial genes are provided by bacteria and fungi in the root region, and they play an important role in pesticide biodegradation. Some pesticides are taken up by plants and converted by enzymes in the cell. Pesticide-degrading microbes from various microbial classes, such as bacteria, fungi, actinomycetes, and algae, were discovered to aid in pesticide bioremediation (Hussain et al. 2009). Bacteria such as *Bacillus* spp., *Burkholderia* spp., *Klebsiella* spp., *Pseudomonas* spp., and fungi such as *Aspergillus* spp., *Phanerochaete chrysosporium*, *Trichoderma* spp., white rot fungi, and algae such as *Chlamydomonas* and marine *Chlorella* are among the microorganisms that can degrade pesticides. Mineralization and co-metabolism are two major reactions in pesticide degradation. Many factors influence pesticide degradation, including the type of pesticide, the type of microbe, the temperature, humidity, and acidity of the environment. Plasmid-located genes typically encode a large number of enzymes that degrade a wide range of pesticides. Horizontal gene transfer from degradative plasmids, alteration of substrate specificity, or altered control of pre-existing enzymes can all be used to obtain pesticide-degrading microbes in soil. Genetically engineered rhizobacteria could be produced to increase bioremediation of contaminants and pesticides. These recombinant microbial communities could be very valuable in the bioremediation of pesticides in the environment.

Table 19.2 Showing list of organisms which are used for bioremediation from different published sources could be included between 2010 and 2021. *NA* Not Available

Country	Research focus	Pesticides	Organisms used for bioremediation	Author/s
Bangladesh	Efficacy of soil-borne Enterobacter sp. for carbofuran degradation: HPLC quantitation of degradation rate	Carbofuran	*Enterobacter* sp.	Ekram et al. (2020)
	Isolation and partial characterization of organophosphate pesticide-degrading bacteria from soil sample of Noakhali, Bangladesh degradation	Organophosphate	*Pseudomonas aeruginosa*, *Bacillus subtilis*	Reza et al. (2019)
	Isolation and identification of pesticides degrading bacteria from farmland soil	Chlorpyrifos, cypermethrin, fenvalerate, and trichlopyr butoxyethyl ester	*Achromobacter spanius*, *Diaphorobacter, Polyhydroxybutyrativorans*	Rahman et al. (2018)
	Selective isolation of a gram negative carbamate pesticide-degrading bacterium from brinjal cultivated soil	Carbamate	*Pseudomonas* sp.	Sharif and Mollick (2013)

(continued)

Table 19.2 (continued)

Country	Research focus	Pesticides	Organisms used for bioremediation	Author/s
India	Pesticide-degrading bacteria from polluted soil are isolated, characterized, and identified for bioremediation.	Chlorpyrifos and malathion	*Kocuria assamensis*	Mehta et al. (2021)
	Bioremediation of pharmaceuticals, pesticides, and petrochemicals with gomeya/cow dung	Chlorpyrifos, cypermethrin, fenvalerate, and trichlopyr butoxyethyl ester	Cow dung slurry	Randhawa and Kullar (2011)
	Bioremediation of organophosphorus pesticide phorate in soil by microbial consortia	Phorate organophosphate	*Brevibacterium frigoritolerans*, *Bacillus aerophilus,* and *Pseudomonas fulva*	Jariyal et al. (2018)
	Residues of endosulfan in surface and subsurface agricultural soil and its bioremediation	Endosulfan	*Bordetella petrii* I GV 34 (NCBI Accession no. KJ022624), B. petrii II GV 36 (NCBI Accession no. KJ022625) and *Achromobacter xylosoxidans* GV 47 (NCBI Accession no. KJ022626)	Odukkathil and Vasudevan (2016)
	Bioremediation of single and mixture of pesticide-contaminated soils by mixed pesticide-enriched cultures	Lindane, methyl parathion, carbofuran	*Bordetella petrii* I GV 34 (NCBI *Pseudomonas aeruginosa*, *Bacillus* sp., *Chryseobacterium joostei*, and *Klebsiella pneumonia*	Krishna and Philip (2011)
	Comparative bioremediation potential of four rhizospheric microbial species against lindane	Lindane	*Kocuria rhizophila*, *Microbacterium resistens*, *Staphylococcus equorum,* and *Staphylococcus cohnii*	Abhilash et al. (2011a, b)
	Comparative bioremediation potential of four rhizospheric microbial species against lindane	HCH, lindane	*Sphingomonas* strains	Manickam et al. (2010)

(continued)

Table 19.2 (continued)

Country	Research focus	Pesticides	Organisms used for bioremediation	Author/s
Pakistan	Enhanced remediation of chlorpyrifos from soil using ryegrass (*Lolium multiflorum*) and chlorpyrifos degrading bacterium *Bacillus pumilus* C2A1	Chlorpyrifos	*Lolium multiflorum* (rye grass) and *Bacillus pumilus* C2A1	Ahmad et al. (2012)
	Enhanced remediation of chlorpyrifos by ryegrass (*Lolium multiflorum*) and a chlorpyrifos degrading bacterial endophyte *Mezorhizobi*um sp.	Chlorpyrifos	*Lolium multiflorum* (rye grass) and *Mezorhizobium* sp.	Jabeen et al. (2016)
Sri Lanka	Isolation of Pseudomonas aeruginosa, a potential petroleum hydrocarbon degrading bacterium from wastewater in Sri Lanka	Petroleum hydrocarbons	*Pseudomonas aeruginosa*	Perera et al. (2013)

19.9 Challenges and Way Forward

Bioremediation technique is considered an environmentally acceptable and economically viable alternative to traditional pesticide abatement approaches. Although bioremediation is perceived more environment friendly than conventional remediation technologies, the over-optimistic speculations must be tested under in contaminated fields. Studies must be done to test the efficiency of the bioremediation technique to different groups of pesticides in several field and environmental conditions to examine the conditions favorable for biodegradative microbe or microbial population. Reportedly, research on its success at the field scale is limited due to the relatively long-time requirement, which can be attributed to the slow rate of plant growth in contaminated environments due to nutrient and water scarcity. Organic and inorganic contaminants have direct toxic effects on plant growth in co-contaminated soils. The inability of plant roots to penetrate the soil and access pollutants is a significant constraint. Plants that accumulate contaminants in their harvestable tissues pose a risk of contaminants entering the food chain through animal consumption of plants (Juwarkar et al. 2010; Rayu et al. 2012).

One of the immediate concern of the bioremediation technology is the employment of organisms, its nature and strategy for survival which requires some type of environment modification that suits their need. To encourage the organisms to uptake or degrade pollutants, some of the practices include using low concentration of pollutants and enhancing metabolic pathways of bacteria and fungi for the digestion of pollutants by adding oxygen or fertilizer.

Extensive scientific studies have shown the success of bioremediation under laboratory conditions, however when done in situ, the success is not guaranteed. Toxic level of pollutants can have adverse impacts on other microorganisms although simple compounds and metals can be phytoaccumulated by the potential phytoremediators. The organisms do not rely on the pollutant diet when other sources of nutrients are available in the environment. Furthermore, the introduction of non-native organisms and genetically modified organisms has the potential to disrupt the environment. Introduction of non-native or genetically altered bioremediation organisms or the "super strains" to degrade the pesticide at a faster rate can cause environmental disturbance more the damage done by the pollutant alone (Singh 2008).

Pesticides and polyaromatic hydrocarbons in contaminated soil and their bioremediation were the main focus of research among the organic pollutants, according to a review of several bioremediation studies. While most bioremediation strategies rely on the intrinsic ability of some bacteria and plants to detoxify pesticides, the pollutant's bioavailability was one of the key constraints (Odukkathil and Vasudevan 2013). Less bioavailability of pesticides can be attributed to unequal spatial distribution of microorganisms and pesticides, as well as the retardation of substrate diffusion by the soil matrix (Harms and Bosma 1997), and pesticide solubility (Harms and Zehnder 1995) can render bioremediation ineffective both in situ and ex situ (Harms and Zehnder 1995). The efficiency of pesticide bioremediation is dependent on the nature of the organisms, the enzyme involved, its concentration and availability, and finally the survival of microorganisms. An improvement in the bioremediation strategies can be made by increasing the bioavailability of the pesticides. Understanding the pesticide metabolism in microbes is equally essential.

Soil contamination has become more complex and diverse as a result of climate change-induced environmental stress. This necessitates the identification and characterization of microbes capable of surviving in harsh environments, such as strains resistant to salinity, alkalinity, drought, and/or extreme temperature. At the Asia and Pacific Plant Protection Commission (APPPC) Regional Workshop on Enhancement of Regional Collaboration in Pesticides Regulatory Management, lack of expertise and capacity to conduct risk assessment of pesticide was reported to be a challenge in almost all countries in Asia (FAO 2012; FAO/WHO 2013). Because risk assessment is expensive and technical, a lack of financial and human capacity in developing countries impedes risk assessment. Governments and industries are hesitant to invest large sums of money to clean up pollution because bioremediation technologies are labor intensive, time consuming, and relatively expensive.

Despite several limitations in bioremediation practice, there is enormous potential to improve bioremediation. Understanding the genetics and biochemistry of the desired microbe, its survivability under environmental stress, and the associated environmental impacts is critical for reducing the environmental impact of pesticides. The selection of microbes with varying degradation abilities may result in increased bioremediation potential (Yang et al. 2020). The development of transgenic and recombinant bacterial strains has the potential to boost phytoremediation and treat multiple pollutants in a variety of environments (Feng et al. 2017). One of the most important aspects of bioremediation is metabolic engineering, which has produced some promising results with effective pathways and superior catalytic abilities on recalcitrant pollutants. Rojo et al. (1987) demonstrated that a particular *Pseudomonas putida* strain that employs enzymes from different organisms could effectively degraded chloro and methyl-aromatics. Lee et al. (1995) reported an improved biodegradation rate of benzene, toluene, and p-xylene by another *P. putida* strain via a combination of tod and tol pathways. Although metabolic pathway engineering can result in the development of engineered microorganisms with improved tolerance to environmental stress (Marconi et al. 1997), the use of genetically modified organisms is limited by the risks associated with uncontrolled proliferation of introduced GEMs (Genetically Engineered Microorganisms), horizontal gene transfer, and low public acceptability (Velkov 2001; Singh 2010). To overcome such constraints, plant microbial remediation strategies have been used. To address the difficult remediation problem, a novel remediation technology based on customized plant systems known as designer plants has been proposed. Plants' ability to remove inorganic pollutants and soil microbes' ability to remove organic pollutants can be combined (Abhilash et al. 2012), resulting in the simultaneous removal of heavy metals and organics. In the remediation industry, such non-transgenic approaches with multi-purpose phytoremediation efficacy hold a lot of promise.

To address the limitation of biological means of pesticide bioremediation, field applications must be performed at various locations rather than being limited to pot experiments. The controlled conditions in laboratory experiments must mimic and stimulate natural conditions such as climatic, weather, and pollutant conditions (aging). Consideration of secondary metabolites of organic pollutants is vital as certain metabolites have been reported to have higher toxicity and longer half-life than the original pollutants. The final treatment of plants and microbes used for remediation must be prioritized to avoid secondary pollution caused to changes in environment and death of microbes.

Bioenergy production, phyto-mining, papermaking, and wood-processing are examples of post-harvest management options for the resulting biomass. Understanding the genetics and biochemistry of desired microbes, as well as selecting multi-member microbial consortia through elective enrichment or chemostat enrichment, may assist in the rapid mineralization of pesticides. Besides soil, river water is polluted by pesticides to some extent. This is due to the erosion of pesticides from agricultural fields due to the excessive use of pesticides in agriculture fields. Future studies must focus on remediating the polluted river sites using common isolated microorganisms that have been proven effective in the terrestrial environment.

With advancing times, several bioremediation treatments systems have been devised and employed for the treatment of various pesticide-polluted sites. However, every treatment, including biological restoration, has its own set of restrictions. The biological remediation of pollutants has resulted in inefficient removal of pollutants that is not close to environmentally acceptable values due to a lack of field application and validation. As a result, potential researchers are becoming less interested in biological treatment options. Traditional bioremediation approaches combined with advanced biotechnological technologies can enhance efficiency and reliability. According to Ward (2004), a mutualistic approach can reduce treatment timeframes for natural attenuation (which can take anywhere from 5 to 25 years), soil-composting treatment (which can take anywhere from 1 to 18 months), slurry phase systems (which can take anywhere from 1 to 12 months), and accelerated slurry phase systems (which only take 15 days).

According to reports, rapid progress has been made in the field of pesticide bioremediation in terms of finding and developing viable and adaptable strains using a combination of genetic engineering and advanced microbiological methods. Further investigations on the identification of biochemical pathway followed by the microbes for pesticide degradation under various environmental conditions and identification of important genes responsible for biodegradation are required. Finding the best conditions for specific microbial growth; the rate of pesticide consumption by microbes; specific microbes-specific pesticide interactions; process parameter optimization; bioreactor efficiency; and verification of natural, feasible, and porous packing media are all areas of interest. To address the current challenges, collaboration among genetic engineers, biochemists, environmental engineers, and microbiologists is critical to enhance current research and give new development directions in the required field (Sun et al. 2020).

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