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

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Abstract Environmental pollution is one of the prominent problems of the twentyfrst 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 effcient 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), diisopropylfuorophosphatase (DFPase), paraoxonase (PON1), SsoPox, organophosphate acid anhydrolase (OPAA).

Keywords Pesticides · Biological methods · Bioremediation · Enzymes

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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

Table 6.1 Pesticides, their characteristics and examples

Source: Duke [\(2018](#page-14-0))

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](#page-18-0)). 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](#page-1-0)). 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\)](#page-17-0). 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, fsh (Sharma et al. [2016\)](#page-17-1).

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\)](#page-2-0) with examples (Table [6.2](#page-2-1)).

Fig. 6.1 Type of pesticides based on the chemical composition

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

Table 6.2 Types of pesticides and their examples

Source: Huang et al. [\(2018](#page-15-0))

6.2 Organochlorine Pesticides

Organochlorine pesticides or chlorinated hydrocarbons are organic compounds consisting of fve 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](#page-13-0)).

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](#page-17-2)).

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\)](#page-16-0).

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 fsh. These pesticides are less toxic as compared to organophosphates and carbamates. Allethrin, cyfuthrin, cypermethrin, deltamethrin, and permethrin are the most used synthetic pyrethroid pesticides (Ortiz-Hernández et al. [2013](#page-17-2)).

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](#page-4-0)) 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 effcacy relies on optimization of environmental conditions, for instance, pH of the soil, temperature, moisture contents as well as microbial community (Chishti et al. [2013;](#page-14-1) Javaid et al. [2016\)](#page-15-1). Various microorganisms that have the potential to degrade pesticides are listed in Table [6.4.](#page-6-0)

Physicochemical		
methods	Characteristics	Limitations
Fenton process	Production of reactive hydroxyl radicals $($ OH) by oxidation of Fe ²⁺ ions in the presence of hydrogen (H_2O_2) , permanganate $(MnO4)$, 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 $TiO2$, 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

Table 6.3 Characteristics and limitations of different physicochemical methods

Table 6.3 (continued)

Table 6.4 Pesticide degradation by microorganisms

Pesticides Organophos

Pesticides	Types	Bacteria	References
Organochlorine	Endosulfan	Pseudomonas sp. TAH	Zaffar et al. (2018)
		Pseudomonas mendocina ZAM1	Mir et al. (2017)
		Stenotrophomonas maltophilia Ozdal et al. (2017) OG ₂	
		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)

Table 6.4 (continued)

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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](#page-14-14)). Several studies that reported pesticides degradation by fungi are listed in Table [6.5.](#page-9-0)

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 detoxifcation 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

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. (2010 _b)
	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)

Table 6.5 Pesticide degradation by fungi

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\)](#page-17-2). Enzymes involved in bioremediation were mainly oxidoreductases, monooxygenase, dioxygenases, carboxylesterases, phosphotriesterases, haloalkane

dehalogenases, haloalkane dehydrochlorinases, diisopropylfuorophosphatase, Paraoxonase (PON1), organophosphate acid anhydrolase (OPAA), carboxylesterases (Table [6.6\)](#page-10-0). Several enzymes that have been applied for the degradation of pesticides from polluted environments are present in Table [6.7.](#page-12-0)

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 $O2$ (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). (1)

Table 6.6 Enzymes and their characteristics

Table 6.6 (continued)

Source: Scott et al. [\(2008](#page-17-15)); Verma et al. [\(2014](#page-18-0)); Bhandari et al. [\(2021](#page-14-18)), Bhandari et al. [\(2021](#page-14-18)); Verma et al. ([2014\)](#page-18-0), Scott et al. ([2008\)](#page-17-15)

	Originating	Cofactor	Documented target	
Enzyme	species	requirements	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	$\overline{Fe^{2+}}$ 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 $(\gamma$ -isomer)	Scott et al. (2008)
LinB	Sphingomonas sp., Sphingobium sp.	None	Hexachlorocyclohexane $(\beta$ – and δ –isomers)	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
AtzA	Pseudomonas sp. ADP	$Fe2+$	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)

Table 6.7 (continued)

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 detoxifcation 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 effcacious nature. Various microorganisms (bacteria and fungi) are used in the removal of pesticides from contaminated sites. Bacterial degradation involves specifc genes and enzymes for the breakdown of functional groups present in the pesticides. In conclusion, although signifcant research has been done on the enzymes associated with the biodegradation of pesticides, further research in relevant environmental conditions is needed to confrm the ability of bacteria and fungi for large-scale decontamination. In addition, signifcant 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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