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REVIEW

Pesticide residues degradation strategies in soil and water: a review

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Abstract

The benefits of using pesticides globally to control pests come at the cost of their ubiquitous occurrence in the ecosystem. The uncontrolled use of pesticides in agricultural practices, manufacturing and food industries and in health sector not only contaminates the environment but also affects non-targeted organisms. There are various biotic and abiotic methods of transforming or removing pesticides, but they may give rise to harmful end products. In this article, various techniques such as photodegradation, phytodegradation and biodegradation used to remove or transform pesticides in the environment are discussed. The current study revealed that use of UV or sunlight to degrade pesticides on soil surface is an effective method, but the results may vary in the laboratory and field conditions. The plants absorb these chemicals from the soil and metabolize it into simpler forms by different processes such as phytovolatilization, phytostimulation, phytoextraction and rhizodegradation. The bioremediation process using microbes or soil microflora to degrade pesticides is a cost-effective technique till date. Actinomycetes and cyanobacteria are the most efficient degraders among the micro-organisms. Microbes possess different enzymes such as Glutathione S-transferases (GSTs), esterases and cytochrome P450 which are involved in the degradation process.

Keywords Biodegradation · Environmental pollutants · Photodegradation · Phytoremediation · Rhizodegradation

Introduction

Pesticides are considered as poisons which not only harm targeted pests but also affect humans, animals and environment. Their exposure to humans causes respiratory, reproductive, gastrointestinal, neurological disorders and even cancers in humans (Nicolopoulou-Stamati et al. 2016). People who are exposed to these pesticides include sprayers, production workers, mixers, formulators, loaders and agricultural farm workers. The workers who manufacture and prepare these pesticide formulations are at greater risks (Aktar et al. 2009). Living beings get exposed to pesticides through direct skin contact, inhalation or ingestion. The pesticides upon entering the human or animal body may get metabolized, excreted, stored or bioaccumulated (Nicolopoulou-Stamati et al. 2016; Stoytcheva 2011).

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Pesticides are chemical substances or biological agents that have been tremendously used in agricultural practices to kill, repel, prevent or control pests and to increase crop production. They are released intentionally into the environment to prevent various pests (Mahmood et al. 2016). They are mainly categorized according to their use such as to control insects (insecticides) or fungi (fungicides), control herbs/weeds (herbicides/weedicides) and control rodents (rodenticides) (Eddleston et al. 2002). Besides agricultural practices, manufacturing and food processing industries also release pesticides through their effluents into the environment. They are toxic and persistent organic pollutants that tend to bioaccumulate in the food chain; hence, there is a need to degrade them (Bapat et al. 2016; Cardeal et al. 2011; Vela et al. 2017).

The use of pesticides to mitigate pests has been increased to many folds in past few decades all over the world. Besides agricultural fields, many pesticides are also commonly used in homes such as in the form of powders, sprays and poisons for controlling rats, fleas, cockroaches, ticks, mosquitoes and bugs. The risks linked with the use of pesticides have exceeded their beneficial effects. Pesticides also affect and even kill or destroy non-targeted animals and plants along with the harmful targeted ones (Mahmood et al. 2016). Only a small amount of pesticides, i.e. less than 1% which is applied to control pests, may reach their target. By run-off, spray drift, off-target deposition and photodegradation, a large volume of pesticides is lost. The low concentrations of certain chemicals may not cause detectable effects in living organisms, but they may cause genetic disorders and physiological changes (Hernández et al. 2013; Bernardes et al. 2015).

Understanding of metabolism of pesticides in plants and micro-organisms is required for their safe development, efficient use and the development of bioremediation approaches for contaminated soil and water (Eerd et al. 2003). Pesticides biotransformation can happen through multi-stage procedures recognized as metabolism or co-metabolism. Co-metabolism is the biotransformation of an organic compound which is not used either as an energy source or as an organism's constituent element. Individual degradation–detoxification process responses consist of oxidation, reduction, hydrolysis and conjugation. Diversity of the metabolic pathway relies on the xenobiotic compound's chemical structure, organism, cultural circumstances, metabolic variables and controlling the activity of these biochemical pathways (Hoagland et al. 2001; Pileggi et al. 2020). Understanding of these enzymatic procedures has developed our knowledge of pesticide science, plant and microbial biochemistry and physiology, particularly ideas linked to pesticide mechanisms of intervention, strength, selectivity, tolerance and economic destiny. There are some basic similarities and distinctions between the metabolism of a plant and microbial pesticides. Abiotic degradation is caused by chemical and physical procedures such as photolysis, hydrolysis, oxidation, reduction and rearrangement of the pesticide (Eerd et al. 2003; Lushchak et al. 2018). Furthermore, pesticides may be biologically inaccessible due to compartmentalization that happens without changing the chemical structure of the initial molecule as a consequence of adsorption of pesticide molecule to soil and soil colloids. Enzymatic conversion, however, is by far the main path of detoxification, which is the consequence of biotic procedures facilitated by crops and micro-organisms. Pesticide metabolism can require a 3-phase method. In Phase I, oxidation, reduction or hydrolysis change the initial features of the parent compound to generally produce a commodity that is more water-soluble and usually less toxic than the parent. The second phase involves the combination of pesticide or pesticide metabolite with sugar, amino acid or glutathione, which increases water solubility and reduces toxicity compared to the pesticide of the parent. Phase II metabolite generally has little or no phytotoxicity and can be deposited in cellular organs. The final stage includes the conversion of Phase II metabolites into secondary conjugates which are non-toxic in nature (Hodgson 2012; Hatzios and Penner 1982).

Pesticide degradation by different methods

Pesticide residue degradation is accompanied by different methods such as by using physical, chemical and biological agents which degrades various insecticides, fungicides, herbicides, etc., into less bioactive degradation products. The main techniques used in the degradation of pesticide residues are photodegradation, phytodegradation and biodegradation.

Photodegradation

It is the process by which the photodegradable molecules get degraded by the absorption of photons especially, whose wavelengths are found in sunlight. It causes alterations in the materials/substances by oxidation and hydrolysis using sunlight and air (Yousif and Haddad 2013). Photodegradation of pesticides by photosensitized and photocatalytic methods is discussed by various authors as given in Table 1.

Mechanism of photodegradation of pesticides

There are numerous reports on the photodegradation of pesticides in the literature. However, only limited data are available on the mechanism of photolysis of pesticides in the natural environments. In this chapter, we have classified the photodegradation of pesticides into two categories, i.e. photosensitized and photocatalytic degradation.

Photosensitized degradation

Photosensitizer-mediated photodegradation involves absorption of light by a molecule in a photochemical process. In the photosensitization process involving redox reactions, the initial transfer of an electron or atom produces free radicals such as hydroxyl radical (·OH), but the oxidized or reduced sensitizers underwent various reactions to convert back to initial species (Fig. 1) (Burrows et al. 2002). Among all the other radicals and active oxygen species such as hydroperoxyl radicals, triplet oxygen, superoxide radical anions and organic peroxyl radicals, only the hydroxyl radical is the strongest oxidizing species which accelerates the process of pesticide oxidation yielding carbon dioxide, water and inorganic ions as final products (Bustos et al. 2019).

There are many studies on organic photosensitizers which accelerate the photochemical reactions, thus increasing the degradation rate. Lin et al. (2000) observed the photodegradation of Butachlor and Ronstar herbicides using diethylamine as photosensitizer under natural sunlight. The amine groups which act as photosensitizers are diethylamine, triethylamine and diethylphenylene diamine which are used to enhance the photodegradation rate (Lin

Table 1 Photodegradation of different pesticides

Pesticide	Pesticide category	Chemical formula	Background	Mode of action	Photodegradation method	References
Chlorpyrifos	Insecticide	$C_9H_{11}Cl_3NO_3PS$	Control insects in agricultural, residential and commercial settings	Inhibit the breakdown of acetylcholine (ACh), a neurotransmitter	Catalytic photodegradation	Muhamad (2010)
Propanil	Herbicide	$C_9H_9Cl_2NO$	Used against numerous grasses and broad-leaved weeds in rice	Inhibit photosynthesis and CO_2 fixation	Photocatalytic degradation over aqueous TiO_2suspensions; Photocatalyst Degradation of Propanil herbicide in water using different analytical methods	Konstantinou et al. (2001), Dhahir et al. (2011)
Fenamiphos	Insecticide	$C_{13}H_{22}NO_3PS$	Used as a systemic and contact insecticide against soil nematodes in golf greens and horticultural crops	Blocks the enzyme acetyl cholinesterase in the target pest. The enzyme regulates inter-cellular activity	Photolysis and photodegradation of Fenamiphos using UV light in absence and in presence of slurry titanium dioxide	El Yadini et al. (2013)
Metamitron	Herbicide	$C_{10}H_{10}N_4O$	Used in fodder beets, redbeets (beetroot and silverbeet) and sugar beet	Disrupt photosystem II, inhibit electron transport	Photodegradation of Metamitron on TiO_2; photocatalytic degradation of Metamitron in ZnO water suspensions; Photocatalytic degradation of Metamitron using CeO2 and Fe/CeO2	Macounová et al. (2001), Mijin et al. (2009), Tambat et al. (2018)
Paraquat	Herbicide		Used for weed and grass control	Inhibit photosynthesis	Photocatalytic degradation in the presence TiO_2 nanostructure thin films; Photocatalytic degradation using nano-sized Cu- TiO_2/SBA-15; Photocatalytic degradation using TiO_2 nanoparticles synthesized from the extract of *Coffea arabica* L.; Titanium dioxide assisted photodegradation	Zahedi et al. (2015); Sorolla et al. (2012), Phuinthiang and Kajitvichyanukul (2019)Florêncio et al. (2004)
Carbaryl	Insecticide	$C_{12}H_{11}NO_2$	Kills both targeted (e.g. malaria-carrying mosquitos) and beneficial insects (e.g. honeybees), as well as crustaceans	Disrupts the nervous system by adding a carbamyl moiety to the active site of the acetylcholinesterase enzyme, which prevents it from interacting with acetylcholine	Photodegradation of Carbaryl in acetonitrile solution	Yousef and El-Khatib (2007)

Table 1 (continued)

Pesticide	Pesticide category	Chemical formula	Background	Mode of action	Photodegradation method	References
Chlorimuron-ethyl	Herbicide	$C_{15}H_{15}ClN_4O_6S$	Emergent herbicide for weed control in soybean (both broad leaf weeds and sedges	Inhibits acetolactate synthase, which regulates plant growth	Phototransformation of Chlorimuron-ethyl in aqueous solution; Photolysis of Chlorimuron-ethyl on a soil surface under sunlight and UV light	Choudhury and Dureja (1996), Choudhury and Dureja (1997)
Atrazine	Herbicide	$C_8H_{14}ClN_5$	Used to prevent pre- and post-emergence broadleaf weeds in crops such as maize (corn) and sugarcane and on turf such as golf courses and residential lawns	Functions by binding tothe plastoquinone-binding protein in photosystem II, which animals lack. Plant death results from starvation and oxidative damage caused by breakdown in the electron transport process	Photodegradation of Atrazine by Ultraviolet Radiation in different conditions; Photodegradation of atrazine with visible light using water-soluble porphyrins as sensitizers; Photocatalytic degradation of Atrazine by heteropolyoxotungstates; Photocatalytic degradation of Atrazine herbicide with illuminated Fe + 3-TiO_2 nanoparticles	Shamsedini et al. (2015), Rebelo et al. (2007), Youssef et al. (2019), Shamsedini et al. (2017)
Thiophanate-methyl	Fungicide	C12H14N4O4S2	A fungicide effective against a broad spectrum of diseases in fruit, vegetables, turf and other crops including eyespot, scab, powdery mildew and grey mould. It has a role as an antifungal agrochemical	Inhibition of mitosis and cell division (Beta-tubulin assembly in mitosis)	Light induced degradation of the fungicide Thiophanate methyl in water	Kouras-Hadef et al. (2018)
Hydramethylnon	Insecticide	$C_{25}H_{24}F_6N_4$	Used for controlling social insects, such as ants or termites	Mitochondrial cytochrome-bc1 complex inhibitor	Phototransformation of Hydramethylnon in aqueous systems	Chakraborty et al. (1993)
Ethiofencarb	Insecticide	$C_{11}H_{15}NO_2S$	Useful in controlling aphids on hard and soft fruits and some vegetables	Ability to inhibit acetylcholinesterase (AChE) in the nervous system	Photodegradation of the pesticide Ethiofencarb in aqueous and non-aqueous media, by gas chromatography–mass spectrometry; Photodegradation of the carbamate insecticide Ethiofencarb on plant surfaces	Sanz-Asensio et al. (1999), Kopf and Schwack (1995)

Table 1 (continued)

Pesticide	Pesticide category	Chemical formula	Background	Mode of action	Photodegradation method	References
Propoxur	Insecticide	$C_{11}H_{15}NO_3$	Used against turf, forestry and household pests and fleas. It is also used in pest control for other domestic animals, anopheles mosquitoes, ants, gypsy moths and other agricultural pests. It can also be used as a molluscicide	Kill insects by reversibly inactivating the enzyme acetylcholinesterase	Photocatalytic degradation of aqueous Propoxur solution using TiO_2 and Hβ zeolite-supported TiO_2	Mahalakshmi et al. (2009)
Molinate	Herbicide	$C_9H_{17}NOS$	Used to control germinating broad-leaved and grassy weeds	Inhibition of lipid synthesis	Heterogeneous photocatalysis using two different types of the semiconductor TiO_2 as photocatalyst	Bizani et al. (2014)
Carboxin	Fungicide	$C_{12}H_{13}NO_3S$	Used as a seed treatment for control of smut, rot and blight on barley, oats, rice, cotton, vegetables, corn and wheat. It is also used to control fairy rings on turf grass	Inhibit succinate cytochrome c reductase in mitochondria	Photochemical degradation of Carboxin in the presence of humic substances and soil	Hustert et al. (1999)
Pentachlorophenol	Herbicide, insecticide, fungicide, algaecide and disinfectant	C_6Cl_5OH or C_6HCl_5O	Used in agricultural seeds (for non-food uses), leather, masonry, wood preservation, cooling tower water, rope and paper mills	Accelerates aerobic metabolism and increases heat production	Photodegradation of Pentachlorophenol catalysed by semiconductor particles; Photodegradation of Pentachlorophenol by sunlight in aquatic surface microlayers; Heterogeneous photodegradation of Pentachlorophenol in the goethite and hematite systems with oxalate under UVA illumination; Photodegradation of Pentachlorophenol using NiO-coupled NiTiO3 nanocomposites from layered precursor as photocatalysts	Barbeni et al. (1985), Chi and Huang (2004), Lan et al. (2010), Gao and Zhang (2012)

Table 1 (continued)

Pesticide	Pesticide category	Chemical formula	Background	Mode of action	Photodegradation method	References
Imidacloprid	Insecticide	$C_9H_{10}ClN_5O_2$	Used to control sucking insects, termites, some soil insects and fleas on pets	Interferes with the transmission of stimuli in the insect nervous system causing irreversible blockage of acetylcholine receptors	Photolytic decomposition of the insecticide Imidacloprid in HPLC grade water; Photodegradation of Imidacloprid in aqueous solution by the metal free catalyst graphitic carbon nitride; Photodegradation of Imidacloprid and Fipronil in rice–paddy water	Wamhoff and Schneider et al. (1999), Liu et al. (2015), Thuyet et al. (2011)
Procymidone	Fungicide	$C_{13}H_{11}Cl_2NO_2$	Used for killing unwanted ferns and nettles, and as a dicarboximide fungicide for killing fungi	Affect mitosis in susceptible fungi but the actual site of action has not been elucidated	UV–visible photodegradation of Procymidone; Photodegradation of the dicarboximide fungicide Procymidone on plant surfaces	Rifai et al. (2013), Schwack et al. (1995)
Trifluralin	Herbicide	$C_{13}H_{16}F3N_3O_4$	Used to control many annual grasses and broadleaf weeds in a large variety of tree fruit, nut, vegetable and grain crops	Inhibition of mitosis and cell division. Microtubule assembly inhibition	Photocatalytic degradation of Trifluralin in acetonitrile/water medium in the presence of titanium dioxide (TiO_2); Photodegradation of Trifluralin in natural waters and soils	Mir et al. (2014), Dimou et al. (2004)
Chlorothalonil	Fungicide	$C_8Cl_4N_2$	Used as a wood protectant, pesticide, acaricide, and to control mould, mildew, bacteria, algae. Typically used on peanuts, tomatoes, potatoes, lawns, turf and roses	Chlorothalonil reduces deactivates glutathione	Photodegradation of Hydroxychlorothalonil in aqueous solutions; Photodegradation of Chlorothalonil was studied in deionized and ground water with sunlight	Armbrust (2001), Peñuela and Barceló (1998)
Warfarin	Rodenticide	$C_{19}H_{16}O_4$	Rat poison	They act by binding to the enzyme vitamin K 2,3-epoxide reductase, thereby interrupting the cellular recycling of vitamin K	Visible light photodegradation of pharmaceutical pollutant, Warfarin by nano-sized SnTe	Vadaei and Faghihian (2018)

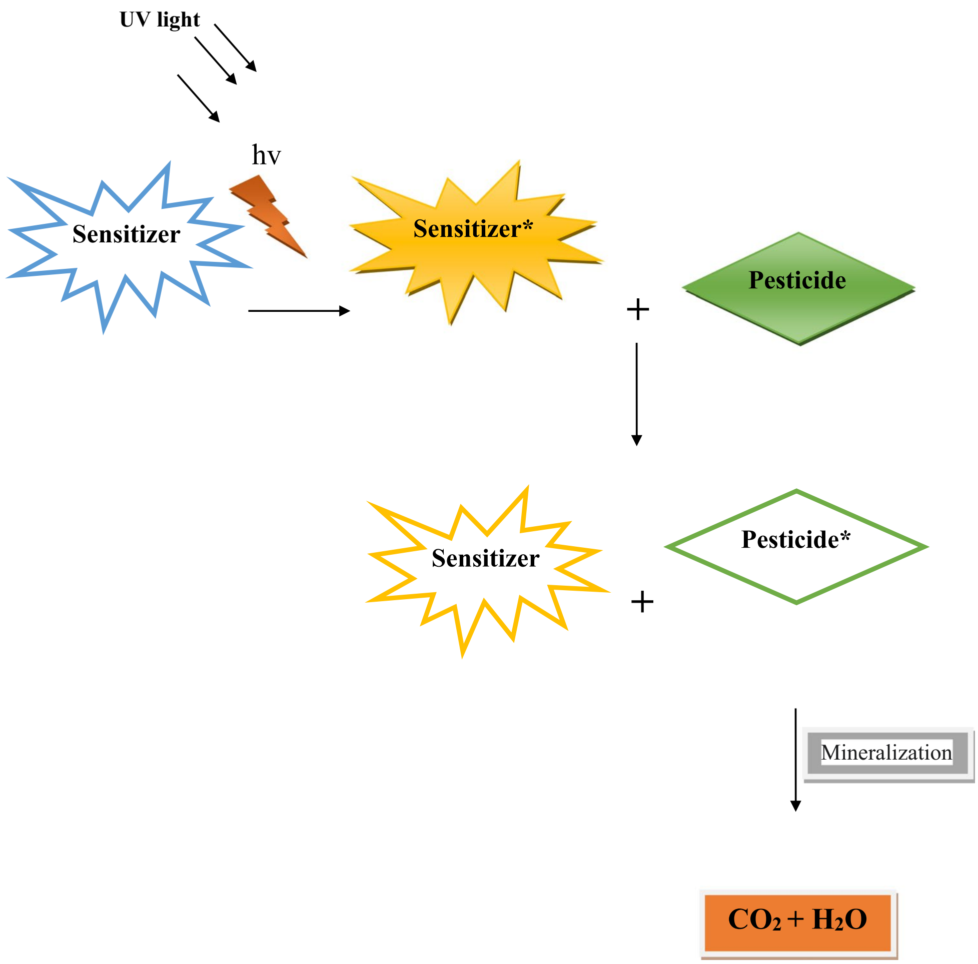

Fig. 1 Photosensitized degradation of pesticides (Figure modified from Burrows et al. 2002)

et al. 2000). In a study, Nayak et al. (2016) observed that degradation of Chlorpyrifos and Diuron was enhanced by the presence of 500 mM fructose as photosensitizer (Nayak et al. 2016).

Furthermore, Bielska et al. (2015) used a hybrid photosensitizer containing Rose Bengal embedded into the halloysite nanotubes. They used this photosensitizer to photodecompose the pesticide 4-n-nonylphenol (Bielska et al. 2015). Gatica et al. (2019) reported the photodegradation of herbicide Isoxaflutole using Riboflavin sensitizer by Fenton and photo-Fenton processes. They observed that only the photo-Fenton process degrades the Isoxaflutole efficiently (Gatica et al. 2019). Liang et al. (2017) studied the photodegradation of Fenvalerate, a synthetic Pyrethroid insecticide using UV light (Liang et al. 2017). Bustos et al. (2019) observed the photodegradation of Dichlorvos (DDVP) using simulated sunlight and dissolved oxygen. Humic acid acts both as an accelerator and inhibitor of Dichlorvos depletion in this photochemical reaction (Bustos et al. 2019).

Photocatalytic degradation

The photocatalytic process involves a catalyst such as TiO_2 to accelerate the degradation process of pesticides in combination with UV light. Due to high efficiency, high stability, low cost and non-toxic nature, titanium dioxide is considered as the best photocatalyst in the photochemical reactions (Fig. 2).

Abdennouri et al. (2016) in a study observed that the photocatalysts titanium dioxide and titanium pillared purified clay were efficient in degrading the pesticides (Abdennouri et al. 2016). Similarly, Jafaria et al. (2016) use the UVC and UVC/TiO_2 process in the photolytic and photocatalytic degradation of Diazinon in water. They observed that mineralization of Diazinon by photocatalytic process is higher than that of photolysis (Jafari et al. 2016). Gupta et al. (2015) observed the photocatalytic activity of $CoFe_2O_4$@TiO_2 nanocomposite for the photodegradation of Chlorpyrifos used to control pest insects. The results of the study revealed that nanocomposite exhibits a strong

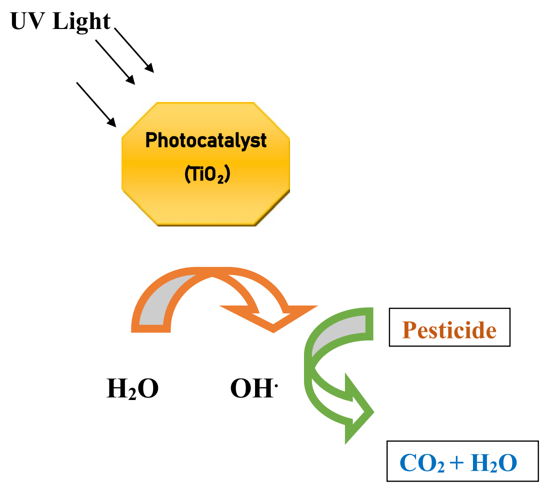

Fig. 2 Photocatalytic degradation of pesticides (Figure modified from Wang et al. 2016)

photocatalytic activity on the photodegradation of Chlorpyrifos (Gupta et al. 2015).

In another study, Peiter et al. (2017) investigated that Cu/CuO electrode acts as photocatalyst and can be used to generate electricity as well as in remediation of natural systems. They observed that pesticides Aminol and Connect were degraded up to 54.46 and 21.02% under UV light (Peiter et al. 2017). Cruz et al. (2017) studied the photocatalytic activity of GO–TiO_2 catalyst under UV–Vis light. They observed that it catalyses the photodegradation of pesticides such as Diuron, Alachlor, Isoproturon and Atrazine (Cruz et al. 2017). Similarly, Jonidi-Jafari et al. (2015) studied the photodegradation of Diazinon using photocatalyst ZnO–TiO_2 (Jonidi-Jafari et al. 2015).

Phytoremediation

Phytoremediation is plant use for bioremediation and has been less studied than methods based on bacteria. However, it has been shown to be more efficient to control soil, water and even air pollution than by bacteria. Plant uptake of pesticides is based on the physico-chemical characteristics of the compound, mode of execution, type of soil, environmental variables and species of plants. Plants use various mechanisms such as phytodegradation, phytoextraction, rhizodegradation, rhizofiltration and phytostabilization to remove pesticides from soil (Yan et al. 2020). In the last century, transgenic crops containing particular pesticide-degrading enzymes were created as the latest breakthrough in phytoremediation. The overexpression of genes engaged in the development, absorption or storage of particular pollutants in transgenic plants makes it possible to resolve some of the disadvantages of phytoremediation, such as elevated levels of pesticides or the storage of organic pollutants. Once pesticides are degraded to non-toxic metabolites or totally mineralized by particular transgenic plants, the crops can be securely disposed-off, while their domain activities have not yet been controlled owing to their potential environmental and biodiversity effects, and this approach may gain growing scrutiny in the close future (Ortiz-Hernández et al. 2013).

Factors influencing phytoremediation

There is a range of variables that govern uptake and degradation of pesticides in plants such as moisture content, pesticide concentration, type of soil and organic carbon. Some of them are given below:

Structure of pesticides

The chemical's composition performs a significant part in the design of its stabilization. A small change in the pesticide's composition causes a dramatic shift in its biotransformation and eventually affects phytoremediation. The attached alkyl or halogen group to a pesticide molecule makes it less bio-available and cannot be remediated by crops (Cork and Krueger 1991). Chlorinated pesticides are hard to phytoremediate due to their water-insoluble nature. After entry to roots, the pesticide molecules can be translocated to shoot through xylem. Therefore, the transportation of non-ionic pesticides differs significantly between species of plants and relies on the chemical properties (Namiki et al. 2018). The absorption and translocation of hydrophobic compounds are therefore restricted, and their phytodegradation is subsequently restricted. On the other side, the pesticide transformation by micro-organisms of the rhizosphere could lead to metabolites being uptake and translocated more effectively by crops. Consequently, any element that enhances the microbial activity in the rhizosphere should also improve the general effectiveness of phytoremediation of pesticides (Yan et al. 2020).

Pesticide concentration

The level of pesticide determines the phytoremediation achievements. When a pesticide's level reaches plant remediation capacity, it impacts the frequency of phytoremediation. Yu et al. reported that Butachlor takes 6318.0; 2919.9; and 10,823.2 days to decrease to half-life when present in non-rhizosphere, wheat rhizosphere and inoculated rhizosphere at 1.0 mg kg^1, 10 mg kg^{-1} and 100 mg kg^{-1} concentrations, suggesting that remediation is fully conditional on pesticide application frequency (Yu et al. 2003).

Soil moisture content, pH and temperature

Soil moisture is a significant parameter for pesticide diffusion and movement within crops. Pesticides indicate higher degradation as the moisture content rises, while the rate of degradation declines when the soil is dry. A study demonstrates that γ-BHC insecticide degrades more quickly in aquatic land than in moist and aerobic land (Racke et al. 1994). When the ground is moist or immersed, DDT is quickly transformed into DDD and stays permanent in dryland (Vidali 2001). Pesticide phytoremediation varies depending on pH of the soil which further depends on the charge that pesticide molecules carry. It manages the adsorption and transportation of pesticides within the plant's root and shoot. According to Mamy and Barriuso, when the pH of the soil reduces, it provides a favourable atmosphere for Glyphosate molecules that can be readily connected to the adverse loads of clay or plant root cells (Mamy and Barriuso 2005). Temperature is also an important factor in pesticide remediation. As temperature increases, pesticides readily dissolved in the aqueous phase which improves their availability to the microbes. Thus, the soil microbial communities may directly or indirectly facilitate the process of phytoremediation. Some pesticides are also seen to be volatized at greater temperatures. Low temperature, however, hampers the pesticide degradation. Research indicates that DDT shows faster degradation at temperatures above 40 °C (Guerin 1999).

Plant enzymes

Within plant cells, there are several plant enzymes that degrade pesticide molecule to simpler forms. Plant enzymes such as GSTs, cytochrome P450, peroxygenases, carboxylesterases, peroxidize and N-, O-glucosyltransferases can transform xenobiotic compounds in phytotransformation (Tripathy et al. 2014). In transgenic plants, the genes engaged in the degradation of pesticides are isolated from microbes and utilized to boost the rate of phytoremediation. In order to produce enzymes that degrade and biotransform pesticides quicker, this genetic engineering method enables crops to convey a specific gene more dominantly. A study indicates that production of cytochrome P450 reductase (YR) linked protein by transgenic potato plant through *Agrobacterium* gene conversion capable of degrading 7- ethoxycoumarin O-demethylation and Chlortoluron in concentrations greater than control crops (Inui et al. 1999).

Microbiology of soil

Some microbes such as bacteria and fungi have a symbiotic association with rhizosphere crops that increases the extraction of pesticides. These micro-organisms are essential as they accelerate the cycle of degradation. Rhizobacteria have escalated the uptake of Thiamethoxam and Acibenzolar-S-methyl by maize and tomato crops, as noted by Myresiotis et al. (2014) (Myresiotis et al. 2014).

Organic acids

Some researchers have indicated that the phytoremediation method is facilitated by organic acid exudates from crops. For example, the effect of weathered 2,2-bis(p-chlorophenyl)-1,1-dichlorethylene on abiotic desorption was investigated by White and Kottler with the concentrations ranged from 0.001 to 0.10 M. They also observed the extraction of polyvalent inorganic ions from the soil. The study results indicated that soil alteration with organic acids such as oxalic acid and citric acid improved the intake of *p,p'*-DDE (White and Kottler 2002).

Age and species of plant

The capacity of plants to remediate pesticides also relies on their age and species. Knuteson et al. (2002) observed that young crops (2-week-old crops) showed higher Simazine uptake (2-chloro4,6-bis(ethylamino)-1,3,5-triazine) as compared to one-month aged crops (Knuteson et al. 2002). Some experiments have shown that mature crops with comparatively higher biomass have accumulated more pesticides that account for their reduced activity (Tu et al. 2004). Similarly, Gawronski and Gawronska (2007) reported that numerous plant families especially *Brassicaceae*, *Fabaceae*, *Poaceae*, *Asteraceae*, *Chenopodiaceae, Salicaceae*, and *Caryophyllaceae* comprise multiple species which show great phytoremediation potential (Gawronski and Gawronska 2007).

There are five techniques for phytoremediation* (Peer et al. 2005*) (Fig. 3)

- **Phytoextraction:** crops collect pollutants to decontaminate groundwater and soil
- **Phytodegradation:** where plants degrade organic pollutants through their own metabolic activities
- **Phytotransformation:** where plants stabilize the pollutants in soil
- **Phytovolatilization:** where plants absorb and transpire pollutants into less harmful volatile forms
- **Rhizoremediation:** filtration with plant roots or whole plants

Phytodegradation and transformation

Phytodegradation is the process of degrading pollutants through phytoenzymes or root exudates into simpler components as a consequence of microbial metabolism

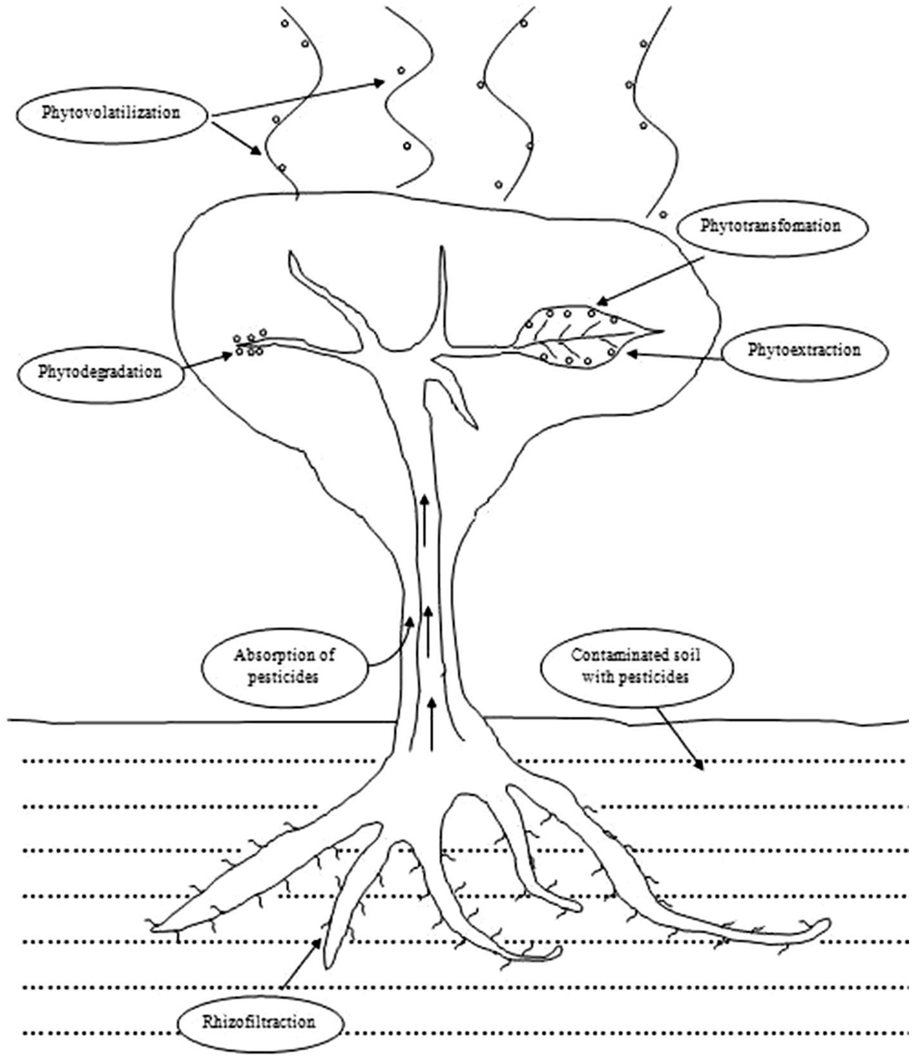

Fig. 3 Different techniques of phytoremediation

that facilitates contaminant detoxification. However, in converting complex and refractory compounds into fundamental molecules via phytocompounds, no process is completely effective. Thus, phytotransformation refers to chemical transformation without complete interruption. Pesticides collected from soil or water are generally metabolized by several metabolic processes in plants into less toxic or non-toxic products. Xia and Ma (2006) revealed that *Eichhornia crassipes* (water hyacinth) had eliminated organophosphate Ethion (Xia and Ma 2006). Similarly, Chang et al. (2005) demonstrated Atrazine translocation and split it into less complicated plant metabolites. (Chang et al. 2005) In another research, dehalogenation of DDT in aquatic plant *Elodea* was noted. Phytotransformation is feasible by catalysing endogenous enzymes that respond with volatile functional groups of pesticides such as NO^{-2}, OH^{-}, NH^{-2}, $COOH^{-}$, Br^{-}, Cl^{-} and I^{-} in Phase I through oxidation–reduction and hydrolysis reactions (Sandermann 1992; Trapp et al. 1994). This is accompanied by the combination of pesticides with modified enzymes in Phase II resulting in detoxification of pesticides (Eerd et al. 2003). Conjugation is caused through the addition of tripeptides such as glutathione or moiety of sugar or novel compound. Glutathione S-transferase as a catalyst has been reported to conjugate glutathione with pesticides through a nucleophilic attack. Most of these metabolic processes resemble the human metabolism of transforming xenobiotic chemicals (Dixon et al. 2002). Many xenobiotics, such as pesticides, induce the activation of GST encoding DNA. Many herbicide safeners are used to remote glutathione conjugation and detoxification by either raising glutathione concentrations or improving GST operation. Examples of pesticides that are conjugated with glutathione are Cyanazine, Atrazine and Simazine, whereas 2,4-D, chloramben and Bentazone prefer glucose conjugation. Conjugated compounds involve adenosine triphosphate-dependent enzymes to migrate into the vacuole, and their transportation across the vacuole has been proved in many plant species. ATP-binding cassette (ABC) transporters are the best identified system for moving pesticides after GST conjugation from root cells and into vacuoles. The metabolism of plants is restricted to compartmentation and retention in Phase III. In contrast to mammals, plants have no way of excreting unwanted compounds. Soluble metabolites are placed in the vacuole or are included in the cell wall structures (Riechers et al. 2005).

Phytovolatilization

In phytovolatilization process, plants uptake and transpire water-soluble contaminants. Contaminants present in soluble form in crops undergo several reactions and eventually volatilize along the stream of transpiration into the atmosphere. There are two types of phytovolatilization:

Direct phytovolatilization This method involves plant-mediated absorption and translocation of contaminants into the shooting part to spread pass through hydrophobic barriers such as cutin or suberin in the epidermis and in plant dermal tissues.

Indirect phytovolatilization By deploying large amounts of soil plants, carrying large amounts of water can increase the flow of volatile contaminants from the subsurface by the following methods (Jasechko et al. 2013):

- Lower the water table.
- Fluctuations in the water table cause gas fluxes.
- Increased soil permeability.
- Redistribution of hydraulics.

Phytovolatilization is important for extremely volatile pollutants such as methyl-tert-butyl alcohol (MTBE), ethylene dibromide (EDB), carbon tetrachloride (CTC) and trichloroethylene (TCE). Methyl-tert-butyl alcohol (MTBE) volatilization was recorded between the leaf, root and wood (Hong et al. 2001). Phytovolatilization may happen in breakdown products through rhizodegradation or phytodegradation. The level of TCE at transpiration sites in Utah ranged from 10 to 100 times greater than at sites in Florida, which were chosen to reduce groundwater pollution because to recurring rains (Doucette et al. 2003). A decrease in xylem volatile compound with a rise in the range from the rhizosphere zone was investigated by Ma and Burken, 2003. Highly unstable compounds such as TCE are therefore immediately oxidized through hydroxyl radicals into the environment. But due to environmental parameters such as lower air circulation, phytovolatilization cannot be effective (Ma and Burken 2003).

Rhizodegradation

Rhizosphere applies to the soil area around the origins of plants that influence the metabolism of plants. Rhizosphere creates a complex atmosphere around the plant to ensure metabolically energetic microbiome (Capdevila et al. 2004). Notably, the existence of crops with a big rhizosphere society may improve the microbial cell count in big fields around them. Plant Growth-Promoting Rhizobacteria (PGPR) are an important microbial community which help in cycling of plant nutrients, soil formation, insect control and detoxification of pesticides (Rajkumar et al. 2010). Together, Arbuscular Mycorrhizal Fungi (AMF) and Plant Growth-Promoting Rhizobacteria (PGPR) form an association against soil contamination. Because of chemical pollutants in soil, microbes appear to live in the chemical-rich surrounding that serves as their energy source. This approach involves various gene pools in the rhizodegradation of pesticides in rhizosphere. Different study findings have shown that parallel gene transfer of degrading genes could provide soil microbes in the soil atmosphere to detoxify pesticides. In Sphingomonas species, the introduction of indistinguishable lin genes clearly displays the concurrent transfer of HCH-detoxifying capacity. Miyazaki et al. (2006) demonstrated the propagation of linB genes to detoxify HCH in the organic settings has been proved (Miyazaki et al. 2006).

Improving rhizodegradation

1. **The best plant–bacteria selection:**
   Rhizospheric bacteria are better suited to colonize the rhizosphere and are the best choice for pesticide degradation. Shim et al. (2000) introduced toluene o-monooxygenase genes from *Bacillus cepacia* G4 into several other bacteria separated from the poplar tree rhizosphere. The authors observed that when recombinant strains of bacteria were introduced in non-sterile soil to cover poplar tree stems, recombinants isolated from plant rhizosphere could survive, while non-rhizospheric recombinant populations were unable to survive in the rhizosphere. These species also expressed toluene o-monooxygenase (TOM) genes and degrade trichloroethylene (TCE) (Shim et al. 2000).
2. **Endophytic bacteria:**
   Families *Pseudomonadaceae*, *Enterobacteriaceae* and *Burkholderiaceae* possess the most prevalent cultivable endophytic species separated from a broad range of habitats, including woody plants, herbaceous plants and grass species. Doty (2008) recognized some endophytic bacteria resistant to elevated levels of heavy metals, benzene, ethyl-benzene toluene and xylenes, trichloroethylene or polyaromatic hydrocarbons (Doty 2008). Siciliano et al. (2002) indicated that some crops can produce

endophytic bacterial genotypes for contaminant degradation (Siciliano et al. 2001). In any event, the benefits of using rhizo- or endophytic bacteria will rely on the sort of contaminant and the ability of each bacterium to degrade (Segura et al. 2009).

3. **Seed colonization:**

    The cheapest method that can be used to introduce micro-organisms to the soil is to coat the seeds with suitable bacteria. Similarly, the initiation of endophytes can be performed using comparable processes (Rocha et al. 2019). Seed adherence was tested using countable numbers of live cells and recently using gfp or lux reporter genes. The number of adhered bacteria can be identified using microscopy (confocal microscopy and scanning electron microscopy). Rhizobacteria attach to the seeds by flagellar and chemotactic proteins. Several studies revealed that membrane proteins are important in cell adhesion and this is in line with the fact that the exterior surfaces are the first point for the contact of the bacterium to the seeds (Pinski et al. 2019; Yousef-Coronado et al. 2008).

4. **Production of biosurfactants:**

    An issue with soil bioremediation is the bioavailability of the pollutants. This absence of bioavailability often reduces efficiencies in extraction of pesticides (Megharaj et al. 2011). Bacteria use various techniques to enhance the bioavailability of hydrophobic compounds such as PAHs, development of extracellular polymeric substances including the excretion of biosurfactants and the formation of biofilms on PAH crystals (Johnsen and Karlson 2004). In the hydrophobic layers of the micelles, hydrophobic pollutants are solubilized to further enhance the transformation of compounds from a solid to a liquid phase where they become more accessible to bacteria. The rhamnolipids out of glycolipids are the main source of bacterial biosurfactants. It has been shown that rhamnolipids can increase the biodegradation level of pesticides (Cui et al. 2008). Therefore, the search for rhizobacteria for promoting contaminant bioavailability is of great interest in the context of bioremediation. This asset is also worrying because a percentage of biodegradable microbes show positive chemotaxis to pollutants. The combined activity of biosurfactant and chemotaxis can therefore contribute to bacterial growth and microbial propagation in polluted areas, helping to remove pesticides (Orozco et al. 2014).

5. **Engineering of rhizoremediation bacteria:**

Genetic modification of bacteria to enhance the ability of bioremediation is a classic strategy (Carpi and ed. 2011). Reports on introducing catabolic genes into distinct bacteria, creating hybrid cells and promoting changes to improve the expression of genes of concern are extensive in the literature. Construction of recombinant species capable of combining distinct characteristics, such as contaminant degradation with biosurfactant production, healthy colonization capabilities and plant growth capability, is still possible. However, the introduction of recombinant species in the sector is limited in many nations and these legal constraints, together with some well-sustained environmental issues, may restrict the growth of this sector (Segura et al. 2009; Gkorezis et al. 2016).

Phytoextraction

Plants have been used to extract pollutants/contaminants from soil, water and atmosphere. The plants which absorb excessive amounts of contaminants from the soil are called hyperaccumulators (Yan et al. 2020). Most of the plants used for phytoextraction are from *Brassicaceae* family (Szczygłowska et al. 2011). Phytoextraction is becoming a remediation technology more commonly used in which field-level outcomes have been shown. It involves the magnitude of contamination, bioavailability of metals and the capacity of crops to capture, receive and store metals from soil that is becoming a task for scientists and executives of phytoextraction enterprises. Researchers use modern techniques such as LCMS-ToF, HPLC and GC–MS for quantitative analysis of pesticides uptake by plants (Chen et al. 2012a; Ghori et al. 2016).

In the event of soil to plant uptake, the capacity for accumulation of pesticides may be influenced by many plant features such as water uptake capacity and soil depth and structure (Pérez-Lucas et al. 2018). Once pesticides are stored by plant root cells, they can either be placed in the roots or transported to the plant's aerial parts where the analytes can be stored, metabolized or volatilized. In general, the accumulation of pesticides in plant roots is ineffective for remediation, although the amount of soil contaminants decreases (Karthikeyan et al. 2003). An apparent exception to this is aquatic plant-based remediation systems, where extraction of contaminants by plant roots can be significant. In root system, *Eichhornia crassipes* (water hyacinth) can accumulate the insecticide Ethion more effectively than in its shooting system. Because the roots built up more than 50% of the plant mass, including the leaves, can be readily collected, this system can be used effectively to phytoremediate water contaminated with Ethion (Xia and Ma 2006). Pesticide molecules can be transferred to the xylem vessels after being collected by plant roots and translocated with the plants transpiration flow. Many experiments have been dedicated to the distribution of pesticides in plant species, mainly due to the elevated productivity and easy cultivability of the crops (Vila et al. 2007). It has been noted that several crops have considerable capacity for accumulation of a wide range of pesticides (Chhikara et al. 2010). Gent et al. (2007)

explored the use of DDE by various cultivars of *Cucurbita pepo* and recorded shoot bioconcentration variables up to 23.7 for the Raven cultivar (White et al. 2005). A part of the pesticide molecules translocated to shoots can be adsorbed in plant macromolecules such as lignin or cellulose. The use of trees, primarily poplar and willow, requires into account this system for phytoremediation and phytopumping (Fernandez et al. 2012). After the phytoaccumulation, crops require to harvest after a specified period. At last shoot tissues need to be burned, composed or disposed-off by other methods (Pascal-Lorber and Laurent 2011). Different plant species involved in the phytodegradation of pesticides are given in (Table 2).

Biodegradation of pesticides

Sunlight and micro-organisms play a vital role in the environmental degradation of different pesticides. The pesticide spraying on crops ended up by making their way into the soil and sediments as well as into the water bodies. Soil and sediments contain different micro-organisms which utilizes these chemical compounds for their growth thus, degrading them into simpler forms (Parte et al. 2017; Huang et al. 2018). The micro-organisms that are capable of degrading the pesticides and thus converting them into non-hazardous substances include bacteria, fungi and algae. Among them, *Actinomycetes* and Cyanobacteria are more efficient degraders inhabiting the soil (Parte et al. 2017; Sehrawat et al. 2021).

The biodegradation studies by various authors revealed many species of bacteria such as *Bacillus, Pseudomonas*, *Brevibacterium*, *Alcaligenes*, *Enterobacter* and K*lebsiella* and fungi such as *Fusarium*, *Aspergillus, Penicillium*, *Rhodotorula* and *Candida* that are capable of degrading the pesticide residues (Parte et al. 2017; Joutey et al. 2013). Microbes involved in the degradation of pesticides reported by various authors are given in Table 3. Micro-organisms are considered as efficient bioremediators as they easily chemically transform pesticides due to their high catalytic activity, fast reproduction rate and large surface to volume area. Some microbes need adaptation time for synthesizing the pesticide-degrading enzymes, while others acquire this ability through random mutations (Ortiz-Hernández et al. 2013; Verma et al. 2014).

Factors affecting microbial degradation of pesticides

There are various factors such as pH of the soil, moisture content, organic matter, carbon and nitrogen content and temperature which affect the rate of pesticide degradation in the soil by microbes. Practices such as tillage and manuring also affect the physical, chemical and biological characteristics of soil along with microbial diversity and activity (Somasundaram et al. 1989).

Soil pH and salinity

The effect of soil pH on pesticide degradation greatly depends upon its susceptibility to acid or alkaline hydrolysis. Soil pH affects the pesticide adsorption on soil surfaces, mobility, chemical speciation and bioavailability. In a study, Singh et al. (2003) examined the effect of soil pH on the degradation of organophosphate insecticide Chlorpyrifos (Singh et al. 2003). The results revealed that the degradation process increased when the soil pH is ≥ 6.7. Soil salinity affects the rate of pesticide degradation to great extent. There are many studies which reported that high salt content decreases the degradation process of pesticides. Siddique et al. (2002) observed that an initial pH of 8 is effective for degradation of isomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH) in liquid culture, while pH 9 is effective in soil slurry cultures (Siddique et al. 2002). Kah et al. (2007) also revealed that pH affects the rate of degradation of six acidic pesticides, namely 2,4-D, Dicamba, Fluroxypyr, Fluazifop-P, Metsulfuronmethyl, and Flupyrsulfuron-methyl) and four basic pesticides, namely Metribuzin, Terbutryn, Pirimicarb and Fenpropimorph (Kah et al. 2007). In a similar study, Fang et al. (2010) showed that neutral pH is required for the effective degradation of DDT, while acidic or alkaline pH inhibits the degradation process by *Sphingobacterium* sp (Fang et al. 2010).

Soil moisture Moisture content of the soil greatly affects the degradation as it is essential for proliferation and microbial activities. The rate of pesticide degradation accelerates with water content and slows down in dry soils (Fishel 1997; Singh and Walker 2006).

Pesticide structure The structure of the pesticide determines its physical and chemical properties, thus affecting its degradation rate. The addition of polar groups such as OH, NH_2 and COOH provides an attacking site to the microbes, while addition of substituents on benzene ring enhances the rate of degradation (Lushchak et al. 2018; Pal et al. 2010).

Pesticide concentration and solubility The concentration of pesticide in the soil is an important parameter in the degradation process. The high initial concentration of the pesticide will affect the number of attacking sites in soil and also have toxic effect on microbes. Fang et al. (2010) in a study observed that the degradation activity of the bacterium *Sphingobacterium* sp. was inhibited by the higher concentration of DDT (Fang et al. 2010). Pesticides with high water solubility will tend to degrade faster than with lower

Table 2 Phytodegradation of different pesticides

Sr. no	Pesticide	Plant species	Pesticide category	Background	References
1	Tebuconazole	*Phragmites australis, Typha latifolia L*	Fungicide	–	Lv et al. (2017), Elsaesser et al. (2011)
2	Cyanophos	*Plantago major L*	Insecticide and avicide	Cholinesterase inhibitor	Romeh (2015)
3	Dimethomorph	*Lemna minor, Spirodela polyrhiza*	Fungicide		Olette et al. (2008)
4	Pyrimethanil	*Caltha palustris, Elodea Canadensis*	Fungicide	Methionine biosynthesis inhibitor	Dosnon-Olette et al. (2009)
5	Atrazine	*Potamogeton crispus, Myriophyllum spicatum, Typha latifolia, Leersia oryzoides, Sparganium americanum, Acorus calamus, Andropogon gerardii,*	Herbicide	–	Qu et al. (2017), Moore et al. (2017), Lin et al. (2008)
7	Flazasulfuron	*Elodea Canadensis, Lemna minor*	Herbicide	–	Olette et al. (2008)
8	Chlorpyrifos	*Myriophyllum verticillatum, Nymphaea alba, Phragmites australis, Eichhornia crassipes*	Insecticide	Inhibitor of acetylcholinesterase	Xu et al. (2018), Mercado-Borrayo et al. (2015)
9	Dimethomorph	*Spirodela polyrhiza, Elodea Canadensis, Lemna minor*	Fungicide	–	Olette et al. (2008)
10	DDT	*Solanum lycopersicum, Achillea millefolium, Traxacum officinalis, Potentilla argentae, Plantago lagopus, Oenotheria biennis, Kanthium strumarium, Erigeron Canadensis, Daucus carota*	Insecticide	Open sodium ion channels in neurons	Mitton et al. (2014, 2018), Moklyachuk et al. (2012)
11	Fenamiphos	*Glycine max*	Insecticide	Inhibitor of acetylcholinesterase	Romeh and Hendawi (2017)
12	Azoxystrobin	*Plantago major*	Fungicide	–	Romeh (2017)
13	Metalaxyl	*Sambucus nigra L., Salix alba L*	Fungicide	–	Fernandez et al. (2012)
14	Trifluralin	*Sambucus nigra L., Salix alba L*	Herbicide	–	Fernandez et al. (2012)
15	Isoxaben	*Salix gracilistylus*	Herbicide		Baz and Fernandez (2002)
16	Oryzalin	*Salix gracilistylus*	Herbicide	Destruction of microtubules	Baz and Fernandez (2002)
17	Dimethoate	*Phalaris arundinacea L., Amaranthus caudate, Lactuca sativa*	Insecticide	Inhibitor of acetylcholinesterase	Elsaesser et al. (2011), Al-Qurainy and Abdel-Megeed (2009)
18	Dicamba	*Typha latifolia L*	Herbicide	–	Elsaesser et al. (2011)
19	Trifloxystrobin	*Typha latifolia L*	Fungicide	Inhibitor of fungal spore germination and mycelial growth	Elsaesser et al. (2011)
20	DDE	*Typha latifolia L., Arachis hypogaea, Brassica juncea, Brassica napus, Cajanus cajan, Cucumis sativus, Cucurbita pepo*	Insecticide	Thinning of eggshell	Chhikara et al. (2010), White et al. (2005), Gent et al. (2007), Åslund and Zeeb (2010)
21	Dieldrin	*Sorghum vulgare Moench, Helianthus annuus L., Glycine max, Brassica rapa, Lagenaria siceraria, Cucumis sativus, Cucurbita pepo L*	Insecticide	–	Murano et al. (2010)
22	Phoxim	*Allium fistulosum, Daucus carota*	Insecticide	–	Wang et al. (2011)
23	Malathion	*Amaranthus caudate, Nasturtium officinale*	Insecticide	Inhibitor of acetylcholinesterase	Al-Qurainy and Abdel-Megeed, (2009)

Table 2 (continued)

Sr. no	Pesticide	Plant species	Pesticide category	Background	References
24	Glyphosate	*Amaranthus caudate,*	Herbicide	Inhibitor of 5-enolpyruvylshikimate-3-phosphate synthase	Al-Arfaj et al. (2013)
25	Metolachlor	*Andropogon gerardii, Sorghum bicolor, Digitaria sp.*	Herbicide	Inhibitor of elongases and geranylgeranyl pyrophosphate	Bogdevich and Cadocinicov (2010)
26	Pendimethalin	*Andropogon gerardii, Leersia oryzoides*	Herbicide	Inhibit cell division and elongation	Zhao et al. (2005)
27	Endrin	*Cucurbita pepo*	Insecticide and rodenticide	Act as neurotoxin and central nervous system	Matsumoto et al. (2009)
28	Dichlorodiphenyldichloroethane	*Curcurbita pepo*	Insecticide	-	Matsuo et al. (2011)
29	Aldrin	*Eichhornia crassipes*	Insecticide	Inhibit calcium ATPase and block gamma-aminobutyric activity	Mercado-Borrayo et al. (2015)
30	Endosulfan	*Eichhornia crassipes*	Insecticide and acaricide	Calcium, magnesium ATPase and GABA gated chloride channels inhibitor	Mercado-Borrayo et al. (2015)
31	Bifenthrin	*Najas marina*	Insecticide	Blocks sodium channels permanently	Chen et al. (2012a, b)
32	Azoxystrobin	*Glycine wax*	Fungicide	Bind complex III of mitochondrial electron transport chain and block ATP synthesis	Romeh (2015)
33	Dodemorph	*Hordeum vulgare*	Fungicide	Sterol biosynthesis inhibitor	Moklyachuk et al. (2010)
34	Fenpropathrin	*Najas marina*	Insecticide	Neurotoxin	Chen et al. (2012)
35	Sulfentrazone	*Nicotiana tabacum*	Herbicide	Inhibit biosynthesis	Ferrell et al. (2003)
36	Diclofop methyl	*Ricinus communis*	Herbicide	Mimic the action of auxins, hormones chemically related to indoleacetic acid that stimulate growth	Rissato et al. (2015)
37	Metalaxyl	*Salix alba*	Fungicide	–	Fernandez et al. (2012)
38	Permethrin	*Typha latifolia*	Insecticide	–	Moore and Locke (2012)
39	Aldicarb	*Zea mays, Vigna radiate*	Insecticide	Cholinesterase inhibitor	Sun et al. 2004
40	Methyl parathion	*Typha latifolia*	Insecticide and acaricide	Inhibitor of acetylcholinesterase	Amaya-Chávez et al. (2006)
41	Butachlor	*Triticum vulgare*	Herbicide		Yu et al. (2003)

Table 3 Micro-organisms involved in the degradation of pesticides

Micro-organisms	Pesticide degraded	Pesticide type	References
Bacteria			
Bacillus safensis, Bacillus subtilis and *Bacillus cereus*	Chlorpyrifos, Malathion and Dimethoate	Insecticides	Ishag et al. (2016)
Alcaligenes faecalis	Endosulfan	Insecticide and acaricide	Kong et al. (2013)
Enterobacter ludwigii	Chlorimuron-ethyl	Herbicide	Pan et al. (2018)
Rhodococcus sp.	Chlorimuron-ethyl	Herbicide	Li et al. (2017)
Stenotrophomonas maltophilia	Chlorimuron-ethyl	Herbicide	Zang et al. (2016)
Bacillus cereus	Deltamethrin	Insecticide	Zhang et al. (2016)
Serratia marcescens	Tebuconazole	fungicide	Wang et al. (2018)
Stenotrophomonas sp.	O,O-dialkyl phosphorothioate and O,O-dialkyl phosphate	Insecticides	Deng et al. (2015)
Stenotrophomonas maltophilia	Methomyl	Insecticide	Mohamed (2009)
Pseudomonas putida and *Acinetobacter rhizosphaerae*	Fenamiphos	Nematicide	Chanika et al. (2011)
Bacillus cereus	Chlorpyrifos	Insecticide	Liu et al. (2012)
Burkholderia gladioli	Profenofos	Insecticide	Malghani et al. (2009)
Serratia marcescens	Nicosulfuron	Herbicide	Zhang et al. (2012)
Bacillus and *Morganella*	Carbaryl	Insecticide	Hamada et al. (2015)
Cyanobacteria and Algae			
Synechocystis sp.	Chlorpyrifos	Insecticide	Singh et al. (2011)
Spirulina platensis	Chlorpyrifos	Insecticide	Thengodkar and Sivakami (2010)
Synechocystis sp.	Anilofos	Herbicide	Singh et al. (2013)
Nostoc muscorum	Malathion	Insecticide	Ibrahim et al. (2014)
Microcystis novacekii	Methylparathion	Insecticide and acaricide	Fioravante et al. (2010)
Fischerella sp.	Methylparathion	Insecticide and acaricide	Tiwari et al. (2017)
Chlamydomonas reinhardtii	Fluroxypyr	Herbicides	Zhang et al. (2011)
Chlamydomonas reinhardtii	Prometryne	Herbicides	Jin et al. (2012)
Chlamydomonas reinhardtii	Isoproturon	Herbicides	Bi et al. (2012)
Scendesmus obliquus	Myclobutanil	Herbicides	Cheng et al. (2013)
Fungi and yeast			
Aspergillus niger	Chlorimuron-ethyl	Herbicide	Sharma et al. (2012)
Aspergillus oryzae	Monocrotophos	Insecticide	Bhalerao and Puranik (2009)
Fusarium oxysporum, *Aspergillus oryzae*, *Lentinula edodes*, *Penicillium brevicompactum* and *Lecanicillium saksenae*	Terbuthylazine, Pendimethalin and Difenoconazole	Herbicides and fungicide	Pinto et al. (2012)
Fusarium sp.	Lindane	Insecticide	Sagar and Singh (2011)
Aspergillus sydowii and Penicillium decaturense	Methyl parathion	Insecticide and acaricide	Alvarenga et al. (2014)
Aspergillus versicolor	Triclosan	Antimicrobial	Taştan and Dönmez (2015)
Cladosporium cladosporioides	Chlorpyrifos	Insecticide	Chen et al. (2012a, b, c)
Trametes versicolor, Pleurotus ostreatus	Thiabendazole, Imazalil, Thiophanate methyl, Ortho-phenylphenol, Diphenylamine and Chlorpyrifos	Fungicides	Karas et al. (2011)
Pichia pastoris	Chlorpyrifos	Fungicide	Kambiranda et al. (2009)
Candida sp.	Lindane	Insecticide	Salam and Das (2014)
Pseudozyma sp.	Lindane	Insecticide	Abdul Salam and Das, 2013
Rhodotorula sp.	Lindane	Insecticide	Salam et al. (2013)
Saccharomyces cerevisiae	4,6-Dinitrocresol or Karathane	Insecticide and fungicide	Zaharia et al. (2013)
Galactomyces geotrichum	Lincomycin	Bacteriocides	Zhang et al. (2015)

solubility as microbes attack only the dissolved fraction of them in the soil (Odukkathil and Vasudevan 2013).

Temperature Temperature affects the pesticide's adsorption in the soil by changing its solubility and hydrolysis. Siddique et al. (2002) observed the effect of temperature on the degradation of Isomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH), used as broad-spectrum organochlorine pesticides against a wide range of soil-dwelling and plant-eating insects (Siddique et al. 2002). They investigated that an optimum incubation temperature of 30 °C was effective for degradation of these isomers in liquid culture as well as in soil slurry. Fang et al. (2010) took different temperatures, i.e. 20, 30 and 40 °C, to check the rate of degradation of DDT by *Sphingobacterium* sp. They observed that temperature of 30 °C was effective for the activity of the bacterium (Fang et al. 2010).

Soil organic matter The presence of soil organic matter either enhances the microbial activities by accelerating the degradation rate by co-metabolism or decreases it by stimulating the adsorption process (Perucci et al. 2000). The presence of organic matter also influences the microbial flora of that area, thus increasing the species diversity which ultimately adds up more enzyme systems to attack the pesticide molecules (Neumann et al. 2014).

Biochemical reactions involved in pesticide degradation

The rate of degradation for different pesticides in the soil varies greatly as it is decided by both biotic and abiotic factors. Some pesticides are considered recalcitrant as they take longer periods for degradation and get accumulated in the food chains (Cawoy et al. 2011). Glutathione S-transferases (GSTs), esterases and cytochrome p450 are the key enzyme families involved in the pesticide degradation (Bass and Field 2011).

Oxidation

Oxygenases are oxidoreductase enzymes which participate in the oxidation of reduced substrates by utilizing FAD/NADH/NADPH as a co-substrate and thus transferring oxygen from molecular oxygen. The most commonly reported bacterial enzymes in the bioremediation of pollutants are mono- or dioxygenases. They increase the water solubility, reactivity and cause cleavage of the aromatic ring (Arora et al. 2009). Oxygenation is the most crucial step in the degradation of the pesticides involving oxidative enzymes such as cytochrome p450s. There are also other oxidative enzymes that catalyse polymerization of various pesticides which are laccase, peroxidase, polyphenol-oxidase and tyrosinase. White rot fungi have been proved as an effective bio-transformer by many authors because of the presence of these enzymes which degrades variety of pollutants in the environment (Pointing 2001). In a study, Torres-Duarte et al. (2009) showed the biotransformation of organic halogenated pesticides by laccase–mediator system. The results revealed that an oxidative dehalogenation is involved in this catalytic process (Torres-Duarte et al. 2009).

Reduction

Most of the environmental pollutants are halogenated chemicals, and dehalogenation is one of the most common reductive reactions. The halogen atom on non-aromatic carbon is replaced by hydrogen atom in these reactions (Matsumura 1982). The halogenated atoms present in the molecules of pesticides increase the carbon oxidation states, thus making the aerobic degradation less favourable for highly halogenated compounds. On the other hand, the anaerobic degradation is more convenient, since more halogens the molecule has, it is easier to produce a reductive dehalogenation. The metabolites of the de-halogenated pesticides are more prone to further aerobic degradation (Baczynski et al. 2004; Kopytko et al. 2016).

Hydrolysis

The enzymes involved in this process are hydrolases which are greatly involved in the pesticide degradation. Pesticides containing peptide bonds, esters, ureas, thioesters or carbon-halide bonds are easily catalysed by the enzymes hydrolases, and the redox cofactors are also not generally required (Scott et al. 2008). These enzymes have broad substrate specificity, and are stable at wide range of pH and temperature (Karns et al. 1987). The hydrolysis of the organic pollutants is mainly done by the bacterial activities. The hydrolytic enzymes involved in the biodegradation process disrupt the chemical bonds in the pesticides, thus converting them into less toxic compounds. This mechanism is effective for the biodegradation of organophosphate and carbamate insecticides (Karigar and Rao 2011). In a study, Singh (2014) revealed the role of carboxylesterase enzymes in the degradation of organophosphate pesticides. Carboxylesterases or carboxylic-ester hydrolases hydrolyse the carboxylic-ester bonds with relatively broad substrate specificity (Singh 2014).

Conclusion

The use of pesticides in agricultural practices is an effective pest management method which significantly affected the farmer's economy, as huge amount of annual food loss could be saved. Pesticides are used in manufacturing industries, food industries and even in homes to manage pests. The application of these chemicals (antimicrobials) also helped in saving many lives in public sector. Despite of many benefits, they also possess disadvantages, as only little amount of these pesticides reach the target organisms and rest pollutes the environment thus, affecting animals and humans to great extent. In this review article, we have discussed the various techniques used for the degradation of these harmful synthetic chemicals in the soils and water bodies. Photodegradation of pesticides on the soil surface by sunlight is an effective technique. The degradation process which uses photosensitizer is called photosensitized degradation, and the sensitizer regenerates back in this process. Nowadays, photodegradation using a photocatalyst gains more interest. The photocatalyst accelerates the rate of degradation to many folds. Plants also uptake these chemicals and metabolize them to non-toxic ones by different processes such as phytovolatilization, phytoextraction, phytoaccumulation, phytostimulation and phytodegradation. Besides photodegradation and phytodegradation, biodegradation of the pesticides by microbes is also an effective and efficient technique. In this chapter, we have discussed the various factors such as pesticide structure, soil moisture, salinity, organic matter and temperature which affects the rate of degradation by microbes. Bacteria, fungi and algae are commonly known for pesticide degradation, and among them, actinomycetes and cyanobacteria are the most efficient ones.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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