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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B. Kamal
Department of Botany, DBS PG College, Dehradun, Uttarakhand, India

R. Goswami
Department of Environmental Science, Graphic Era Hill University, Dehradun, Uttarakhand, India

A. Mishra (✉)
Department of Chemistry, Graphic Era (Deemed to be University), Dehradun, Uttarakhand, India

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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

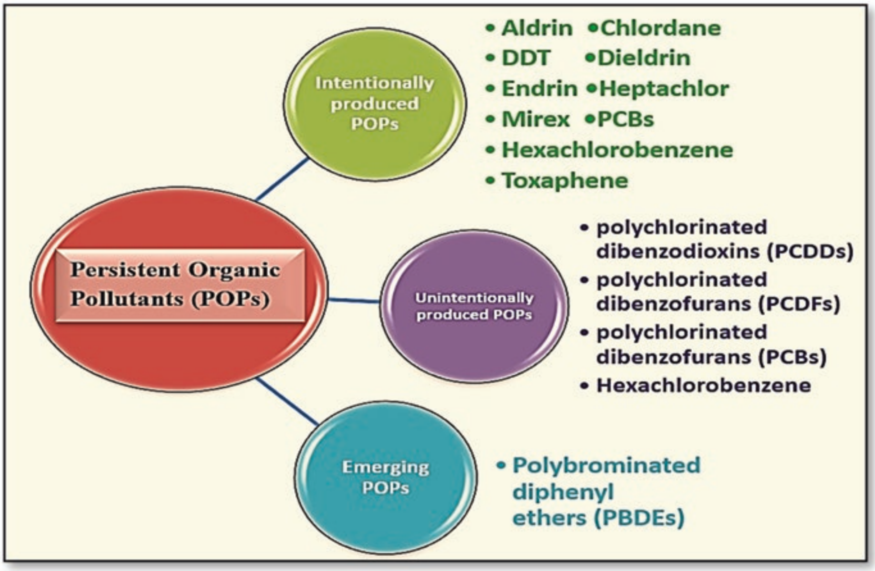

Fig. 7.1 Different types of persistent organic pollutants (POPs)

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

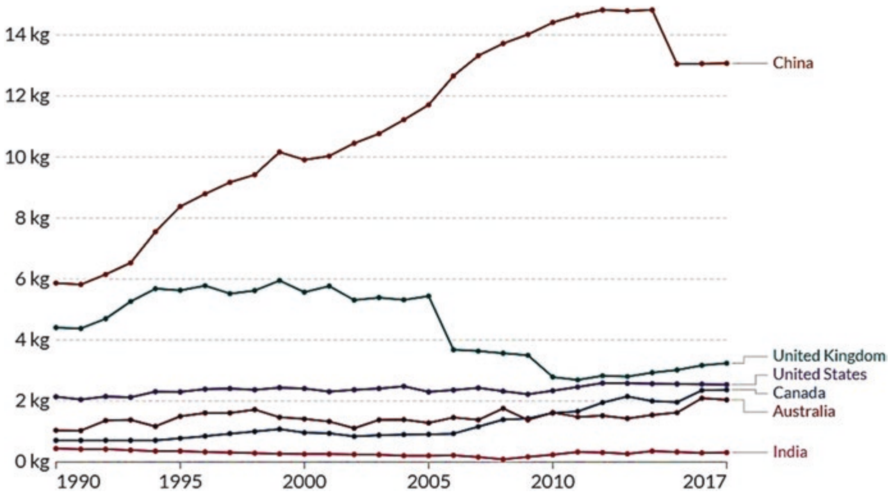

Fig. 7.2 Average pesticide use per hectare cropland from 1990 to 2017 (Max Roser 2019)

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

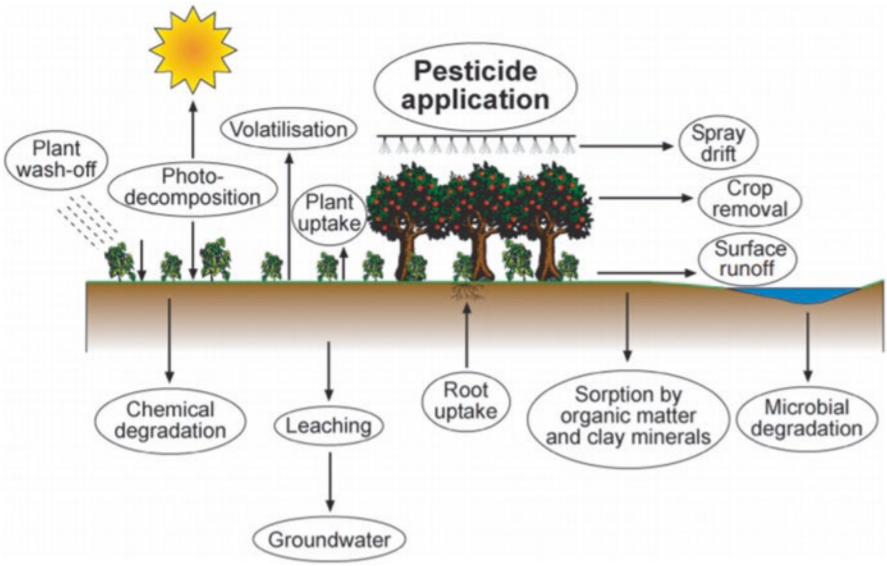

Fig. 7.3 Various processes for the fate of pesticides in the environment. (Reproduced with permission from Sarmah et al. 2004)

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

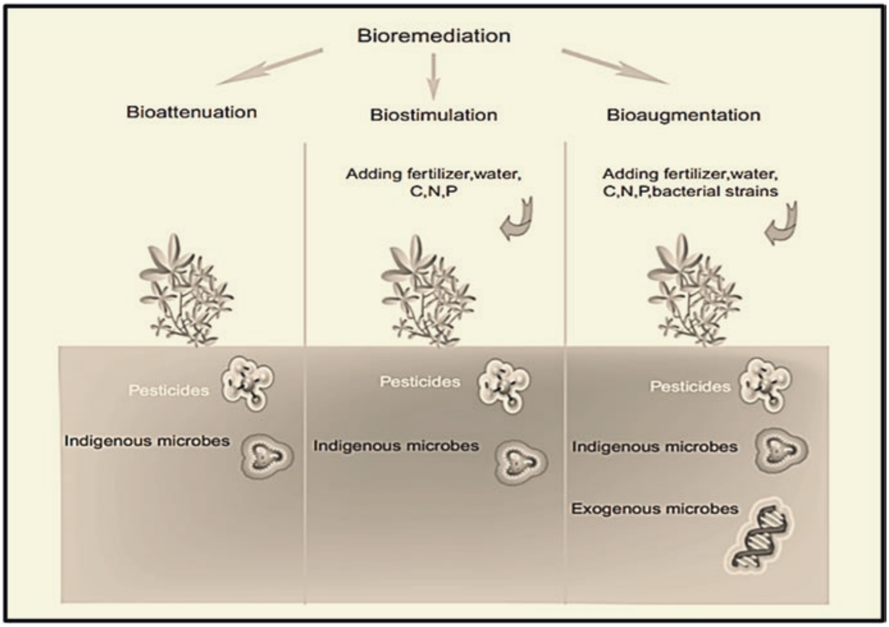

Fig. 7.4 Bioattenuation, Biostimulation, and Bioaugmentation processes (Reproduced with permission from Ying 2018)

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)
Cyp1A1/1ª2	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

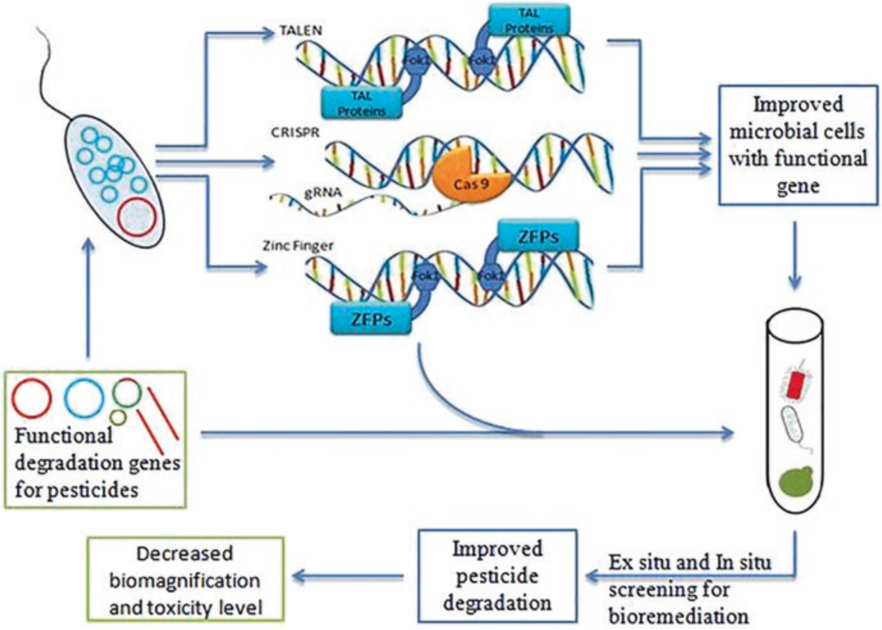

Fig. 7.5 Gene editing tools for bioremediation (reproduced from Jaiswal et al. 2019 available under CC BY 4.0)

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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