World Journal of Pharmaceutical and Life Sciences
WJPLS
www.wjpls.org
SJIF Impact Factor: 5.008

NEW ASPECTS ON REMEDIATION OF PESTICIDE THROUGH PHYSICAL, CHEMICAL AND BIOLOGICAL SOURCES

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Article Received on 19/09/2018 **Article Revised on 10/10/2018** **Article Accepted on 31/10/2018**

ABSTRACT

The pesticides are being used for enhancing agricultural yield. With the increase in industrial revolution, the demand of pesticides has also increased. Moreover, pesticides are also involved in protecting crops from pests. In addition, pesticides provide economic benefits to farmers annually by saving their crops from pests but the use of pesticides in agricultural fields is a major concern now-a-days as pesticides are involved in causing serious issues to human health and environment. The pesticides harmful effects are more as compared to their benefits. The methods more commonly used for remediation are thermal, chemical, and physical methods. These methods do not undergo complete degradation of pesticides and they are costly. There is another method which is effective, not harmful to nature, and cost effective. This method comes under biological technique and known as Bioremediation. There is a need to work on this method for future benefits. The objective of this document was to review literature for new aspects of bioremediation methods of pesticides by defining several sources, its profile related to microorganisms characterization and advanced remediation methods.

KEYWORDS: Pesticides; Degradation; Remediation methods; Bioremediation; Characterization.

INTRODUCTION

The chemical substances used to kill pests at tolerable levels are known as Pesticides. The word 'Pesticide' comprise of two words (Pest: Insects and cide: to kill). The pesticides classification on the basis of its functions has shown in figure 1.[1] The globalization has resulted in chemicals pollution in the environment. Therefore, there is a need to eliminate these hazardous chemicals from environment. For this new technologies were implemented. In these clean up technologies landfills, recycling, and pyrolysis are more common. The negative impacts on environment were only the main problem with these technologies because they resulted in toxic substance formations.[2] Moreover, these technologies are not easy to handle and cost-effective.[3] As compared to these clean up technologies, bioremediation is a better choice. In this, microorganisms' ability is utilized to clean up the contaminated site. This method is environment friendly and cost-effective.[4] Many serious environmental concerns, human health problems and biodiversity issues (soil quality degradation) have resulted due to increase use of pesticides.[5,6] Pesticides persistence in soil makes them low biodegradable. Thus biodegradation of pesticides depend on its persistence and biodegradability.[7]

Contamination of Soil

Heavy metals, pesticides, and municipal garbage are most common sources of soil contamination. The heavy metal soil contamination consists of atmospheric deposition, sewage, irrigation, industry, pesticides and fertilizers,[8] and the municipal garbage soil contamination consists of home and industry discarded materials i.e. paper, plastic and organic matter.[9] The heavy metals and municipal garbage contamination inhibit microbial activity and loss of biodiversity respectively.[10]

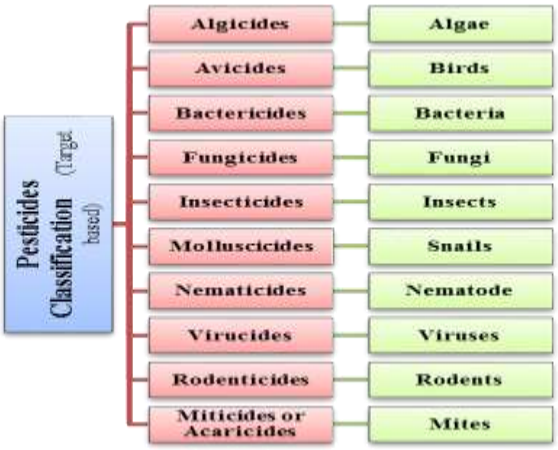

Figure 1: Target based classification of pesticides.

Contamination of Water

Water is an important medium for many life forms. The water pollution on earth has led to shortage of fresh water. The water pollution mainly occurs due to excessive usage of fertilizers, and pesticides. The 98% pesticide contamination is severely toxic for water bodies i.e. fish and crustaceans.[11]

History of Pesticide

The history of pesticides turns back to a long time when plant and animal derivatives such as neem, chrysanthemums, and rotenone derivate or common chemicals such as sulphur, mercury and arsenic were used as pesticides. These pesticides were used to prevent crop damages. These traditional pesticides were either ineffective or toxic for both humans and animals. In addition to it, non-chemical methods were also used to control pests. The history of modern synthetic pesticides goes back to World War I when DDT was introduced. In 19th century, several chemicals were yielded by active research. These chemicals have adverse effect on human health. Moreover, "the chemist's war" is the other name of World War I due to usage poison gas and nitrates. For this reason, many companies and governments agencies continued the active research on these chemicals after the war.[12]

Scenario of Pesticides Use in Pakistan

The pesticide use in Pakistan is mainly consists of six intervals. If we talk about the scenario before 1980, the Plant Protection Department under Government of Pakistan was responsible for pesticides import in the country. Most of the import at that time was related to locust control program, malaria control programm, aerial spray of cotton, sugarcane, rice, tobacco, etc. This import and distribution has its own advantages and disadvantages. There were no extra charges on pesticides and aerial spraying. Actually they were almost free at that time. Large containers were used for pesticides storage and transfer. Storage and handling of pesticides is very important. A large number of accidents have occurred due to this reason.[13] In the same era, the private sector overtook pesticide business with an agreement. Due to this reason, there is no proper data available for pesticides import and distribution. The most important thing is Pakistan pesticide business started from 1954 and the import is that era goes to about 254 metric tons 3, the increase in import was seen in the year 1986- 1987 to about 20,648 m tons. In addition to it, where pesticides have played an important role in protecting plants from pests. It has also hazardous effects on human health and environment. The pesticides harmful effects are more as compared to their benefit.

In Pakistan, there is no sufficient knowledge about farming activities and how to maximize the benefits of farming. In increasing cotton production, two institutes in Pakistan have played a pivotal role. These two institutes are: the Central Cotton Research Institute, Multan, and Nuclear Institute for Agriculture and Biology, Faisalabad. For increasing cotton production, pest management practices are also very crucial. When the pesticide business was transfer to private sector, the import was increased. It also tends to increase sprayed area.[14]

Government Regulations

In 1971, Agricultural Pesticides Ordinance is done by pesticide import and distribution under the 1973 rule of Agriculture Pesticides. The registration process of pesticide takes place periodically. Now, some pesticides are de-registered and their distribution is banned. It is given in figure 2.[14] The inspectors' appointment is under Pesticide Ordinance provision. It also defined the procedure for quality analysis of samples. But this process was not sufficient. Moreover, the inspectors were also not sufficient and were not trained. In addition to it, the court proceedings take a lot of time. In 1988, import policy of pesticide is governed by pivotal moderations. These are as follows: (i) Generic names will be given to the pesticides for import. (ii) Pesticides local registration is not necessary if it is already registered internationally. Still many improvements are needed in government regulations to make new policies.

Figure 2: Banned pesticides in Pakistan.

Institutional Arrangements for Pesticide Monitoring and Research

The pesticides in Pakistan are usually imported from foreign countries and the pesticides business of Pakistan depends on this import. If we talk about local production pesticides then it is in very small amount in Pakistan. In Pakistan Ministry of Food, Agriculture and Cooperatives is controlling ministry for pesticide business. The registry and regulatory matters of pesticides is the duty of Plant Protection Department. There is another committee known as Agricultural Pesticide Technical Advisory (APTA) Committee whose responsibility is to form pesticides law. The monitoring of pesticides which is a main task is under Pakistan Agricultural Research Council. There are some projects which are going on pesticides and agriculture research but still it is a requirement to find some fruitful methods to verify the findings and results of those projects. The results and

findings of these projects have been published in various local journals.[14]

Types of Pesticides

There are different types of pesticides depending on the pests. These pesticides mainly are herbicides, insecticides, fungicides and rodenticides. The classification of pesticides on the basis of its structure has given in figure 3.[15]

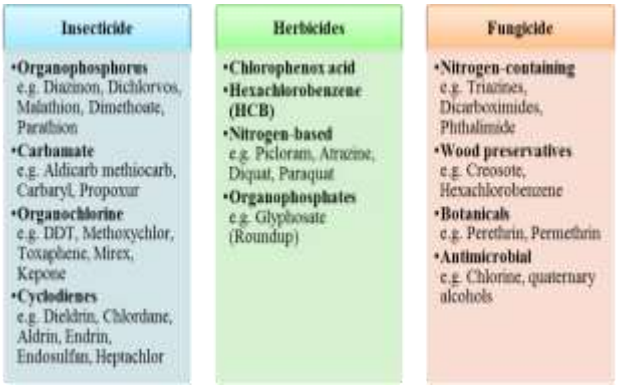

Figure 3: Types and examples of pesticides.

Table 1: Pesticides with their effects on health.

Pesticide	Persistence (Half-life)	Health Effects
Aldrin	20 days to 1 year	Nervous system effects. Probable carcinogen. Large doses: convulsions, death. Moderate doses: dizziness, headaches, vomiting, uncontrolled muscle movement
Dichlorodiphenyltrichloroethane (DDT)	2 to15 years	Nervous system effects (tremors, seizures); probable carcinogen
Chlordane	4 years	Nervous system, digestive system, liver effects. Headaches, irritability, confusion, weakness, vision problems, vomiting, stomach cramps, diarrhea, and jaundice for lower doses. Higher doses: convulsions and death.
Dieldrin	Up to 7 years	Nervous system effects. Probable carcinogen. Large doses: Convulsions, death. Moderate doses: Dizziness, headaches, vomiting, uncontrolled muscle movement.
Heptachlor	0.4 to 2 years	Nervous system damage, liver and adrenal gland damage, tremors

Pollution and Health Effects of Pesticides

The use of pesticides is mainly on agriculture land. Pesticides are usually used to increase crop production and to kill pests which are harmful for plants. More crop production is the demand now days due to increase population. The pesticides exposure is harmful for human health and environment. The pesticides are extremely toxic in nature and due to this reason pesticides are responsible for serious health concern to human health and environment. The major part which is contaminated due to pesticide is agriculture area and pesticides are also released in environment through agriculture waste water and pesticides manufacturing industry.[16] The effects of pesticide in environment depend on thing given. These are pesticides environmental behavior, pesticide toxic nature and amount of pesticide applied.[16] In addition to it, pesticides are responsible to cause serious environmental concern due to Biomagnifications (Figure 4; Table 1).[15,17]

There are various health risks and side effects of using pesticides. Majority of the farmers still mainly used DDT, Malathion, endosulphan, organophosphates, carbamates, and other organochlorides as pesticides. The method of pesticides application on soil is aerosols and hand sprayers. There are various health effects of using pesticides on human health. These health effects with their percentages have given in figure 5 graphically.[18]

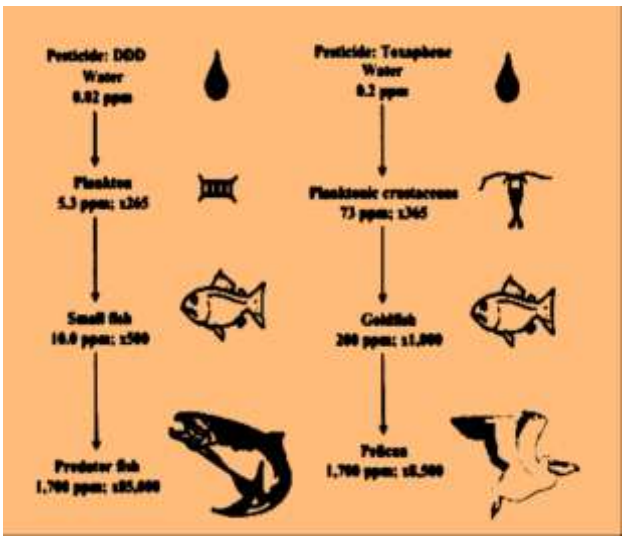

Figure 4: Toxic chemicals bio-magnification.

Bioremediation of Pesticides

There are many methods available for pesticides treatment. These methods are given in Table#2. These are thermal, chemical, physical and biological methods. These methods are better shown in table 2 as given.

Table 2: Methods of bioremediation.

Thermal Methods	Chemical Methods	Physical Methods	Biological Methods
Incineration	Ozonation/ UV radiation	Adsorption	Biodegradation technique for pesticides wastewater treatment
Open burning	Fentonoxidation	Reverse osmosis	
	Electro-oxidation: innovative technologies, cost intensive and are not ecofriendly in nature	Nanofiltration	
	Electro-coagulation: innovative technologies, cost intensive and are not ecofriendly in nature	Electro dialysis	
	Phytoremediation	Membrane distillation	
	Photo-catalytic degradation		
	Advance oxidation processes: Pollutants are adsorbed on the surface of adsorbate using activated carbon, inorganic material, organic material and naturally available material		
	Coagulation: It promotes the interaction of small particles to form larger particles		
	Flocculation: process of producing interparticle contacts that lead to the formation of large particles		

The disadvantages of these techniques involves high cost, not eco-friendly, and not suitable for less concentration.[19-20] Now days, advanced oxidation processes that come under coagulation and adsorption technologies are more demanding for treatment of waste water. This method is thought to be more attractive as compared to conventional purification methods. The details of the procedures which are more commonly used have given in the table. In addition to it, the methods which have less energy requirement, cost effective, involves simple method of coagulation are more effective for bioremediation. If we talk about water purification method, the integration of coagulation and adsorption is most common and attractive technology for the research to grow. The pesticide toxic nature demands some bioremediation method to eradicate.

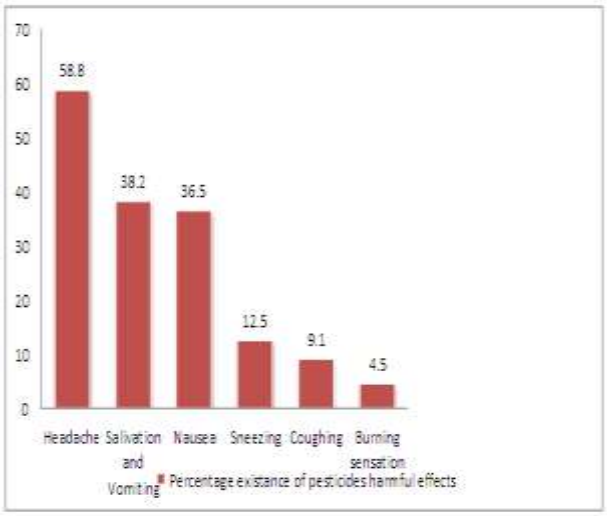

Figure 5: Graph representing pesticides harmful effects percentages.

The pollutants are rapidly increasing. Sometime, microorganisms in polluted environment are responsible for intrinsic bioremediation. The bioremediation process requirements are summarized in figure 6.[15,21]

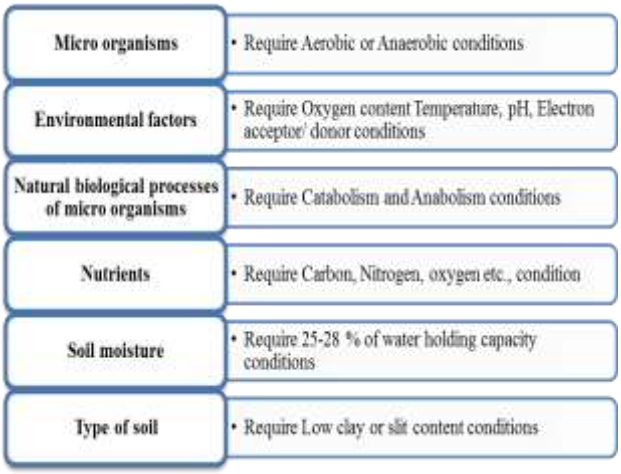

Figure 6: Pesticides bioremediation requirements.

Strategies for Pesticide Remediation

Pesticide pollution is a serious environmental problem and their remediation is necessary. Ideal treatment should result in destruction of the compounds without generation of intermediates. The strategies are shown in figure 7.[22,23]

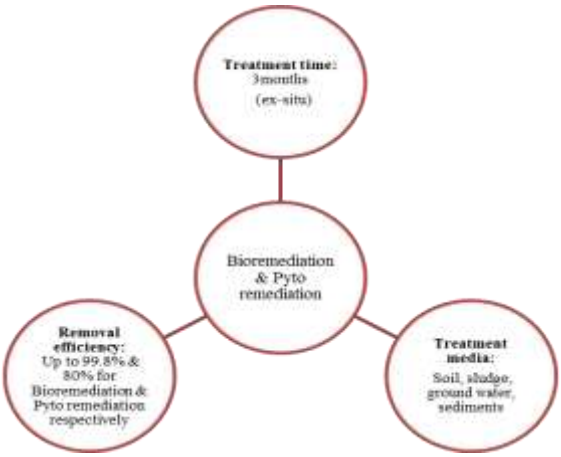

Figure 7: Pesticide-contaminated sites treatment technologies.

Role of Bacterial, Fungal and Enzymatic Degradation of Pesticides

Bacterial species that are involve in biodegradation of pesticides are *Flavobacterium, Arthobacter, Aztobacter, Burkholderia, Bacteruim* and *pseudomonas.*[24]

The pesticide biodegradation if occur completely then pesticides initial compound convert into carbon dioxide and water. This reaction also gives energy to microorganisms. The soil in which innate microorganisms are not able to degrade pesticides, other microorganisms addition is recommended to make soil suitable for pesticides degradation. The microbial degradation of pesticides depends on enzymes, temperature, pH and nutrients. In pesticides, some of them are can degrade easily while on the other hand some microorganisms due to their structure capability are not easily degraded. It is better to say these pesticides recalcitrant and these aspects of pesticides is due to anionic structure. In addition to it, *Pseudomonas* species are involved in degradation of organophosphorus compounds, and the Neonicotionoids as shown in the figure 8.[25]

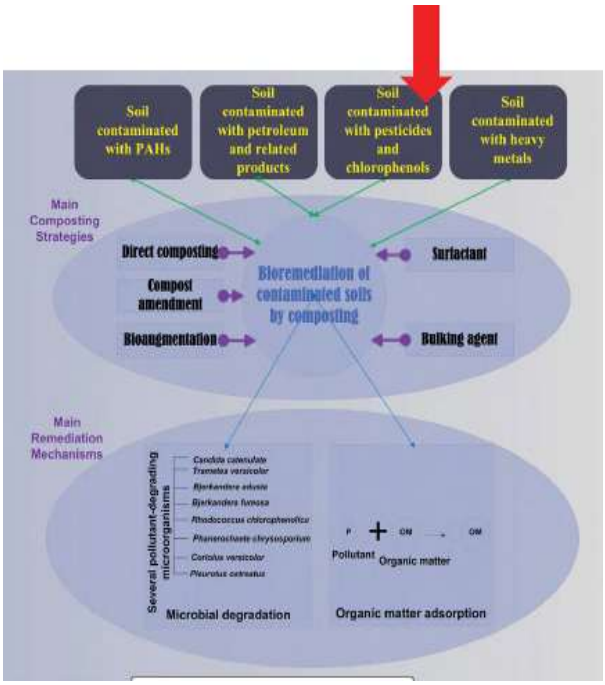

Figure 8: Phenanthrene bioavailability and degradation (compost amended soil).

The pesticides are degraded by fungi when it undergoes structural changes. The fungi with minor change in structural details convert parent toxic pesticide compound into non-toxic compounds. Then this compound is released into soil where its further degradation takes place if necessary. The different fungi which have shown ability to degrade pesticides are given in figure 9.[26]

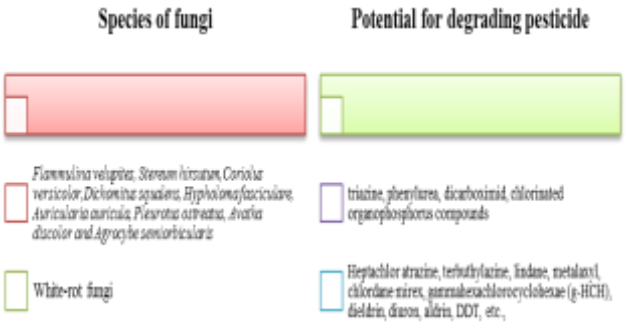

Figure 9: Pesticides degrading fungi.

If we talk about enzymes, enzymes have ability to degrade many xenobiotics biologically. Moreover, enzymes have also ability to renew pollutants into less toxic compounds. Actually enzymes have potential to renovate polluted environment to a noticeable rate.[27] In

addition to it, enzymes follow mechanisms of intrinsic detoxification and biodegradation for pesticides degradation. An organism that is *P. putida*, its enzyme consists of larger family of biocatalysis enzyme. These biocatalysis is involved in reactions that are relevant to environment. Fungal enzymes have additional attribute of removing contaminants of polyaromatic hydrocarbons (PAHs). Their action takes place mostly in fresh, marine water or terrestrial. The most common fungal enzymes are oxidoreductases, laccase and peroxidases.[28] Furthermore, these enzymes are also important for xenobiotics biodegradation.

The organophosphorus compounds are also investigated and enzymes are also identified to degrade organophosphorus compounds. In literature the first bacterium i.e. *Flavobacterium* sp. ATCC 27551 was isolated from soil of Philippines in 1973. This bacterium was having ability to degrade organophosphorus compounds. Till now, many bacteria, fungi and cyanobacteria have isolated which have characteristics to degrade organophosphorus compounds. These microorganisms use OP compounds as carbon, nitrogen or phosphorus sources as shown in figure 10[29] and table 3.

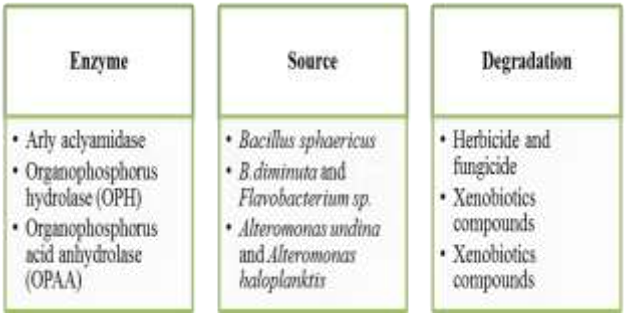

Figure 10: Enzymes their Source and degradation ability.

Table 3: Organisms role in bioremediation- An insight.

Process	Source	Pollutant	Microbes/plants	References
Biodegradation	Garden, beach and mud	Saw	*Aspergillus* sp *Trichoderma* sp	[30]
Degradation	Cellulosic materials	Blue dye 2B	*Bacillus* sp	[31]
Phytoremedtion	Soil	Pb, Cd	*Vetiveria zizanioides* and *Eichornia crassipes*	[8]
Phytoremedation Adsorption	Sewage irrigated soils wastewater	Heavy metals	Flagellate sp. Of *Dunaliella* algae	[32]
Adsorption	Soil	Cu, Mn, Zn, Pb, Cr and Pd	Three herbaceous plants (*Plantago major*, L., *Taraxacum officinale* and *Urtica diocia*	[32]

Much works have done on the discovery of plant products. These plant products are used as biopesticides. It is much more easy strategy for the destruction of target pests.

Many organisms are found to degrade pesticides.[33,34] A WHO toxic pesticides class also exists. This class is found to degrade by microorganisms. Ample work has been done to find out these microorganisms. These organisms are beneficial to degrade pesticides. In addition, these organisms can accelerate the process of bioremediation as shown in figure 11.[35]

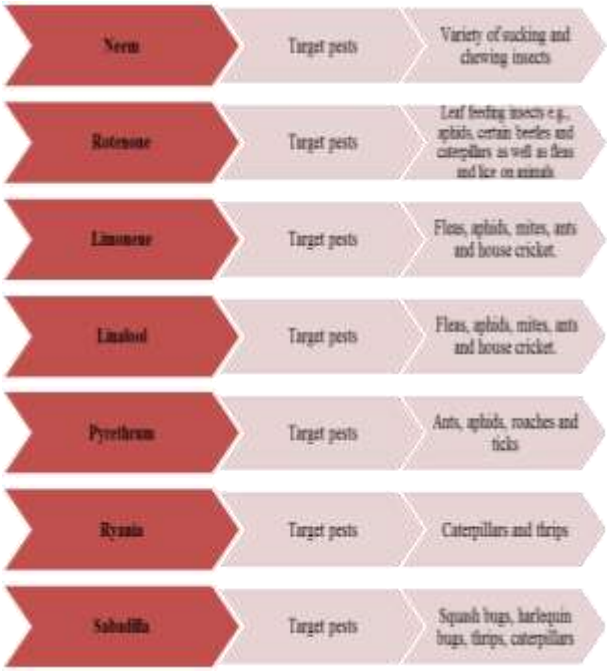

Figure 11: Products of plant use to target pests.

CONCLUSION

This review illustrates the use of pesticides has severe impacts on soil fertility. The pesticides application on soil causes serious concern to human health and ecosystems. From an industrial point of view, the strategy of bioremediation has prospective of eliminating pesticides contaminants from soil. The innate microorganisms of soil have potential of degrading pesticides from environment. The microorganisms use their enzymes for degradation of pesticides, pollutants and other persistent chemical compounds. These microorganisms are known to have bioremediation potential. There is a need to explore this field as it can surely solve the issues related to human health and environmental hazards. More research on this aspect of bioremediation is required for safe environment and hence future.

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