

## Review on Bioremediation of Pesticides

Baba Uqab, Syeed Mudasir, Ruqeya Nazir\*

Department of Environmental Sciences/Centre of Research for Development, University of Kashmir, Jammu and Kashmir, India

### Abstract

With the onset of industrial revolution and manufacture of various pesticides has no doubt enhanced yield in our agricultural products and also protect our majority of crops from the pests. As we cannot lose the majority of crops to these pests. Pesticides at present play an important role in enhancing the yield and provide an economical benefit to our farmers, but the use of pesticides in the agricultural fields is a major concern today. Increase in soil pollution has caused a serious concern. Large numbers of contaminants in which pesticide is one the major concern have pose a serious threat to human health as well as to the natural ecosystem. The available methods (physical or chemical) are either incomplete or costly. Bioremediation provides a novel tool or such process. Bioremediation provides an eco-friendly, economical and efficient method for detoxification of pesticides.

**Keywords:** Pesticides; Bioremediation; Detoxification; Pollution; Fertilizers

### Introduction

Pesticides are the chemical substances use to kill or manage pests at tolerable levels. The suffix “cide” literally means to kill. Pesticides consist of different products with different functions. Table 1 but the designation is formed by combining the names of pest with suffix [1].

The rapid increase in population has resulted in accumulation of variety of chemicals in the environment. Thus the production of these xenobiotics has forced to implement new technologies to reduce or eliminate them from the environment. Earlier techniques or technologies which were used to eliminate them from environment were landfills, recycling, pyrolysis etc., but these also have adverse effects on the environment and leads to formation of toxic intermediates [2]. These methods proved to be expensive and difficult to execute especially in case of pesticides [3].

The promising technology which utilizes the ability of microorganisms to remove pollution from the environment and are eco-friendly, economical and versatile is Bioremediation [4]. The extensive use of pesticides has resulted in serious environmental as well as health problems besides has effected biodiversity as well [5,6].

The use of pesticides not only degrade the soil quality but also reaches the water table hence enters aquatic environment also, so it can be infer that fate of pesticides is often uncertain, thus decontamination off pesticide polluted areas is very complex process [5]. Low degree of biodegradability has classified them into persistent toxic substances [7].

### Contamination of soil

Soil being important resource on the planet earth is being degraded from variety of sources. Heavy metals, pesticides, municipal garbage. Municipal garbage contains discarded materials from home and industry contains paper, plastic and organic matter [8]. Heavy metals in soil come from atmospheric deposition, sewage, irrigation, industry and use of pesticides and fertilizers [9]. Effect of contamination may result in the loss of biodiversity and functioning of soil like nutrient cycling etc. Heavy metals also inhibit microbial activity [10].

### Contamination of water

Water is arguably the most important resource on the planet earth providing the unique habitat to variety of organisms. Pollution levels in the water ecosystems had resulted in loss of fresh water content on

planet earth. Lack of access to toilet facilities among Indians has crossed 700 million mark and about 1000 Indians die of diarrhea every day. Lack of fresh water has acute scarcity in china and 500 million people lack access to safe drinking water Excess use of fertilizers, herbicides and pesticides cause serious damage to life present in waters. Excess Phosphorous results in the Eutrophication. Among the pesticides 98% were classified as acutely toxic for fishes and crustaceans [11].

### Pesticide scenario of India and world

Pesticide consumption in world has reached to 2 million tones as per Abhilash and Nandita [12] and from these 2 million tones Europe utilizes 45% followed by USA 24% and rest 25% in rest of the world. Pesticide consumption in Asia is also alarming. China uses highest percentage followed by Korea, Japan and India. In India use of pesticide is about 0.5 kg/hectare and large contribution is from organochlorine pesticides. The usage is because of warm humid climatic conditions [13]. The concept of green revolution has played a important role for utilization of variety of pesticides for high yield varieties. Presently India is largest producer of pesticides in Asia and ranks 12<sup>th</sup> in world. Pesticide residue in several crops has also affected the export of agricultural commodities in the last few years. In this context, pesticide safety, regulation of pesticide use, proper application technologies, and integrated pest management are some of the key strategies for

| Pesticide    | Target   | Pesticide               | Target   |
|--------------|----------|-------------------------|----------|
| Algicides    | Algae    | Molluscicides           | Snails   |
| Avicides     | Birds    | Nematicides             | Nematode |
| Bactericides | Bacteria | Virucides               | Viruses  |
| Fungicides   | Fungi    | Rodenticides            | Rodents  |
| Insecticides | Insects  | Miticides or Acaricides | Mites    |

Table 1: Classification of pesticides according to their target.

\*Corresponding author: Nazir R, Department of Environmental Sciences/Centre of Research for Development, University of Kashmir, Jammu and Kashmir, India, Tel: +91-9419023191; E-mail: ruqiyaya.du@gmail.com

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minimizing human exposure to pesticides and to maintain the fertility of the soils for proper productivity. There is a dearth of studies related to these issues in India Uttar Pradesh is the largest consumer followed by Punjab, Haryana and Maharashtra. Regarding the pesticide share across agricultural crops, cotton account for 45% followed by rice (25%), chillies/vegetables/fruits (13-24%), plantations (7-8%), cereals/millet/oil seeds (6-7%), sugarcane (2-3%) and other (1-2%) [12,14].

### Pesticide classification

Pesticides encompass a variety of different types of chemicals including herbicides, insecticides, fungicides and rodenticides. Pesticides are usually classified on the basis of structure (Table 2). The structural classification include organochlorine, organophosphorus, carbamates, nitrogen based pesticides [14].

### Bioremediation history and use

Bioremediation from its root meaning means to use microorganisms to remediate/ destroy or to immobilize pollutant from environment [15]. Natural Bioremediation has been used by civilizations for the treatment of waste water but intentional use for reduction of hazardous waste is more recent development. Modern bioremediation and use of microbes to consume pollutants are credited in part to George Robinson He used microbes to consume an oil spill along the coast of Santa Barbara, California in the late 1960s.

### Pesticide concerns

Pesticides are not only toxic to humans but they pose a threat to safety of soil water and air quality [16]. The pesticide contamination of surface and ground water pose a serious threat to surrounding ecosystems. The organochlorine and organophosphates cause tumors, irritability and convulsions [14]. Besides this organochlorine pesticides cause serious environmental issues due to Biomagnifications (Figure 1; Table 3).

### Pesticide bioremediation methods

The level of toxicity caused by the pesticides leads to the great need for bioremediation. No doubt in some cases intrinsic bioremediation occurs because of microbes that are already present in polluted ecosystems, but it is also true that in some cases intrinsic bioremediation is not adequate. The requirements for the process of bioremediation of pesticides given by Ref. [14] are summarized in Table 4.

### Strategies for pesticide remediation

Pesticide pollution is a serious environmental problem and their remediation is necessary. Ideally treatment should result in destruction of the compounds without generation of intermediates (Table 5).

### Bacterial degradation of pesticides

Bacteria species that degrade the pesticides belongs to genera *Flavobacterium*, *Arthobacter*, *Azotobacter*, *Burkholderia*, and *Pseudomonas* [17]. Recently *Bacterium raoultella* sp is also found to degrade pesticides.

The complete biodegradation of the pesticide involves the oxidation of the parent compound resulting in to carbon dioxide and water, this provides energy to microbes. The soil where innate microbial population cannot be able to manage pesticides, the external addition of pesticide degrading micro flora is recommended. Degradation of pesticides by microbes not only depends on the enzyme system but also the conditions like temperature, pH and nutrients. Some

of the pesticides are easily degraded however some are recalcitrant because of presence of anionic species in the compound. Besides organophosphorus compounds, the Neonicotinoids are degraded by the *Pseudomonas* species (Figure 2).

### Role of fungi

The minor structural changes that fungi does to degrade pesticides and render them into nontoxic substances and release them into soil where it is susceptible to further degradation. The various fungi which have shown ability to degrade pesticides are given in Table 6.

### Role of enzymes

Enzymes take part in key role in Biodegradation of any xenobiotics and are able to renovate pollutants to a noticeable rate and have prospective to restore polluted environment [18]. Enzymes are also involved in the degradation of pesticide compounds, both in the target organism, through intrinsic detoxification mechanisms and evolved metabolic resistance, and in the wider environment, via biodegradation by soil and water microorganisms. *P. putida* theoretical oxygen demand (TOD) enzyme is a representative of a much larger family of enzymes with application in the biocatalysis of environmentally relevant reactions. Fungal enzymes especially, oxidoreductases, laccase and peroxidases have prominent application in removal of polyaromatic hydrocarbons (PAHs) contaminants either in fresh, marine water or

| Pesticide           | Examples  |
|---------------------|---|
| Insecticide         |   |
| Organophosphorus    | Diazinon, dichlorvos, dimethoate, malathion, parathion      |
| Carbamate           | Carbaryl, propoxur, Aldicarb methiocarb                     |
| Organochlorine      | DDT, methoxychlor, toxaphene, mirex, Kepone                 |
| Cyclodienes         | Aldrin, chlordane, dieldrin, endrin, endosulfan, heptachlor |
| Herbicides          | Chlorophenoxy acids, hexachlorobenzene (HCB)                |
| Nitrogen-based      | Picloram, Atrazine, diquat, paraquat                        |
| Organophosphates    | Glyphosate (Roundup)  |
| Fungicide           |   |
| Nitrogen-containing | Triazines, dicarboximides, phthalimide                      |
| Wood preservatives  | Creosote, hexachlorobenzene                                 |
| Botanicals          | Perethrin, permethrin                                       |
| Antimicrobial       | Chlorine, quaternary alcohols                               |

Table 2: Types of Pesticides and Examples from Ref. [14].

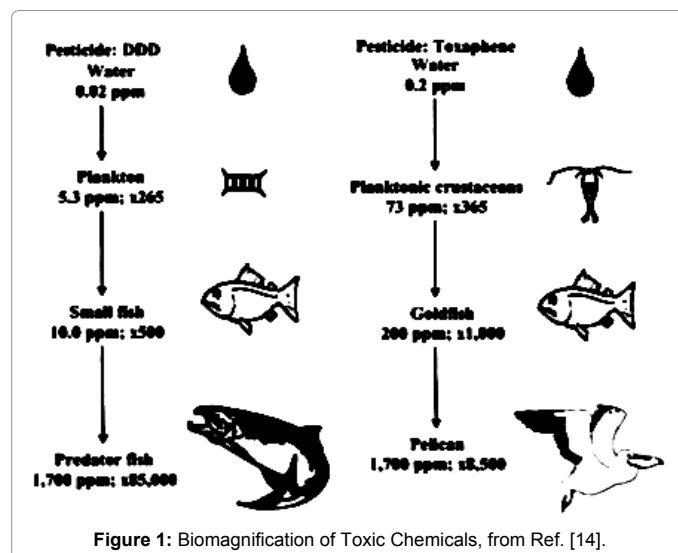


Figure 1: Biomagnification of Toxic Chemicals, from Ref. [14].

| Pesticide                             | Persistence (Half-life) | Health Effects   |
|---------------------------------------|-------------------------|--|
| Aldrin                                | 20 days to 1 year       | Nervous system effects. Probable carcinogen.<br><b>Large doses:</b> convulsions, death.<br><b>Moderate doses:</b> dizziness, headaches, vomiting, uncontrolled muscle movement   |
| Dichlorodipe nyltrichloroethane (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.<br><b>Higher doses:</b> convulsions and death. |
| Dieldrin                              | Up to 7 years           | Nervous system effects. Probable carcinogen.<br><b>Large doses:</b> Convulsions, death. <b>Moderate doses:</b> Dizziness, headaches, vomiting, uncontrolled muscle movement.   |
| Heptachlor                            | 0.4 to 2 years          | Nervous system damage, liver and adrenal gland damage, tremors   |

Table 3: Health effects of common pesticides, from Ref. [23].

| Factor  | Conditions required                                      |
|---|--|
| Micro organisms                                 | Aerobic or Anaerobic                                     |
| Natural biological processes of micro organisms | Catabolism and Anabolism                                 |
| Environmental factors                           | Oxygen content Temperature, pH, Electron acceptor/ donor |
| Nutrients                                       | Carbon, Nitrogen, oxygen etc.,                           |
| Soil moisture                                   | 25-28 % of water holding capacity                        |
| Type of soil                                    | Low clay or slit content                                 |

Table 4: Requirements for the process of bioremediation of pesticides, from Ref. [15].

| Technology        | Treatment time in months | Treatment media                       | Removal efficiency | References |
|-------------------|--------------------------|---------------------------------------|--------------------|------------|
| Bioremediation    | 3 ( <i>ex-situ</i> )     | Soil, sludge, ground water, sediments | Up to 99.8%        | [24]       |
| Phyto remediation | 3 ( <i>ex-situ</i> )     | Soil, sludge, ground water, sediments | Up to 80%          | [29]       |

Table 5: Technologies available for treatment of pesticide-contaminated sites.

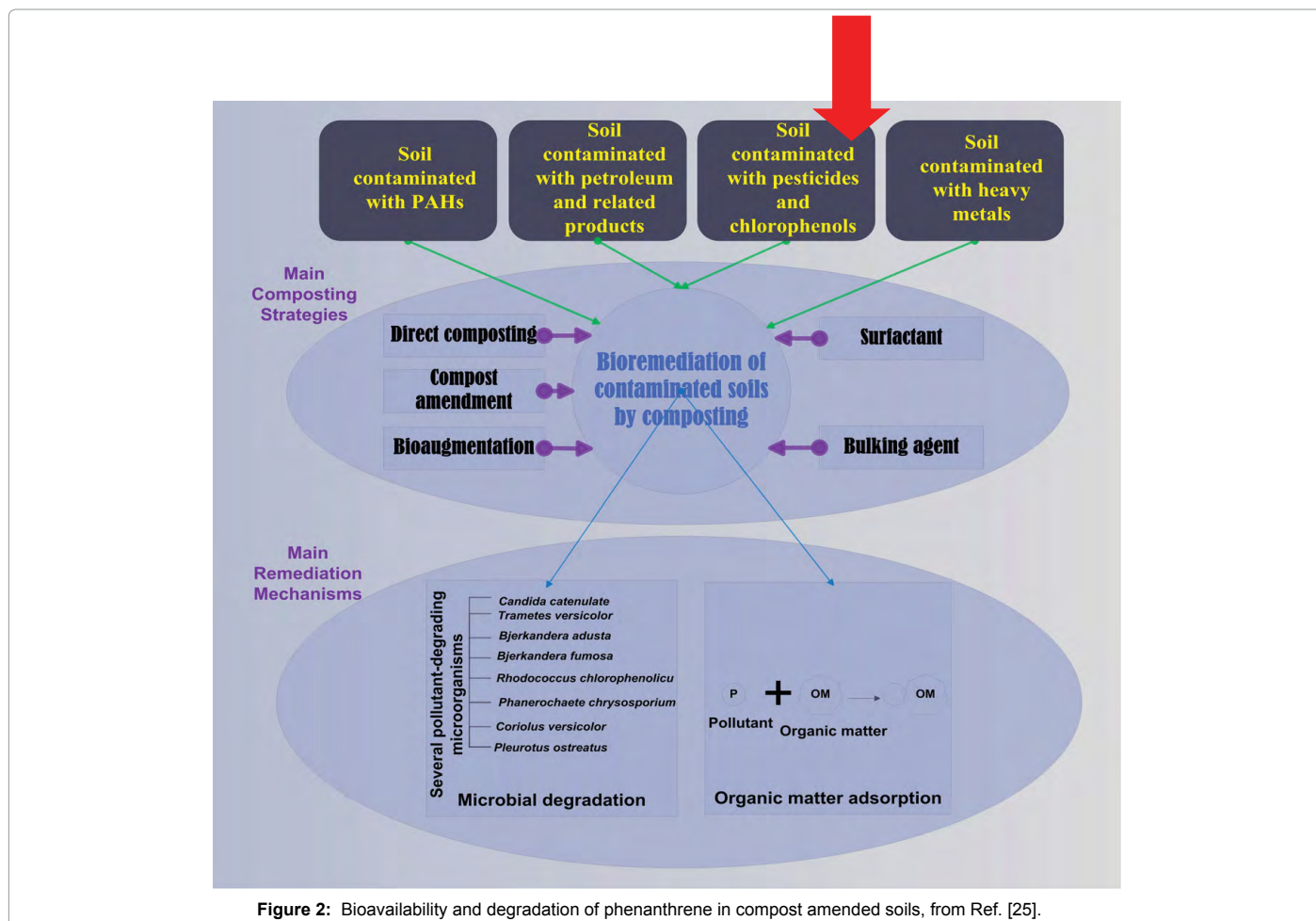


Figure 2: Bioavailability and degradation of phenanthrene in compost amended soils, from Ref. [25].

| Species of fungi   | Potential for degrading pesticide  | Reference |
|--|--|-----------|
| <i>Flammulina velupites</i> , <i>Stereum hirsutum</i> , <i>Coriolus versicolor</i> , <i>Dichomitus squalens</i> , <i>Hypholoma fasciculare</i> , <i>Auricularia auricula</i> , <i>Pleurotus ostreatus</i> , <i>Avatha discolor</i> and <i>Agrocybe semiorbicularis</i> | triazine, phenylurea, dicarboximid, chlorinated organophosphorus compounds   | [30]      |
| White-rot fungi  | Heptachlor atrazine, terbuthylazine, lindane, metalaxyl, chlordane mirex, gammahexachlorocyclohexane (g-HCH), dieldrin, diuron, aldrin, DDT, etc., | [30]      |

Table 6: Various fungi which have shown ability to degrade pesticides.

| Enzyme                                   | Source  | Degradation             |
|--|---|-------------------------|
| Arly acylamidase                         | <i>Bacillus sphaericus</i>                                    | Herbicide and fungicide |
| Organophosphorus hydrolase (OPH)         | <i>B. diminuta</i> and <i>Flavobacterium</i> sp.              | Xenobiotics compounds   |
| Organophosphorus acid anhydrolase (OPAA) | <i>Alteromonas undina</i> and <i>Alteromonas haloplanktis</i> | Xenobiotics compounds   |

Table 7: Sources of enzymes and there degradation property.

| Process                     | Source                            | Pollutant                 | Microbes/plants  | References |
|-----------------------------|-----------------------------------|---------------------------|--|------------|
| Biodegradation              | Garden, beach and mud             | Saw                       | <i>Aspergillus</i> sp <i>Trichoderma</i> sp  | [28]       |
| Degradation                 | Cellulosic materials              | Blue dye 2B               | <i>Bacillus</i> sp   | [21]       |
| Phytoremediation            | Soil                              | Pb, Cd                    | <i>Vetiveria zizanioides</i> and <i>Eichornia crassipes</i>  | [8]        |
| Phytoremediation Adsorption | Sewage irrigated soils wastewater | Heavy metals              | Flagellate sp. Of <i>Dunaliella</i> algae  | [26]       |
| Adsorption                  | Soil                              | Cu, Mn, Zn, Pb, Cr and Pd | Three herbaceous plants ( <i>Plantago major</i> , L., <i>Taraxacum officinale</i> and <i>Urtica dioica</i> | [26]       |

Table 8: Role of different organisms in bioremediation.

| Plant products used as pesticides | Target pests   |
|-----------------------------------|--|
| Neem                              | Variety of sucking and chewing insects   |
| Rotenone                          | Leaf feeding insects e.g., aphids, certain beetles and caterpillars as well as fleas and lice on animals |
| Limonene                          | Fleas, aphids, mites, ants and house cricket.  |
| Linalool                          | Fleas, aphids, mites, ants and house cricket.  |
| Pyrethrum                         | Ants, aphids, roaches and ticks  |
| Ryania                            | Caterpillars and thrips  |
| Sabadilla                         | Squash bugs, harlequin bugs, thrips, caterpillars  |

Table 9: Plant products used in pesticides to target pests.

terrestrial [19]. The enzymes play a key role in the biodegradation of any xenobiotics compounds.

The organophosphorus compounds have been studied in detail and hence much of the literature is available describing the OP degrading enzymes. In 1973, the first bacterium to degrade OP compounds was isolated from a soil sample from the Philippines and was identified as *Flavobacterium* sp. ATCC 27551. Since then, several bacteria, a few fungi and cyanobacteria, have been isolated that can use OP compounds as a source of carbon, nitrogen or phosphorus (Tables 7 and 8).

Ample work has been done to discover various plant products that can be used as biopesticides, hence made it easier to destroy target pests with these products a list of such plant products in given in table given below [20].

Variety of organisms has been involved to degrade pesticides and the result has been a success [21-25]. Toxicity class of pesticides given by WHO in which the pesticides have been classified into three classes which represent their hazardous potential have also been found degradable by the microorganisms. Hence, the process of bioremediation has been accelerated by the use of such organisms [26-30] (Table 9).

## Conclusion

No doubt the pesticides have caused serious impact on the soil fertility. Soils contaminated with pesticides have attracted high

attention because it impacts human health and natural ecosystem. Bioremediations has a tremendous potential for remediation of the soils that are affected by pesticides. Microorganisms that are present in the soils can remove pesticides from the environment. Biopesticide enzymatic degradation of polluted environment represents most important strategy for pollutant removal and degradation of persistent chemical substances by enzymatic reactions have been found high bioremediation potential. Hence bioremediation is much promising approach to overcome the pesticide pollution that can surely solve the problem of pesticide pollution of soils. This technology has proved again and again its potential to degrade not only pesticides but also the various in organic compounds. So time is to utilize this eco-friendly technology for better and safe future.

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