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### INVESTIGATING THE DEGRADATION PATHWAYS OF VARIOUS ENVIRONMENTAL POLLUTANTS

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### ABSTRACT

The preservation of Earth's three primary environmental components—water, soil, and air is crucial to the maintenance of life as we know it. Multiple forms of physical, biological, and chemical pollution are present in the environment at varying intensities. There are a plethora of biological, chemical, and physical remediation methods that have been created for environmental protection, both in situ and ex situ. High cost, processing time, and environmental feasibility are a few of the constraints of most approaches. When opposed to chemical and physical methods, biological ones tend to be less harmful to the environment. The intricacy of the pollutant composition further adds to the difficulty of the clean-up process.

Keywords: Environmental, Organism, Biodegradation, Pollutants and Chemicals

## INTRODUCTION

Environmental contamination has been caused by the massive production and use of many synthetic organic compounds in both agricultural and industrial settings. Discharges into the environment can be intentional or unintentional and include a wide variety of synthetic chemicals, including but not limited to: herbicides, pesticides, plasticizers, dyes, detergents, pharmaceuticals, petroleum products, and industrial chemicals like lubricants, coolants, insulators, hydraulic fluids, solvents, and synthetic waste (Hutzinger and Veerkamp, 1981). The majority of industrial facilities release harmful chemicals into the environment. As a result, their concentrations in the environment are steadily rising to concerning levels.

There have been reports that indicate a number of these compounds and the results of their biotransformation may be harmful, mutagenic, or carcinogenic to both humans and other animals. Serious pollution and ecological problems might result from the accumulation of these substances in the soil if they are not broken down. Polluting the environment are many kinds of aromatic chemicals that seep into soil, including polycyclic aromatic hydrocarbons, nitroaromatics, sulphoaromatics, haloaromatics, and polychlorinated biphenyls. The different parts of the ecosystem are affected by the toxicological and other bad impacts of the environmental pollutants.

It is arguable that these harmful compounds are alien to the environment as they did not exist in the biosphere before humans synthesised them. Many different types of microbes in the biosphere contribute to the breakdown of substances in the environment. A wide variety of synthetic organic chemicals may be degraded into intermediates that can enter the main metabolic pathways by the diverse microbial communities found in soil and water. The natural carbon cycle cannot continue to function without the mineralization of organic compounds. Studies on the microbial degradation of environmental chemicals and its potential biotechnological uses in the decontamination of polluted sites and effluents have received a lot of attention because microorganisms are important agents for destroying synthetic chemicals in the natural environment.

## LITERATURE REVIEW

**Mukherjee** (2021) When soil, groundwater, or even whole ecosystems are damaged, bioremediation may help restore them by enhancing natural biological processes. Toxic or hazardous materials may be "bioremediated" by using biological agents to break them down into less harmful compounds. The biosphere is teeming with microorganisms. These microbes play a crucial role in cleaning up contaminated and hazardous environments. The use of appropriate bioremediation processes and treatments may restore severely contaminated environments. To mitigate the negative impacts of pollution on the ecosystem, this review has examined several bioremediation as a more effective alternative to conventional physical and chemical procedures for restoring a healthy environment.

Anbalagan (2020) when thinking about global warming, two big problems are water contamination and the use of fossil fuels. Green technology for pollution cleanup and energy generation is being developed via photocatalysis research. A process known as photocatalysis uses semiconducting materials to transform the energy of light, in the form of photons, into chemical energy. These photocatalytic compounds are synthesized using various ways. The creation of photocatalytic materials involves the use of metal and linked metal frameworks. We take a look back at photocatalyst synthesis and its uses in decontaminating the environment and making biodiesel, methanol, and hydrogen. Some examples of pollutants include phenols, antibiotics, pesticides, herbicides, and dyes.

**Nishat (2022)** Polluted water and soil may be caused by a wide variety of physical, chemical, or biological contaminants, including but not limited to: pesticides, chemical fertilisers, heavy metals, nutrients that do not break down, biological agents, and many more. National and international legislation have been slow to respond to the growing concern about the environmental impact of these chemicals and compounds. Finding solutions to these problems is a difficult task for human civilization. To combat environmental contamination, scientists and technologists have discovered new, isolated bacteria that show promise. The role of their enzymes and metabolites in environmentally friendly toxin removal is significant. Current consensus and representative reports in this field are also highlighted in this chapter, as is the use of technology based on microorganisms to remove developing contaminants from the environment. Utilizing naturally occurring organisms like as bacteria, fungus, actinomycetes, and others, this remediation method destroys or detoxifies substances that pose a threat to people and the environment. Among its many benefits, this technique is popular because to its all-natural process, low energy and equipment requirements, and friendliness to the environment.

Wahyuni, Endang & Kunarti, Eko. (2022). Chemical analysis and techniques for pollutant removal that adhere to some of the 12 principles of Green Chemistry are discussed in this chapter. This chapter provides an overview of Green Chemistry and its 12 guiding principles. Chemical identification and concentration determination, using either traditional or instrumental approaches, are addressed by presenting a number of chemical analysis

techniques. The instrumental methods offered in this chapter are limited to atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF) for determining the analyte concentration and infrared spectrometry (IR) and X-ray diffraction (XRD) for chemical identification. The conventional methods evaluated in this chapter include gravimetric and volumetric analysis. Methods for removing pollutants using both traditional and cutting-edge techniques are also discussed. Typical chemical removal techniques including adsorption, precipitation, and coagulation are shown. Topics covered in this chapter include ozonation, Fenton and Photo-Fenton, photocatalytic degradation, photo-oxidation/reduction, and advanced approaches for chemical pollutants are detailed with an assessment of how well they adhere to or depart from certain Green Chemistry principles.

**Sharma, Indu.** (2020). Degradation, elimination, immobilization, or detoxification of various physical and chemical harmful chemicals from the environment via the activity of microbes is a key component of bioremediation. Degrading and transforming pollutants into less harmful forms is the primary premise. Several variables, such as cost, site conditions, type, and concentration of contaminants, determine whether bioremediation is done ex-situ or in-situ. Therefore, the most suitable bioremediation method is chosen. Environmental elements determine the completeness of bioremediation, and the main strategies to develop it include bio stimulation, bioaugmentation, bioventing, bio piles, and bio attenuation. Bioremediation is the best method for cleaning up contaminated areas since it is efficient, cheap, and environmentally safe. Because each bioremediation method is tailored to a particular set of circumstances, it has its own set of pros and cons.

## MICROBIAL DEGRADATION OF AROMATIC COMPOUNDS

Soil and water microbes break down or change many different aromatic compounds, both naturally occurring and man-made, which is a big part of the biogeochemical cycles (Alexander, 1981). Aromatic compound metabolism is best shown by bacteria and fungi. Here are several bacteria: Pseudomonas, Bacillus, Micrococcus, Rhodococcus, Alcaligenes, Nocardia, Flavobacterium, Azotobacter, Acinetobacter, and Mycobacterium. According to Fewson (1981), the most adaptable genera of fungus belong to the Phanerochaete family, namely Aspergillus and Cunninghamella. While it's true that some organisms like yeasts, algae, diatoms, and even higher plants and animals can metabolise a wide range of substances, the impact of these transformations is often far larger than that of the heterotrophic bacteria and fungi found in the same environment (Alexander, 1981). Therefore, the primary agents responsible for biodegradation of environmental contaminants are the bacterial and fungal communities found in soil and water. As their only carbon and energy source, microbes may use a wide variety of aromatic chemicals.

Intricate catabolic routes allow these molecules to reach the major metabolic cycles, where they may be converted into energy or cellular components. The majority of these routes are aerobic. The metabolism of aromatic compounds relies heavily on molecular oxygen, which also serves as a terminal electron acceptor. Oxygenases are enzymes that allow organic substrates to absorb one or both oxygen atoms, catalysing these processes. According to Hayaishi (1974), oxygenases may be categorised as either monooxygenases or dioxygenases. Hydroxylation of the benzene nucleus to dihydroxyphenolic intermediates such catechols, protocatechuate, gentisate, etc. is an important step in the microbial breakdown of aromatic compounds. In order for these intermediates to reach the TCA cycle, dioxygenases break their aromatic rings, releasing aliphatic molecules. A new family of dioxygenases has been discovered, and it catalyses the double hydroxylation of aromatic substances. This sets the aromatic nucleus up for assault by ring cleavage dioxygenases, according to recent research (Subrainanian et al. 1978).

When an organism relies only on aromatic compounds for its carbon and energy needs, such compounds are often mineralized after they undergo full degradation. However, even if a chemical isn't directly used as a growth substrate, it may nonetheless undergo partial or full degradation if an organism uses another substrate. Cooxidation and cometabolism are crucial steps in the biodegradation of resistant chemicals including pesticides and halogenated hydrocarbons Since these structures do not exist in nature, microbes have just lately been introduced to synthetic organic molecules, which make them resistant to microbial breakdown (Hutzinger and Veerkamp, 1981).

Enzymes and other cellular components needed for dissimulation of ambient chemicals may be synthesised over time by microorganisms that renew quickly in the environment. Collaborative metabolism allows diverse microbial communities to provide essential enzymes for the breakdown of resistant substances. A microbe that can catalyse the first stage of the catabolic pathway but not the second step is one example. This causes it to expel the metabolic byproduct, which is then used as a substrate by another microbial community. Therefore, for comprehensive chemical biodegradation in the wild, the whole microbial population's gene pool is crucial.

## PESTICIDES AS ENVIRONMENTAL POLLUTANTS

The widespread use of several pesticides—some of which are quite harmful—increases agricultural output by preserving crops, preventing spoilage, eliminating infections, and controlling disease vectors. Pesticides are an integral part of our daily lives. Insecticides, herbicides, bactericides, and other pest control agents are a wide range of synthetic organic compounds with a wide range of chemical and biological activities. Insecticides, fungicides, herbicides, nematicides, rodenticides, and a plethora of other pest control agents are constructed from a wide variety of chemicals.

Organochlorine, organophosphorus, carbamates, synthetic pyrethroides, thiocarbamates, nitrochlorophenol derivatives, metal salts, and organometallic compounds are among the most common types of pesticides used today. Table 1 provides the structures and usage of many commonly used insecticides. There is a black side to these advantages, too, since these pesticides pose dangers to nontargets, ecosystem productivity, biodiversity, and human health. Pesticide residue is present in large concentrations in the food chain, which poses dangers to beneficial species like earthworms, honeybees, fish, and birds. This is supported by several studies and criteria papers (Jaffery el al. 1992). Pesticides' negative impacts must be included in any attempt to evaluate pollution's environmental impact.

## Table 1. Pesticides, their common and chemical names, structures and uses

Classes	Examples		Structure	Uses
	Common Name	Chemical Name		- Sea
I) Organochlorine Pesticides	DDT	1,1,1-trichloro-2,2-bis(p- chlorophenyl) ethane	CL H Cl	Insecticide applied to malaria eradication by control of mosquito, grass grub, fly house and flea vectors of plant, human and animal diseases. Also used for hundreds of species of orchard, garden field and forest pests.
	Lindane	gamma-1,2,3,4,5,6- bexachlorocyclohexane		Soil poison, seed treatment, toxicant for the grasshopper, cotton insects and rice stem borer control, insect killing shelf papers.
	Heptachlor	l,4,5,6,7,8,8-heptachloro- 3a,4,7,7a-tetrahydro-4,7- methanoindene		Cockroaches, ants, termites, soil insects, grasshopper control.
II) Organophosphorous Pesticides	Parathion	O.O-DiethylO-p-nitrophenyl phosphorothionate	C <sub>2</sub> H <sub>3</sub> O	Most widely used of this class, gartic odour high toxicity to warm blooded animals, mosquito control broad spectrum insecticides, originally used on potato beetle.
i i	Methyl parathion	O.O-Dimethyl O-p-nitrophenyl phosphorothionate	CH <sub>3</sub> O CH <sub>3</sub> O	Most widely used of this class, garlic odour high toxicity to warm blooded animals, control of plant pests broad spectrum insecticides, originally used on potato beetle.
	Malathion	Diethyl(dimethoxy thiophosphorylthio)succinate	$\begin{array}{c} & & & \\ & & & \\ &$	Household, home garden, vegetable and fruit insect control, control of mosquitoes, flies and lice.
II) Carbamates Pesticides.	Carbaryl	1-naphthyl N-methylcarbamate		General purpose insecticides, can be useful for 100 or more crops, especially cotton, forage, fruit, vegetables, lawn and garden insecticide, low toxicity to mammals.
	Carbofuran	2,3-Dihydro-2,2-dimethyl-7- benzofuranyl N-methylcarbamate	$ \begin{array}{c} 0 \\ \parallel \\ 0 \\ -C \\ -N \\ -CH_3 \\ -CH_3 \end{array} $	Systemic insecticide, acaricide and nematicide
	Aldicarb	2-methyl-2- (methylthio)propionaldehyde <i>O</i> -methylcarbamoyloxime	$\begin{array}{c} \overset{CH_3}{\underset{H_3C=S-C-CH=N-O-C-N-CH_3}{\overset{H}{\underset{CH_3}{\overset{H}{\underset{H_3C}{\overset{H}{\underset{H}{I}}{\overset{H}{\underset{H_3C}{\overset{H}{\underset{H_3C}{\overset{H}{\underset{H}{I}}{\overset{H}{\underset{H}{I}}{I}}}}}}}}}}}}}}}}}}}}}}}}}}$	Systemic action, seed and soil treatment.
	Propoxur	2-isopropoxyphenyl N-methylcarbamate		Nonsystemic insecticide, aphides, bugs, flies, jassids, millipeds, mosquitoes, cockroaches, ants and other household pests, useful in malaria control programme.

The word "pesticides" encompasses a wide variety of compounds with varying structures; this study will focus on the broad strokes; the toxicity of pesticides will not be discussed here since there are already several monographs and reviews covering that topic. Knowledge derived from reading Toxicology atlas of India (Jaffery et al. 1990), Disaster preparation in the chemical sector (Viswanathan et al. 1986), and Compilation of pesticide toxicology data handbooks (Jaffery et al. 1989a,b) forms the foundation of this article. The number of reported incidents of pesticide poisoning throughout the agricultural belt of the nation has been steadily rising over the last several years. The World Health Organisation reports that

every minute, someone in a developing country is poisoned by pesticides. There is a high prevalence of acute pesticide poisoning, including some foetal instances, among workers in impoverished nations who handle and spray agricultural pesticides. The term "Economic Poisons" has been used to characterise the insecticides.

## **Chlorinated Pesticides**

Over the last half-century, a flood of chlorinated aromatic pesticides have been produced for distribution all over the globe. Many chlorinated aromatic chemicals, including DDT, Lindane, pentachlorophenol, and many more, find employment in industrial, agricultural, and public health contexts as pesticides. Due to their toxicity and resistance to microbiological decomposition, these pollutants remain in the environment for the longest periods of time. But new research shows that chloroaromatic chemicals may break down in the body (Leisinger et al. 1981). In 1939, Muller of Switzerland was the first to notice that DDT had insecticidal capabilities.

Excessive and incorrect pesticide usage, together with the production of millions of tonnes of chlorinated pesticides, leads to the release of many harmful intermediate products and effluents into water and soil (Vollener and Klotz, 1997). Bioaccumulation and food poisoning caused by DDT occurred in the 1960s because, despite widespread restrictions, certain developing nations, like Mexico and India, kept using it heavily, particularly for public health purposes (WHO, 1969). In order to preserve crops, increase agricultural production, control disease vectors, and make industrial goods, many businesses rely on chlorinated aromatic pesticides, which are very harmful and long-lasting compounds. Contaminated locations on the EPA National Priority List include structurally similar compounds such as DDT and BHC, which are dispersed worldwide and are among the most resistant pollutants (Federal Register, April 29, 1996). When it comes to pesticides used in India, the three most wellknown ones are DDT, BHC, and melathion. Their extended persistence in nature magnifies the toxicity and health risk concerns in regions of pollution, therefore affecting the environmental profile of wide areas. This is in addition to the fact that they are carcinogenic and poisonous. It was first noticed that injected DDT into animals, including humans, was stored in adipose tissue (Jack, 1973). The second finding was that DDT might cause liver tumours and damage in rats when fed chronically.

There have been reports of DDT residues in different foods, air, water, and even breast milk Additionally, vegetables, fruits, seeds, and cereals have been discovered to be contaminated with DDT Direct and indirect exposure to pesticides may occur via the food chain, personal contact, and occupational exposure. But over 90% of these substances that people consume get up in their bodies via food Of all pesticides, only 17% were studied, and out of them, 70% were shown to be genotoxic in some way Due to their poor solubility, delayed biodegradability, toxicity, hydrophobicity, and bioaccumulation, DDT and its metabolites are among the most persistent environmental contaminants Because of their toxicity and estrogenic effects, which may alter reproductive development in animals and reptiles, this bioaccumulation poses a significant threat to humans Bioaccumulation is made worse by the fact that DDT naturally turns into l,l-dichloro-2,2-bis(p-chlorophenyl)ethylene, a more stable noninsecticidal compound that has been linked to human malignancies Given that India is still mostly an agricultural nation. There will be an inevitable increase in pesticide use in the future.

## **Carbamate Pesticides**

When organochlorine pesticides proved too difficult to control, researchers turned to carbamate insecticides (Bull, 1981; Rodriquez and Dorough, 1977). In the 1950s, carbamates were developed into insecticides for commercial use. Active herbicides, fungicides, and insecticides are chemicals that belong to this class. Esters of N-alkyl carbamic acids are the only ones that can kill insects. Aiyl esters of N-methylcarbamic acid show the most action. These pesticides have a wide range of effects and are very potent both topically and in the stomach. These compounds work by blocking the enzyme acetylcholinesterase in nerve cells, which is how they affect insects and mammals. Accumulation of acetylcholine disrupts nervous system function, which is the outcome of blocking acetylcholinesterase action in nerve tissue. The insects get paralysed and eventually die as a consequence.

Pesticide carbamates are very harmful to both humans and other animals; the rat LD50 is 16,250 mg/kg. Carbamates are harmful to embryos and cause mutations when injected into people and animals, even at low dosages. They also have a deleterious impact on the neurohumoral and endocrine systems. Extracts from the West African calabar bean were the first to yield the carbamates. There was a methylcarbamate ester in these extracts known as phytostigmine (Baron, 1991). The research of carbamates and its derivatives has provided evidence of several of their effects. Figure 1 shows the general structure of carbamates.

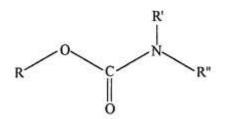


Fig. 1 General Structure of carbamates.

Such that R" is a methyl group (CH3), R is a hydrogen (H), and R is an alkyl (OH) or phenyl ring.

Pesticides and pharmaceuticals both make use of carbamate molecules. The Table is a list of certain carbamates that are important. section I.3b Many species of birds, fish, bees, and earthworms are said to be extremely poisoned by carbamate insecticides (Kidd & James, 1991; Dupont de Nemours, 1989; 1991).

### Table 2. Carbamates.

Aldicarb	Methiocarb	
Aminocarb	Methomyl	
Banol	Oxamyl	
Bendiocarb	Phenoxycarb	
Carbaryl	Promecarb	
Carbofuran	Propoxur	
Carbosulfan	Swep	
Chlorpropham	Thiodiocarb	
Isoprocarb	Zectran	
Landrin		

To protect agricultural goods stored in warehouses or shops, as well as domestic items, against weeds, insects, pests, and illnesses, the carbamate insecticide propoxur (Baygon, 2-isopropoxyphenyl-N-methylcarbamate) has seen considerable application. Various insect pests that attack crops including strawberries, potatoes, and barley have been controlled with soil-incorporated N-methylcarbamate insecticides (Chapalamadugu and Chaudhary, 1992). Groundwater in several US states has been shown to be contaminated with the N-methylcarbamate insecticide and its byproducts (Jones and Black, 1984; Zaki et al. 1982; Anonymous 1990). Inadequate storage and management of pesticides, unintentional spills, and the discharge of trash from manufacturing and consumption facilities can contribute to pollution concerns. With an LD50 of 100 mg/kg for rats, propoxur is a very toxic acetylcholinesterase inhibitor that is harmful to both humans and other animals.

Multiple human investigations have shown that propoxur is harmful. Increasing rates of sister chromatid exchange and micronuclei were reported as genotoxic effects of propoxur and its nitrosoderivatives on human cells in vitro, according to recent reports (Cid et al. 1990). It has a wide range of effects and is a very potent contact and gastric pesticide. Insects such as ants, aphids, beetles, cockroaches, flies, Jassids, millipedes, and mosquitoes may be effectively controlled using the non-systemic pesticide propoxur, which has a quick knock-down effect (Kumar and Shaxma, 1992). Damage to ecological systems is a result of its toxicity and longevity. Therefore, it is crucial to study the metabolic destiny of these pesticides in nature, since their widespread usage in warehouses and household items poses a risk of environmental contamination.

### **BIODEGRADATION OF PESTICIDES**

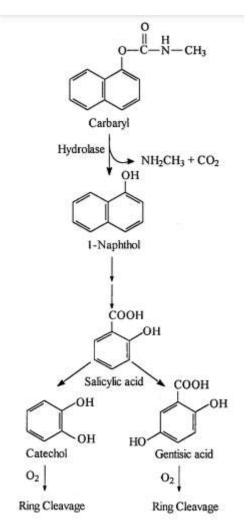
The environmental destiny of pesticides is crucial since the chemicals' usefulness or possible danger is determined by their persistence, change, or elimination. Pesticides undergo biodegradation in the environment, mostly due to the actions of microbes. various pesticides biodegrade at various rates. Some pesticides, such dieldrin, lindane, and DDT, have shown to be difficult to remove. Therefore, they remain in the environment for an extended period and end up in food chains many years after they are applied to soil. The more lasting chlorinated pesticides are being replaced by more biodegradable alternatives, such as organophosphates, in the pest control industry. In certain soil circumstances, the fast biodegradability of pesticides like carbofuran and diazinon renders them ineffective for insect management (Felsot, 1989). A pesticide's environmental latency and efficacy are significantly impacted by

the microbiological breakdown of the chemical. When pesticides break down at a normal pace, they remain effective against pests without becoming an environmental hazard. An insufficient level of pest control may result from a pesticide that degrades too quickly. It has been shown that the 'problem' or 'aggressive' soil phenomena seen following repeated application of certain pesticides absorbed into soil is partly caused by the rapid microbial breakdown of these chemicals. Economic loss due to failing crops occurs when some insecticides, even after repeated applications over many years, fail to control insects. The possibility that soil microbes exposed to these substances on a regular basis may evolve strategies to break them down is one proposed explanation. Pesticides in problematic soils degrade quickly, maybe due to microbes that have recently gained certain characteristics.

The metabolic processes used by microoganisms to degrade pesticides are crucial to understanding their environmental destiny (Somasundaram and Coats, 1990). Both the insecticides and the metabolites produced may be predicted using this data. Metabolites formed during pesticide biodegradation may be much more harmful than the original chemical. For instance, DDE, an intermediate in the breakdown of DDT, may accumulate in the environment (Boul et al. 1994). Many different types of microorganisms, both aerobic and anaerobic, have been found in various environments and have the ability to break down pesticides. Metabolism of pesticides is carried out by a broad range of bacteria, which includes species of Rhodococcus, Flavobacterium, Pseudomonas, and Alcaligenes. Bacteria may either use the pesticide as their only carbon source or break it down into its component parts. There are many environmental conditions that influence microbial breakdown, including the existence of bacteria with the right degradative enzymes. Hill and Wright (1978), McRae (1989), Wallnofer and Engelhardt (1989), Somasundaram and Coats (1990), Cork and Krueger (1991), and Aislabie and Jones (1995) are among the reviews that discuss the microbial metabolism of pesticides. The biodegradation of carbamate and chlorinated insecticides has been the subject of recent discussions.

1. **Microbial degradation of carbamate pesticides** Carbaryl, carbofuran, and propoxur are carbamate insecticides that have seen extensive usage in the management of various insect pests. The formation of N-nitrosocarbamates, which are strong carcinogens, and the chemicals' potency as acetylcholinesterase inhibitors make them ecologically dangerous (Fahmy et al., 1970; Elespuru et al., 1974). Carbate pesticides, on the other hand, do not remain in the environment for very long. Pesticide decontamination relies heavily on microbial breakdown. On the other hand, the rate of deterioration might be so high that it defeats the purpose of protecting against the specific pests. As a result, carbamate pesticide microbial breakdown has received a lot of research interest. It is believed that microbes with carbamate pesticide-degrading capabilities play a key role in the environmental detoxification of pesticides. Due to their effects on the environmental destiny of carbamate pesticides and their possible use in detoxifying pesticide waste, these microbes have attracted a lot of research. Carbamate insecticides may be rendered inactive with only one step that involves hydrolyzing the N-methylcarbamate bond (Cain and Head, 1991).

**Carbaryl Carbaryl** The pesticide sevin, which has been widely used to safeguard crops, contains the active component (1-naphthyl-N-methylcarbamate). The hydrolysis of carbaryl to 1-naphthol and degradation of the latter were documented by Bollag and Liu (1971) in their study of Fusarium solani and two unknown soil bacteria. Bollag and Liu (1972) used radioactive 1-naphthol in their tests to establish that F. solani degrades the drug. According to Sud et al. (1972), chromatographic analysis of ether-extracted cultures of an Achromobacler



grown on carbaryl for three days showed the presence of pyruvate, 1-naphthol, catechol, and quinol

Fig. 2. Bacterial degradation of carbaryl.

Enrichment cultures and Bacillus species accumulate 1-naphthol and 1,4-naphthoquinone during the metabolism of 14C-labelled carbaryl (Rajagopal et al. 1984). Three bacterial isolates from garden soil, Pseudomonas sp. (NCIB 12042 & 12043) and Rhodococcus sp. (NOB 12038), were found to metabolise carbaryl by Larkin and Day (1986). On the other hand, the gentisic acid pathway was shown to be responsible for the carbaryl metabolism in Pseudomonas sp. (NCIB 12043) and Rhodococcus sp. (NCIB 12043) and Rhodococcus sp. (NCIB 12038). The Pseudomonas sp. (NCIB 12042) is an alternative to gentisate that degrades carbaryl via 1-naphthol and salicylic acid via the catechol pathway. In Fig 2, we can see the many methods in which carbaryl is broken down by bacteria.

## Carbofuran

An extensively used insecticide in agriculture is carbofuran (2,3-dihydro-2,2dimethyl-7benzofuranylmethylcarbamate). Williams et al. (1976), Venkateshwarlu et al. (1977), Felsot et al. (1981), Rajagopal et al. (1984a), Kams et al. (1986), and Chaudhary and Ali (1988) are among the publications that discuss the bacterial degradation of carbofuran. Carbofuran is a growth substrate used by bacteria belonging to the Achromobacter, Pseudomonas, and

Flavobacterium genera. For their carbon and nitrogen needs, many of the isolates mentioned relied on methylamine, a product of carbofuran hydrolase's hydrolysis of the N-methylcarbamate ester bond. They were divided into three categories according to how they used

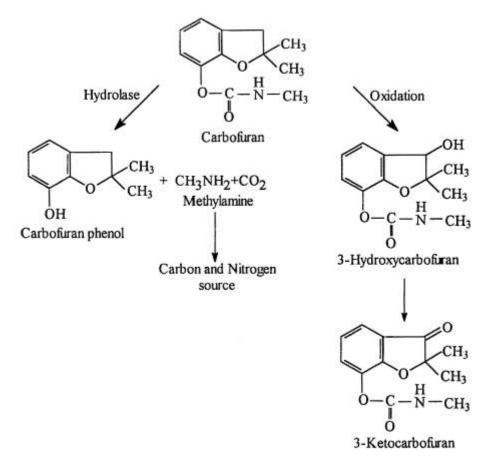


Fig.3. Bacterial degradation of carbofuran.

the drug carbofuran. As a nitrogen source, the pesticide was used by group I, whereas carbofuran was used by groups 11 and III. Cyclofuran phenol was produced when group I and group II isolates degraded carbofuran. The specific oxidative route via which group III isolates quickly destroyed carbofuran remains unknown. However, it was shown that three metabolites were produced from carbofuran after its degadation by Bacillus sp. and enrichment cultures. The metabolism of 3-hydroxycarbofuran and 3-ketocarbofuran was accelerated, although the carbofuran phenol remained stable (Rajagopal et al. 1984b). Figure 3 shows the suggested process by which bacteria break down carbofuran. While bacteria can identify their degradation products, fungal cultures such as Aspergillus niger, Trichoderma viride, and Helminthosporium sp. may generate an intermediate molecule called hydroxycarbofuran (Kandasamy et al. 1977).

## 2. Microbial Degradation of Chlorinated Pesticides

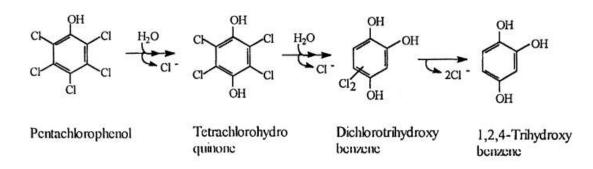
## DDT

DDT, or l,l,l-trichloro-2,2-bis(4-chlorophenyl)ethane, was the mosquito killer that was used the most all across the globe. The distribution of DDT and its metabolites is worldwide, however its usage is now restricted to poor nations (Siinonich and Hites, 1995). Among all pollutants, DDT has the longest half-life in the environment. Several bacteria may cometabolize DDT to DDD [l,l-dichloro-2,2-bis(4-chlorophenyl)ethane] under anaerobic circumstances, and it has been shown that bacterial transformation of DDT occurs under these conditions as well (Aislabie et al. 1997). The primary process by which facultative anaerobic bacteria biodegrade DDT is an initial reductive dechlorination that produces DDD. Subsequently, DDD is subjected to additional dechlorination, oxidation, and decarboxylation, ultimately yielding DDM [bis (4-chlorophenyl)methane] (Focht and Alexander, 1970). P-chlorophenylacetic acid, a byproduct of aromatic ring breakage in DDM, may be further broken down by microbes.

Subsequent dechlorination of l,l-dichloro-2,2-bis(4-chloroplienyl)ethylene (DDE) to l-chloro-2,2-bis(p-chlorophenyl)ethylene (DDMU) is possible under methogenic and sulfidogenic conditions; this process was described by Quensen et al. in 1998. According to recent reports (Nadeau et al. 1994 ; 1998), Alcaligenes eulrophus A5 may aerobically degrade DDT to 4-chlorobenzoic acid. It seems that A. eutrophus's first DDT transformation is analogous to biphenyl and 4-chlorobiphenyl degradation, which included biphenyl dioxygenase enzyme-catalyzed 2,3-hydroxylation (Gibson et al. 1973). 4,-chlorobenzoic acid is the end product of 2,3-dihydroxy-DDT, which is formed when DDT is oxidised by a dioxygenase and then mela-xmg cleaves it.

**Pentachlorophenol** The most common insecticide, wood preservative, and herbicide is pentachlorophenol (PCP). It was Crosby in 1981. Despite several findings demonstrating biodegradation of PCP, the rate of breakdown in natural environments is often poor (Crosby, 1981; Rao, 1978; Rochkind et al. 1986). Soil and groundwater have been severely polluted by PCP's accumulation in the environment due to its persistence (Crosby, 1981; Haggblom and Valo, 1995). Among the most dangerous pollutants, PCP is on the US Environmental Protection Agency's list of priorities (USEPA, 1989). In both aerobic and anaerobic environments, PCP and chlorinated phenolic compounds have been shown to biodegrade.

According to Reineke (1988), Commandeur and Parsons (1990), and Mannisto et al. (1999), microbes may break down mono, di, tri, tetra, and pentachlorophenols. Steriert and Crawford (1986) found that anaerobic Flavobacterium strains degraded PCP by a process that began with hydrolytic dechlorination in the para position to produce tetrachlorohydroquinone and then proceeded via its reductive dechlorinations. According to Steriert et al. (1987), this particular strain could break down and remove chlorine from various di-, tri-, and tetrachlorophenols. As seen in figure 4, it has been demonstrated by Rhodococcus chlorophenolicus can break down PCP into tetrachlorohydroquinone, which may then undergo a process combining hydrolytic and reductive dechlorination to transform into dichlorotrihydroxybenzene (Apajalahti and Salkinoja - Salonen, 1987).



### Fig. 4. Bacterial degradation of pentachlorophenol by Rhodococcus chlorophenolicus.

Anaerobic sewage sludges undergo reductive dechlorination of PCP (Boyd and Shelton, 1984; Mikesell and Boyd, 1986). Degradation of PCP in soil revealed full reductive dehalogenation to CO2 and methane.

### CONCLUSION

We have investigated the biodegradation of DDT and propoxur, two pesticides that are recognised as harmful to the environment. The current study aimed to clarify the biodegradative pathways of propoxur and DDT by Pseudomonas species. These species were isolated from soil through enrichment cultures. Propoxur hydrolase, an enzyme involved in the biodegradation of propoxur by Pseudomonas sp., was partially purified and characterised.

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