

Review Article

An Overview on Biodegradation of Carbamate Pesticides by Soil Bacteria

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ABSTRACT

Carbamates are poisonous pesticides which have been used widely in agriculture production for decades. Unlike other pesticides such as organophosphate, carbamate pesticides are not persistent in the environment however, their degradation is crucial due to their toxicity to living system. The World Health Organization, categorized carbamate pesticide as toxic, hazardous and restricted for use. Example of carbamates pesticides include Carbaryl, Aldicarb, Methomyl, Carbofuran, and Propoxur. They are extensively used to control many insect and pests of crops. Presently, there is significant awareness regarding the negative effects of pesticides due to their ability to pollute soil and water bodies. Most pesticides are readily degraded or metabolized by microbes. Carbamate pesticide

degradation by microorganisms relies not only on the availability of microbes with suitable biodegradative enzymes, but also on the various ecological factors. This review-article outlines the present development in biodegradation of carbamate pesticides, their toxicity and enzymatic degradation as well as their degradative pathways.

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INTRODUCTION

Pesticide is a substance or formulation of substances used in controlling, destroying and preventing any pests, that include rodents, insects, weeds, birds, nematodes, microorganisms or mammals that interfere or destroy things. Apart from their toxic effect, pesticides are also beneficial to humans in many ways. Pesticides may be categorized by chemical structure, physical form or their target species. They can also be categorized as inorganic, synthetic or biological (bio pesticides). Furthermore, pesticides may be grouped into chemical families. The most common pesticide families include the organophosphate, pyrethroid, organochlorine and carbamate pesticides which are further categorized as rodenticides, weedicides, fungicide, herbicide, and insecticide. Carbamate consists of a wide spectrum of biologically active pesticides used worldwide to control insects and nematodes. Carbamate pesticides are generally categorized into *N*-methyl-carbamate insecticides and *N*-allyl-carbamate herbicides in view of their chemical structures and biological actions (Ozturk et al., 2016; Parks et al., 1987). Carbamates are closely linked with organophosphorus compounds in mode of action and resistance meaning they are inhibitors of acetyl cholinesterase causing very similar symptoms. They have high polarity, soluble in water and thermally unstable. They are poisonous to living organisms due to their acute toxicity (Alvarez et al., 2017). The use of carbamate has received great concern not only because of their widespread use, but also due to its higher toxicity to plants and animals (Chin-Pampillo et al., 2015). Carbamates pesticides are usually converted into several products through different paths such as oxidation, biotransformation, hydrolysis, bio-augmentation, photolysis, biodegradation as well as metabolic reactions in living organisms (Cai et al., 2015). Many scientists have reported biodegradation of several pesticides by bacteria under different physiological conditions. Soil bacteria that are constantly exposed with synthetic toxic chemicals may develop new capabilities to degrade such chemicals (Wu et al., 2014). Microbial populations in soil have the ability of metabolizing (hydrolyzing) carbamate pesticide and can easily adapt themselves to various form of carbamates. However, carbamates pesticide and their metabolites can affect the micro flora and soil productivity (Gupta et al., 2016). Even though carbamate pesticides do not persist longer in aquatic environment and are very stable under aquatic conditions, the application of these toxic compounds may cause a major reduction of non-target organisms. Therefore degradation of carbamate using microbes is of great interest since many conventional approaches of removing pesticides contamination proved to be ineffective and expensive. Hence an effective and inexpensive techniques is required for treating such pollutant. Table 1, below gives details of carbamate type, chemical formula year of production and the rat LD₅₀ in mg/kg values for some carbamate insecticides. It also notes their half-lives in soil.

Table 1
History, toxicity and half-life of some Carbamates pesticides

Name	Trade Name	Type	Formula	Year of introduction	Rat LD50 (mg/kg)	Half-life soil (Days)
Carbofuran	Furadan	Insecticides	$C_{12}H_{15}NO_3$	1967	8-14	3-60
Cabaryl	Prokoz® and Sevin®	Insecticides	$C_{12}H_{11}NO_2$	1958	250 to 850	4-72
Aldicarb	Temik®	Insecticides	$C_7H_{14}N_2O_3S$	1965	0.9 - 1.0	1-15
Propoxur	Baygon®	Insecticides	$C_{11}H_{15}NO_3$	1959	80 - 191	80 - 210
Oxamyl	Vydate®	Nematicide	$C_7H_{13}N_3O_3S$	1974	2.5 - 3.1	4 - 20
Methomyl	Lannate®	Insecticides	$C_5H_{10}N_2O_2S$	1966	12-48	30-45
Methiocarb	Mesuro®	Molluscide	$C_{11}H_{13}NO_2S$	1960	23-140	15 to 50
Carbendazim	Mecarazole, Bavistin	Fungicide	$C_9H_9N_3O_2$	1972	>2000	42 to 175
Primicarb	Primor, Abol	Insecticides	$C_{11}H_{18}N_4O_2$	1970	68-221	53
Carbosulfan	Alachlor, Lasso, Pillarzo	Insecticides	$C_{20}H_{32}N_2O_3S$	1979	90 to 250	1.4
Fenoxycarb	omply, Insegar, Logic, Pictyl, Regulator	Growth Regulator	$C_{17}H_{19}NO_4$	1987	>16,800	14-45

STRUCTURES AND TOXICITY OF CARBAMATE PESTICIDES

Carbamates are acetylcholinesterase inhibiting compounds, and they are used worldwide and are responsible for poisoning and prevalent occurrence of an infectious diseases in many developing countries (Anguiano et al., 2017). Carbamate pesticides, have high acute toxicity. Chemically, carbamate insecticides remain as esters of carbamates as well as organic components derived from N-methyl carbamic acid (C_2H_5NO) which take weeks or months to break down in soil (McDonald et al., 2005). Carbamates are insecticides, herbicides, and fungicides that act like organophosphates pesticides for insecticides and nematocides by inhibiting acetyl-cholinesterase, except that the action is reversible. The toxicity is generally low, with the except for compounds such as aldicarb. Carbamate pesticides play a vital role in agriculture because of their broad spectrum nature as well as varied degree of compounds, degradable in soil and usually have small amount of toxicity on living organisms (Chapalamadugu & Chaudhry, 1992; Cycon et al., 2017). Carbamates are inhibitors of acetylcholinesterase (AChE) which become acetylcholine in synapses and neuromuscular junctions and eventually produce serious disorder of central nervous system (Berman et al., 2017; Vidair, 2004). The inhibition of the hydrolysis response of AChE results in the accumulation of ACh, which brings about many symptoms, such as hyper salivation, sweating and seizure (Guo et al., 2017). Carbamate pesticides are less hazardous with respect to human exposure than organophosphorus (Hernandez et al., 2013). The use of pesticides has brought a chain of uninterrupted effect to the environment and health of rural workers in Brazil rural environment (Soares et al., 2003). The clinical effects of pesticide carbamate usually depend upon the type carbamate involved, the dose and route of exposure (Lamb et al., 2016). Carbamate pesticides toxicity are responsible for many cases of poisonings in the rural environment (Gupta, 1994). Carbamates pesticides are absorbed via oral or dermal route, even though the last has a tendency to be the less toxic route (Lamb et al., 2016). For instance, carbofuran insecticide has a rat oral LD_{50} of 5-6 mg/kg, compared to rat dermal LD_{50} of 120 mg/kg, making the oral absorption nearly 24 times more toxic when consumed (Li et al., 2009; Yu et al., 2009). LD_{50} is the way of measuring toxicity. The dosage has to be considered as compounds with high LD_{50} may yield lethal indications if high dose is ingested (Purushothaman & Kuttan, 2017). Carbamate toxicity is likely to be of shorter in duration compared with organophosphate toxicity due to the reversibility of the (AChE).

The clinical effects of carbamate pesticides depend on the type of carbamate pesticide used and the dose and mode of exposure (Ahmad et al., 2004). The study on biodegradation of toxic insecticides is useful, because the reactions that discharges poisonous insecticides transform most of the insecticide residues in the environment to harmless and less toxic metabolites (Cycon et al., 2017). Figure 1 shows the different structures of carbamates pesticides. However, the toxicity of the carbamate compounds differs in terms of molecular

structure, but generally the AChE inhibition is of shorter time than other forms of pesticides. Figures 2, 3 and 4 show some of their degradative pathways.

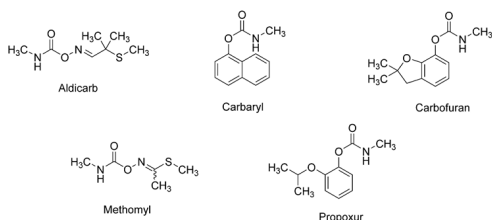


Figure 1. Structures of some carbamate pesticides

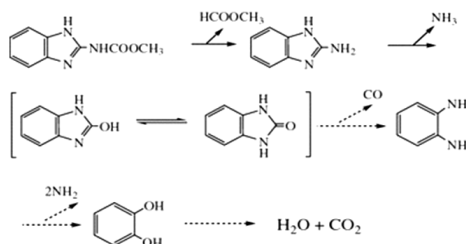


Figure 3. Degradation pathway of carbendazim by Bacterial strain (Fang et al., 2010)

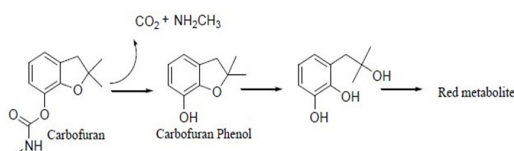


Figure 2. Proposed Biodegradation pathway of carbofuran by *Spingomonas* sp. (Satish et al., 2017)

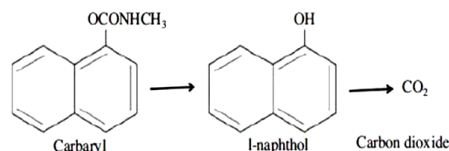


Figure 4. Generalized degradation pathway of carbaryl (Jones et al., 2003)

SOURCES, TRANSPORT AND DISTRIBUTION OF CARBAMATE

Production of chemical pesticides and marketing have continued to increase from 1950s (Munnecke, 1979). Fungicidal chemical, Benzimidazole was made available in market around 1970. Carbamate pesticides are derived from carbamic acid. Generally, carbamate is characterized by low vapour pressure at room temperature, they have low evaporation or sublimation rate, which resulted in volatilization from soil. Nevertheless, dispersal through air will be a less significant factor. Carbamates are characterized by light absorbance, thereby contributing to its photolytic decomposition in water. Therefore, persistent hazardous contamination of carbamates is small. The insecticide are mostly applied to plants, which will subsequently reach the soil, however, herbicidal and nematicidal carbamates are directly applied to the soil (Kazano et al., 1972). Factors such as soil type, soil moistness, adsorption, soil pH, volatility and photo-decomposition affect the biodegradation of carbamates pesticides in the soil (Wang et al., 2009). Some carbamates may decompose easily, while some are strongly absorbed in the soil (Ozturk et al., 2016). Soil type and solubility in aqueous medium are very vital in these processes. However, it should be noted parent compound should not be the only consideration, but also the breakdown products or metabolites (Sahoo et al., 1990).

The initial stage in the metabolic break down of insecticide carbamates in soil is hydrolysis. Several factors influence the fate and transport of pesticides which includes, their adsorption, absorption, Run-off, microbial degradation, volatilization, photochemical decomposition uptake by plant and chemical degradation. The products of this process would then metabolize further in the soil plant system (Tien et al., 2013). Plants metabolize carbamates in which aryl-hydroxylation and conjugation or hydrolytic decomposition are the important pathways of the detoxification. Many studies suggested that carbamates pesticides were entirely dispersed through the apoplectic system in plants (Miyamoto, 1975). They are also broken down by microbes, flora and fauna in water and soil environment.

METABOLISM OF CARBAMATE PESTICIDE

The metabolic product of carbamates pesticide is generally similar in mammals, insects, and plants. Carbamates pesticides are commonly absorbed simply via respiratory tract, dermal contact and mucous membrane. Generally, carbamate metabolites are less toxic as compared with their parent compounds. In some circumstances, the metabolites are even more toxic than the original compound (Cycon et al., 2017). Environmental circumstances that favor the growth of microbial community equally favor the degradation of pesticides carbamates. The primary phase in metabolic degradation of carbamate pesticide in soil is the hydrolysis leading to carbamic acid, then breakdown to carbon dioxide (CO₂) as well as similar amine (Chanika et al., 2011). The mechanisms of hydrolysis is not the same for N-methyl carbamate and N-dimethyl derivatives. The N-methyl carbamates pass via an isocyanate metabolites, while in the hydrolysis of N-dimethyl carbamates, a product containing hydroxyl ion is formed resulting in alcohol and N-dimethyl replaced acid (Rosman et al., 2009). Apart from hydrolysis, oxidation also happen which consists of: hydroxylation of the aromatic ring, N-dealkylation, oxidation of aliphatic side chains, O-dealkylation, N-methyl hydroxylation, and sulfoxidation to the corresponding sulfone (Chaudhry & Ali, 1988; Otieno et al., 2010).

MICROBIAL DEGRADATION OF CARBAMATE PESTICIDES

Pesticides biodegradation by microorganism is not new. Microorganisms simply supply all the required energy source for simple chemical reactions to take place (Pandey et al., 2010). Numerous factors are involved in pesticide biodegradation such as physicochemical mechanism, photochemical mechanism, microbial degradation and bioremediation. The biodegradation of carbamates by diverse microbial consortia that metabolize the pesticides has been studied extensively (Onunga et al., 2015; Satish et al., 2017). Mostly, the studies did not undermine the involvement of abiotic processes in the microbial degradation (Rangasamy et al., 2017). The use of pesticides over decades, has caused numerous

microbes to develop mechanism to degrade toxic compounds, including pesticides, by means of different mechanisms, approaches and enzymatic pathways. Organophosphate degrading bacterial strain was first isolated in Philippines in 1973 in a paddy field area. Subsequently, many phylogenetically diverse strain capable of metabolizing pesticides by co-metabolism, and use them as nutrient and carbon sources, have been isolated by many researchers from different geographical locations (Das et al., 2005; Talwar et al., 2014). Pesticides are mainly used to protect damages of crops and fruits while, these chemicals are applied directly to soil. When these pesticides are used in soil they undergo different process such as volatilization, degradation, sorption, or surface transport to other places (Li et al., 2016). Studies showed that soils with a history of pesticide application mostly have shorter half-lives compared with soil that has no history of pesticide application (Cycon et al., 2017). Moreover, the chemicals considered as non-degradable become biodegradable after several years in soil. Thus, the soil is a major source of microorganisms that can degrade pesticides. Other microbial sources include; microbes from pesticide industry wastewater and sediment, activated sludge, sewage slurry, surface waters and their sediments, as well as areas closed pesticide manufacturing industries. Many groups of microorganisms characterized by growth and degradation ability of pesticides (Ishag et al., 2016). Isolation and characterization of microbes for pesticides degradation bring about new tools to restore environments polluted with pesticides. Several microbial species capable of degrading pesticide such as *Pseudomonas*, *Flavobacterium*, *Achromobacterium sp.*, *Sphingomonas sp.*, *Arthrobacter* and *Bacillus species* have been isolated and characterized in effort to know their mechanism to remove pesticides. Degradation of Carbofuran was first carried out through degradation to carbofuran phenol and subsequently degraded to 2-hydroxy-3-(3-methylpropan-2-ol) phenol by *Sphingomonas sp.* and *Arthrobacter sp.* strains (Chaudhry & Ali, 1988; Kim et al., 2004). Carbaryl is another carbamate that is widely used and poisonous to living organism (Anguiano et al., 2017). Bacterial identified as *Aeromonas*, *Pseudomonas*, *Bacillus* and *Morganella genera* isolated from Gaza Strip utilized carbaryl as source of nutrient. *Bacillus* and *Morganella* degraded carbaryl up to 94.6% and 87.3% degradation rate (Hamada et al., 2015). In another study, *Pseudomonas sp.* C5pp isolated from soil was described to have mineralize carbaryl by means of 1-naphthol, salicylate and gentisate (Trivedi et al., 2016). The genomic investigation of C5pp strain shows that carbaryl pesticides catabolic genes are arranged into three operons; middle, lower and upper. The study mentioned the role of horizontal gene transfer events in the evolution of carbaryl degradative pathway in C5pp isolate. Table 2 shows the summary of microbial species used for biodegradation of carbamate pesticides in which different bacterial and fungal strains from different sources were studied by different scholars.

Microorganisms have the capability to degrade multiplicity of environmental pollutants, including carbamate pesticides. It is highly significant to understand the biochemical

bases for the development of new degradable capacities of microorganisms involve in pesticide degradation (Sogorb & Vilanova, 2002). Enzyme-based degradation method are potentially capable of qualitatively faster action than traditional microbial remediation methods (Nguyen et al., 2014). Several enzymes that hydrolyzed carbamates compound are either esterases or amidases. The hydrolysis of carbamate compound is influence by the chemical structure of the side chains and substrate (Lei et al., 2017). The parent compound is often detoxified by these hydrolytic process. Carbamate insecticide enzymes mediated hydrolysis typically yield an alcohol and methylamine as well as carbondioxide (Lei et al., 2017). Several carbamate hydrolyzed enzymes responsible for degradation have been isolated and also carboxylesterases from various bacteria were previously reported (Ufarte et al., 2017; Wang et al., 2017).

Table 2

Biodegradation of different carbamate pesticide by microbes

Pesticides	Microbial species	Environmental media	Mechanism involve	References
Carbofuran	Consortia	Soil	Degradation	Tien et al. (2017)
	<i>Pseudomonas</i> sp.	Soil	Degradation	Devi et al. (2017)
	<i>Pseudomonas</i> and <i>Alcaligenes</i>	Soil	Degradation	Omolo et al. (2012)
	<i>Enterobacter cloacae</i> strain TA7	Soil Soil	Degradation Degradation	Fareed et al. (2017) Seo et al. (2007)
	<i>Mucor ramannianus</i>			
	<i>Novosphingobium</i> sp	Soil	Degradation	Nguyen et al. (2014)
	<i>Aspergillus</i> sp.	Soil	Degradation	Devi et al. (2017)
Carbaryl	<i>Bacillus</i> , <i>Morganella</i> , <i>Pseudomonas</i> , <i>Aeromonas</i> , <i>Corynebacterium</i> sp.	Soil	Degradation	Hamada et al. (2015)
	<i>Micrococcus</i> sp.	Soil	Degradation	Doddamani et al. (2001)
	<i>Enterobacter cloacae</i> sp. <i>Paecilomyces</i>	Soil Soil	Degradation Degradation	Fareed et al. (2017) Chan-Cupul et al. (2016)
Propoxur	<i>Corynebacterium kutscheri</i> , <i>Staphylococcus aureus</i> , <i>Bacillus pasteurii</i> and <i>Aeromonas</i> sp.	MSW	Degradation	Anusha et al. (2009)
	Consortia	Sediment	Degradation	Dewi et al. (2015)
	<i>Pseudomonas</i> sp.	Soil	Degradation	Kamanavalli et al. (2000)

Table 2 (Continue)

Pesticides	Microbial species	Environmental media	Mechanism involve	References
Methomyl	<i>Escherichia coli</i>	Soil	Degradation	Kulkarni et al. (2018)
	<i>Pseudomonas</i> sp.	Soil	Degradation	Kulkarni et al. (2014)
	<i>Stenotrophomonas</i> sp.	Soil	Degradation	Mohamed (2009)
Oxamyl	<i>Pseudomonas</i> sp.	Soil	Transformation	Rousidou et al. (2016)
	<i>Micrococcus luteus</i>	Soil	Degradation	Mohamed (2017)
	<i>Aminobacter</i> sp.	Soil	Degradation	Osborn et al. (2010)
	<i>Trichoderma</i> sp.	Soil	Degradation	Helal et al. (2015)
Aldicarb	<i>Aspergillus niger</i>	Soil	Degradation	Aemmr et al. (2013)
	<i>Enterobacter cloacae</i>	Soil	Degradation	Fareed et al. (2017)
	<i>Stenotrophomonas maltophilia</i>	Soil	Degradation	Aemmr et al. (2013)
	Consortia	Sediment	Transformation	Kazumi et al. (1995)
Carbendizim	<i>Sphingomonas</i> sp.	Soil	-	Xiao et al. (2013)
	<i>Rhodococcus</i> sp.	Soil	Degradation	Xiao et al. (2013)
	<i>Trichoderma</i> sp.	Soil	Degradation	Tian et al. (2009)
	<i>Nocardioideis soli</i>	Soil	-	Sun et al. (2014)

GENETICALLY MODIFIED ORGANISMS FOR CARBAMATE DEGRADATION

Microorganisms genetically engineered for bioremediation would be an environmentally friendly and economical alternate for the removal of contaminants in polluted areas (Li et al., 2007). Diverse categories of engineered microorganisms have been developed through recombinant DNA and RNA technologies, which have been used for the remediation of several pollutants from polluted environments (Jiang et al., 2005). Genetic manipulation bids a means for engineered microbes to deal with contaminant, such as pesticides in polluted sites. The strategy is to prolong the degradative abilities of already present metabolic pathways in an organism by introducing extra enzymes from other organisms or by modifying the specificity of the catabolic genes previously present (Lan et al., 2014). Microbial genes were aimed to form new metabolic pathways so as to increase degradative processes. GM microorganisms can be favorite tool for biodegradation because of the special features of their metabolic pathways. Recent researches have shown the way that lead to development of degradation pathways and the organization of catabolic genes, hence making it simpler to produce genetically modified microorganisms (GMO) for the degradation of organic compounds such as carbamates (Liu et al., 2016; Zhang et al., 2016). Biodegradation is an environmentally friendly, economical, highly efficient approach

compared to the conventional techniques which were typically costly and has negative effect on the environment. The genetically engineered microbes have ample ability to degrade organic compounds such as pesticide as they discharge several specific enzymes that contain specific catabolic gene into plasmids. The studies of recombinant DNA provide the means to develop DNA and RNA examinations for the purpose of identifying microorganisms from varied populaces with unique capability to degrade pesticides (Jiang et al., 2005).

CONCLUSION

The continuous application of pesticides in agricultural field, has a negative effect on the environment. Bioremediation using microbes is an emerging technology and useful phenomenon for the degradation of toxic pesticides in soil. Resistant microbes from the soils with a history of pesticide application shows the existence of pesticide degrading bacteria in the soil. Alterations in the structure and diversity of microbial populations after exposure to pesticides may result from toxic effects of pesticides on some communities of microbes. Some microorganisms have the ability of using pesticides as nutrients and energy source and may benefit from these pesticide exposure. The isolation of novel microbes for biodegradation of toxic compounds has long been a key challenge, but the emergent knowledge of the genetic and biochemical bases of the metabolism of substances has increased. Various species of bacterial and fungal species having capability to degrade carbamate pesticides have been identified by many scientists. The application of molecular-based approaches in the remediation of pollutants is being increasingly used and has provided valuable evidence for improving biodegradation methods. Moreover, environmental meta-genomic information from soil and sea can be an important source of genes. The viability of the remediation technique has to be assessed bearing in mind its real applicability, its possible limitations and shortcomings as well as its benefits. Furthermore, a great deal of effort is essential to resolutely establish comprehensive knowledge of the molecular basis for catabolic sequences, to limit inactivation of enzymes at high threshold concentration of toxic organic contaminants to increase the compounds bio-availability in the environments. These species of microorganisms are enabling us to suggest an alternative pathway for pesticide biodegradation. In order to fully understand the mechanism of carbamate degradation, a detail explanation of the mechanisms involved in the degradation of pesticides should be conducted as this study is about the carbamates toxicity and their degradation pattern by microbes.

FUTURE PROSPECTS

Microorganisms have the ability to degrade different compounds, including carbamate pesticides in the field or under laboratory conditions. Nevertheless, effective methodologies have yet to be established to remove residues and recalcitrant pesticides from soil and water

bodies. Advances in several aspect of contaminants degradation by microbes, have further explained the mechanisms, and pathways for their degradation as well as developing viable remediation approaches for different polluting compounds. The system of bio molecular engineering should be exploited more to improve the capabilities of degradative enzymes. The advance of genetically engineered microbes with enhanced abilities to degrade diverse types of pesticides under field conditions should be made. Future research should explore towards faster and economic restoration of pesticide polluted soil in order to protect the soil quality and agricultural produce for the health of human beings.

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