Microbial Flora and Biodegradation of Pesticides: Trends, Scope, and Relevance

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Abstract

Pesticides, although proving as a fast remedy in pest control, are polluting the environment in a number of ways acting as havoc to mankind and environment. The presence of pesticides above tolerance level has raised concerns about their removal from soil and environment through novel ways like microbial bioremediation. The present book chapter highlights about the microorganisms and their degradation pathways used in removal of a number of pesticides like carbendazim, chlorpyrifos, endosulfan, and sulfosulfuron. There are a number of living and nonliving factors such as pH, temperature of soil, and availability of degrading microbes. Research has been done on isolation of pesticide-degrading microbes, which could act as an efficient and novel bioremediation agents in the future like *Brevibacillus borstelensis* and *Streptomyces albogriseolus* that have the ability to remove carbendazim and sulfosulfuron.

Keywords

Bioremediation • Carbendazim • Degradation • Pesticides • Sulfosulfuron

15.1 Introduction

A pesticide is a chemical compound, such as lindane, parathion, thymol, and heptachlor or even a biological agent like virus or bacteria as per defined by the Environmental Protection Agency, USA. Pests are living organisms which damage the crops, humankinds, or other animals. These may include insects, fungi, mice, other animals, unwanted weeds, and even microorganisms such as bacteria and

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viruses. The vast increase in use of pesticides, herbicides, and insecticides in agriculture as well as increased industrialization has led to ecological contamination around the world. Pesticides and their degradative products in the top layer of soil have become a serious threat not only to humans and animals but to the soil microbes especially the nitrifying and ammonifying ones. It is considered that the rate with which pesticides are being used at present would malign the environment rendering it unfit for human health. Most of the applied pesticides approximately 20–70% and their breakdown products that are percolated to the soil cause many undesired effects to the environment (Arya et al. 2015).

For controlling the huge range of growing pests, great arrays of pesticides have been used in food production technologies (Osteen and Livingstion 2007; Ghaly and Dave 2012; Ahemad and Khan 2012a, b). In a survey of food commodities, 51% pesticide contamination were detected; however, 20% was found to be pesticides above the maximum tolerance level. The presence of pesticides above tolerance level has raised an alarm for human health concern (Selvaraj et al. 2014). A number of pesticides like aldrin, chlordane, ethyl mercury chloride, methomyl, carbofuran, benzyl hexachloride, 2,4-T, endosulfan, and many more have been banned by the Government of India. While others like DDT, lindane, methyl parathion, and diazinon have been restricted in use, use of pesticides has raised an alarm as these have shown adverse health effects on even nontarget organisms including man. Breakdown of pesticides occurs in soil and water and could be caused by plants, microbes, other chemicals in environment, and UV radiations as well. But the most important type of degradation occurs by microorganisms especially fungi and bacteria. In literature, previous studies have shown that the microbes use pesticides as supply medium and energy source and obtain essential elements from them.

Nowadays, herbicides/weedicide like fenoxaprop-p-ethyl, clodinafop, and sulfosulfuron are efficiently used in weed crop for weed control (Chhonkar and Malik 2002). The use of these herbicides/weedicides especially sulfosulfuron at more than recommended doses or imperfect calibration and wrong methods of application have raised a concern about the health hazards for animals and humans because of the residues left in soil and crops after the pesticide application. The use of benzimidazole fungicides started way back in 1960s and had increased thereon. These fungicides are found to be efficient at low doses and act by inhibiting cell division and thus play a crucial role in modern agriculture (Maltby et al. 2009).

The most commonly used systemic fungicides include thiabendazole, benomyl, thiophanate-methyl, fuberidazol, and carbendazim (Delp 1987). The excessive use of these fungicides has sharply reduced the resistance of healthy crop plants against pathogen attack (Medina et al. 2007; Garcia et al. 2001). Using of pesticides symbolizes the agricultural development where they are used to control pests and vectors, but the environmental and health hazards caused by them have raised a concern on the excessive use of these harmful chemicals. Increase in environmental contamination is the result of excessive use of pesticides in agriculture which causes the long-term harmful effects to human health (Bhanti and Taneja 2007). Contamination of foods associated to pesticides' used in agriculture has increased a major concern of human health such as nausea, headaches, reproductive problem, cancer, and endocrine disorder (Berrada et al. 2010). In countries like India, Colombia, Argentina, Zimbabwe, Mexico, and Kenya, floriculture has increased nowadays because of the optimization of greenhouse conditions (Illing 1997; Ribeiro et al. 2012). In the greenhouse production of medicinal herbs and vegetables, application of carbendazim increased nowadays making it compulsory to discover the ways to remediate carbendazim from the contaminated soil and environment. Likewise, sulfonylurea herbicides are very much persistent in environment and are used more often. As compared to conventional herbicides, the herbicides from sulfonylurea group have showed higher potency even at low concentration (Brown 1990). Moreover, it has been observed that even at lower concentration of herbicides as low as 1% causes the damage to sensitive plants (Beyer et al. 1987).

15.2 Classification of Pesticides

Pesticides is a class of agrochemicals including a large group of chemical compounds classified into various subclasses of herbicides, fungicides, insecticides, rodenticides, garden chemicals, etc. based on their target.

They can be classified as botanical, synthetic, and inorganic pesticides. These are also divided on the basis of their mode of action, targeted pest species, and their chemical composition.

Pesticide classification has been done according to the type of pest as follows:

- Algicides are used to control the algae.
- Avicides are used to control the birds.
- Bactericides are used to control the bacteria.
- Fungicides are used to control the fungi.
- Herbicides are used to control the weeds.
- Insecticides are used to control the insects.
- Molluscicides are used to control the slugs and snails.
- Nematicides are used to control the nematodes.
- Rodenticides are used to control the rodents.

Pesticide classification on basis of mode of action:

- Systemic or noncontact
- Nonsystemic or contact

Systemic pesticides are those pesticides such as 2, 4-D and glyphosate, which are absorbed through the plant tissues efficiently and reach to the vascular system of plant showing its consequence. The nonsystemic or contact ones are those pesticides which target the pest like paraquat when they come in contact without entering in plant tissue.

Pesticide classification on basis of chemical composition:

- Organochlorines
- Organophosphates
- Carbamates
- Pyrethroids

Organochlorine pesticides contain five or more chlorine atoms in their structure. In agriculture they were the first synthetic pesticides. Examples include DDT, endosulfan, Lindane, and aldrin.

Organophosphates consist of a phosphate group in their chemical moieties. Examples include parathion, glyphosate, and malathion.

Carbamates are carbamic acid derivatives. Examples include carbofuran and aminocarb.

Pyrethroids are the chemical molecule, which is an analogue of pyrethrins, secondary metabolites of flower chrysanthemum. Examples include cypermethrin and deltamethrin.

15.3 Mode of Formulations of Pesticides

Pesticides are marketed as various formulations. Pesticide formulation is composed of an active ingredient and an inert ingredient. The active chemical moiety in a pesticide controls the target pest. Most of the pesticides also consist of chemically inert ingredients, which mainly reduce their toxicity for human handling making them more effective; usually, they are diluted in water, a petroleum-based solvent, or other diluents. Formulations are further of two types: liquid and dry.

15.3.1 Liquid Formulations

These formulations are in liquid form and further of following types:

1. *Emulsifiable concentrates (EC)*

These formulations consist of one or more organic solvents, an active liquid ingredient, and a chemical agent which allows the formulation to be emulsified with water. Usually, 25–75% of the active ingredient is present in one gallon of EC.

2. *Solutions (S)*

An active counterpart of some pesticides is easily solubilized either in water or organic solvent. After forming a solution, they do not easily sediment or cannot be separated. Further, they are of the following three types:

(a) *Ready to Use (RTU)*: These agrochemical solutions hold the recommended amount of solvent. Therefore, there is no need to dilute these solutions before application. These formulations contain small amounts of active ingredient usually.
(b) *Concentrate Solutions (C or LC)*: These agrochemicals should be further diluted with either organic or inorganic solvent application. Occasionally, the solvent is liquid; more often the solvent could be a petroleum-based solvent or refined oil.
(c) *Ultra-Low Volume (ULV)*: These concentrate solutions could have 100% of the active ingredient. These can be used by diluting with a small quantity.

3. *Flowables (F)*

Flowables are the suspension, which contains active ingredients in a liquid solvent with inert ingredients. Mostly, the suspensions are prepared with water.

4. *Aerosols (A)*

Aerosol formulation consists of few active ingredients in a liquid solvent. However, the amount of the active ingredient is very low.

5. *Formulations for Smoke or Fog Generators*

These types of formulations are made to be disintegrated into aerosol using a machine which uses a rapidly moving disk or heated surface.

6. *Invert Emulsions*

Invert emulsion is a mixture of pesticide in 40% water added in oil. In this emulsifier pesticide is dispersed in oil/water suspension, which forms large droplets that hinder their slide.

15.3.2 Dry Formulations

These formulations are in dry powder forms and further of following types:

1. *Dusts (D)*

The dust formulations consist of dry inert carrier such as clay, talc, and volcanic ash mixed with lesser amount of active ingredients (0.5–10%). They are often applied dry and easily dispersed on the target or nontarget sites.

2. *Baits (B)*

This formulation consists of an active ingredient added in food. The bait attracts the pests, and when they consume it, they die due to the presence of pesticide in it. Normally, the amount of active ingredients in the bat formulations is less than 5%.

3. *Granules (G)*

Granular formulations are similar in some extent to dust formulations; moreover, this formulations contain larger and heavier granular particles. These granular particles consist of absorptive material like walnut shells, corncobs, or clay. These formulations are made up of 1–15% of active ingredient.

4. *Pellets (P or PS)*

Most of the pellet formulations are similar to granular formulations. Moreover, in the pellet formulation, the active particles are of alike shape and weight.

5. *Wettable Powders (WP or W)*

Wettable powders are similar in some extent to dust formulations. Prior to application they must be mixed with water. This formulation contains 5–95% of active ingredient. As they do not dissolve in water, therefore, constant mixing is applied to maintain the suspension.

6. *Soluble Powders (SP or WSP)*

These formulations are alike of wettable powders. They form the true solution when dissolved in water. The formulation consists of 15–95% of active ingredients.

15.4 Effect of Pesticides on Environment, Man, and Other Living Organisms

Residue pesticide levels for 253 different pesticides in 100 samples of 13 different dried vegetables were tested in Seoul, Korea, and residual pesticides were found in exceeded MRLs in 2 samples out of 11 agricultural products tested and 1 dried pepper leaf sample (Seo et al. 2013). In Iran, pesticide use has increased in previous years as insecticides being used are 33% followed by herbicides 30%, fungicides 20%, acaricides 6.2%, rodenticides 3.8%, and nematicides 1.5% (Sara et al. 2013). China is the global leader in the use of pesticides since the 1990s (Wang 1999) with the use of chemical pesticides found to be threefold greater than in developed countries (Zhang 2001; Yu 2006). Application of pesticides worldwide has guaranteed production potential, but their heavy use, persistence, and transfer in cross-ecosystems and trophic food webs have caused major environmental contamination (Pimental 2007;

Ackerman 2007). Pesticide application has led to changes in soil nutrient levels and alterations to soil microbial activity, diversity, as well as genetic structure (Girvan et al. 2004; Ros et al. 2006). A major impact of herbicides is on aquatic environment which enters by spray drift, runoff, and leaching to field drains which then passes into the food chain (Davies et al. 2003). For the sustainable agricultural fertility and productivity, soil health with special reference to biological features maintaining the functions of both natural and managed ecosystems is very much required (Enriqueta-Arias et al. 2005).

The most widely used active ingredient in the benzimidazole carbamate fungicides has been carbendazim or methyl-2-benzimidazole carbamate (MBC), which has both protective and curative activities against fungal pathogens. The fungicidal property of carbendazim has been embattled by disruption of microtubule formation and stopping mitotic cell division (Foster et al. 1987). The residues of carbendazim have been detected from orange (Shen et al. 2009) and sandy soil (Yarden et al. 1985). A study carried out on degradation and dissipation of pesticides such as carbendazim, difenoconazole, and azoxystrobin in the pomegranate fruit has shown the residues of carbendazim and difenoconazole in outer rind of the pomegranate. All these pesticides, viz., azoxystrobin, difenoconazole, and carbendazim, have been found to follow the first-order kinetics for their dissipation (Utture et al. 2011). About 208 litchi soil samples of Guangdong area of China have been investigated by the authors for the detection of nine pesticides, viz., cyhalothrin, mancozeb, cypermethrin, metalaxyl, dichlorvos, dipterex, deltamethrin carbendazim, and dimethoate. Cypermethrin, mancozeb, metalaxyl, and cyhalothrin along with carbendazim ranges from 3.4 to 59.1% (Yao et al. 2010).

Residues of pesticides have been determined in tomato samples in Bogota, Columbia. Among pesticides carbendazim, acephate, dimethomorph, and pyrimethanil are among the frequently detected ones (Arias et al. 2014). Study carried out by Hernandez et al. (2012) on soil samples and surface waters used for cultivation of rice crop from different sites of Usosaldaña, Colombia, revealed the occurrence of fungicides like azoxystrobin, carbendazim, epoxiconazole, propiconazole, and herbicides like atrazine, diuron, and insecticides such as thiacloprid. Residues of ten pesticides have been detected in paddy rice, eight in rice bran, and seven in brown rice. These residues are obtained after industrial processing of paddy rice from the 14 pesticides including carbendazim evaluated for their persistence in the cropping and processing of rice crop in the season 2009–2010 in Uruguay (Pareja et al. 2012). In 204 samples of 19 different vegetables, 215 pesticide residues have been monitored, and most commonly detected pesticides are organophosphorous followed by pyrethroids, triazoles, and carbamates.

Carbendazim (methyl-1*H*-benzimidazol-2-yl-carbamate) or MBC has mutagenic and teratogenic effects in animals even at low concentration and can harm the liver and endocrine system (Zuelke and Perreault 1995; Moffit et al. 2007; Rajeswary et al. 2007; Yu et al. 2009). After an oral exposure to carbendazim, it gets well absorbed (80–85%) and subsequently metabolized into many compounds within the organism, and main metabolites include 5-hydroxy-2-benzimidazole carbamate and 5, 6-hydroxy-2-benzimidazole carbamate-N-oxides. These metabolites are poorly catabolized in humans and animals and thus retained in tissues, such as gonads, liver, skin, adrenals, adipose, and other organs as reported by WHO in 1990. Carbendazim at higher doses reduces sperm production in male rats and fetal viability in female rats. Alteration in morphology of sperm, weight of testis and epididymis, sperm motility, and post-implantation losses were also observed (Gray et al. 1990). Carbendazim is investigated to be behind the benomyl-induced toxicity of testes as well as inhibition of the microtubular assembly of the testes in rats. Within an hour of carbendazim administration, sloughing of the seminiferous tubules starts and reaches severity in 2 h (Lim and Miller 1997). A number of abnormalities in sexual differentiation and reproduction are found to occur because of endocrine disruptor chemicals. In a study on human, ovarian granulose-like cells possessing high levels of aromatase activity is carried out to demonstrate the effect of benomyl, the only known benzimidazole fungicide, and a microtubule-interfering agent, which is found to induce aromatase activity. This activity is presumed to be mediated by its metabolite, carbendazim (Morinaga et al. 2004).

Benomyl, isothiocyanates, captan, iprodione, and carbendazim have been found to inhibit the respiratory and fermentative metabolism in yeast (Chiba et al. 1987). Quinlan et al. (1980) studied the effect of carbendazim on the cell cycle and nuclear division in yeast *Saccharomyces cerevisiae* and found it to result in the accumulation of large doublets of cells, spindle and cytoplasmic microtubule disappearance, alteration in morphology of spindle polar bodies, increase in nuclear size, and showing inhibition of microtubule polymerization. Carbendazim causes loss of mitotic chromosomes at high frequency, disruption of the mitotic spindle structure, and function along with nondisjunction of chromosomes in *Saccharomyces cerevisiae* (Wood 1982).

The effects of carbendazim and chloramphenicol on the soil bacterial/fungal ratios and on soil enzyme activities both singly and together were studied, and it was found that carbendazim had an inhibitory effect on the bacterial/fungal ratios. The inhibitory effect of chloramphenicol on neutral phosphatase was found to be increased in the presence of carbendazim (Yan et al. 2011a, b). Effects of carbendazim, 2, 4-D, and atrazine were studied on rhizospheric soil of groundnut crop, and it was found that the total counts of bacteria, fungi, and actinomycetes were lower in treated soil than in the untreated soil along with reduction in number of *Rhizobium*, *Azospirillum*, and phosphate-solubilizing bacteria. Also there was reduction in soil enzyme activities (Mohiuddin and Mohammed 2014).

A study was conducted on Canadian prairies for checking dissipation behavior of some herbicides like tribenuron-methyl, metsulfuron-methyl, rimsulfuron, thifensulfuron-methyl, ethametsulfuron-methyl, sulfosulfuron, and nicosulfuron from cropland to surrounding aqueous systems. Of these, three most persistent pesticides, viz., metsulfuron-methyl, sulfosulfuron, and ethametsulfuron-methyl, are among the majority of detected pesticides in swamp sediments (Degenhardt et al. 2010). A study was conducted on the activity, adsorption, mobility, and field persistence of sulfosulfuron in a silty clay loam and sandy loam soil. There was an increase in activity of sulfosulfuron observed with the increase in sulfosulfuron concentration, which is slightly greater in sandy loam soil than silty clay loam soil (Eleftherohorinos et al. 2004). A sensitive and very fast analytical method was developed for simultaneous detection of 16 sulfonylurea herbicides including sulfosulfuron in surface water (Yan et al. 2011a, b). Residues of the sulfosulfuron and their harmful effects were detected in crops including sunflower, canola, bean, soybean, lens, sorghum, pea, sugar beet, corn, barley, and sorghum (Hadizadeh 2010).

A survey during the crop season of 2005–2006 was conducted on 286 farmers belonging to different districts of Punjab regarding bio-efficacy of herbicides used by the Punjab farmers for the control of *Phalaris minor* in wheat, and it was disclosed that 38.5% farmers use sulfosulfuron and 36.0% used clodinafop in agriculture. However, 13.6% farmers used unrecommended herbicides. It was discovered that more than 27% farmers use unrecommended herbicides or unapproved brands of recommended herbicides, and more than 19% of the farmers were found to use under- or overdoses of herbicide (Walia and Brar 2006).

Herbicide residue analysis for isoproturon, clodinafop-propargyl, fenoxaprop-p-ethyl, and sulfosulfuron in samples of postharvest soil, grain, and straw of wheat was analyzed by HPLC in a field experiment carried out at Gwalior, M.P., India, and higher values for isoproturon and clodinafop were detected (Arora et al. 2013).

15.5 Degradation of Pesticides in Soil, Water, or Environment by Abiotic and Biotic Factors

The pesticides undergo a complex series of interdependent reactions following their release in environment collectively called chemodynamics of pesticides. Abiotic factors like pH, salinity, temperature, moisture, precipitation, light intensity and topography, and inherent physicochemical properties affect the chemodynamic processes of pesticides. Major fate of pesticides is in the form of transportation, retention, degradation, and biota uptake. Degradation is the important path of environmental removal of pesticides, which entails the chemical degradation, photodegradation, and microbial degradation.

Pesticide degradation is the breakdown or chemical transformation of pesticide molecules into simpler forms that are less toxic as compared to the parent molecule. Sometimes, the molecules converted still remain toxic like that of the case with DDT. The DDT is converted to DDD, which is also toxic and acts as a pesticide. Chemical transformation of pesticides normally occurs in soil due to various interactions with soil components. These reactions are of oxidation, reduction, and hydrolysis type.

Photodegradation of pesticides occurs in the presence of sunlight as a result of rupturing of chemical bonds. Photocatalytic degradation of various pesticides like carbendazim, chlorpyrifos, simazine, and acetochlor has been investigated to form different degradation compounds resulting from the loss of the chloro, hydroxyl, and alkyl groups along with cleavage of the amide, ester, amino-alkyl, and alkyloxy bonds finally leading to deamination and opening of the ring (Kiss and Virag 2009). Effective phototransformation of carbendazim has also been studied (Abdou et al. 1985; Panades et al. 2000).

Microbial degradation is the breakdown or transformation of pesticides by microorganisms present in soil, water, or air. Rate of degradation depends on the nature and amount of pesticide present in soil, microbial population in soil, and the abiotic factors of soil like temperature, pH, salinity, moisture, aeration, and organic matter. Pesticides are acted upon by bacteria, fungi, and other microbes which probably use them as a substrate for carbon or energy source. Some examples include bacterial genera like *Pseudomonas*, *Clostridium*, *Bacillus*, *Thiobacillus*, *Achromobacter*, etc. and fungal genera like *Trichoderma*, *Penicillium*, *Aspergillus*, *Rhizopus*, and *Fusarium*, etc. which are playing an important role in the degradation of the toxic chemicals or pesticides in soil (Kaufman 1987). A number of isolates capable of carrying out some form of degradation of carbofuran have been isolated from soils, and several bacterial taxa were recorded for the same including *Pseudomonas* sp. (Parekh et al. 1995), *Flavobacterium* (Chapalamadugu and Chaudhry 1991), *Achromobacter* (Chaudhry and Ali 1988), *Arthrobacter* sp. (Ramanand et al. 1988), and *Sphingomonas* sp. (Feng et al. 1997). Microorganisms serve as important agents to detoxify these harmful chemicals which affect human and animal health, helpful soil microbes, and crop production (Kale et al. 1989). A newly classified strain *Brevibacillus laterosporus* has been observed to use as biological control agent in crop field against bacterial brown strip of rice caused by *Acidovorax avenae* subsp. avenae (Li et al. 2015).

Carbendazim is known to be degraded up to 99.1 and 87.1% by a bacterial strain, a member of *Pseudomonas* sp., isolated from soil in mineral salt medium containing 10 ug/ml and 1 ug/ml, respectively (Fang et al. 2010). Carbendazim removal efficiency was found to increase effectively by combining carbendazim-degrading bacteria *Bacillus subtilis*, *Paracoccus* sp., *Flavobacterium*, and *Pseudomonas* sp. with *Sedum alfredii* and Cd (Xiao et al. 2012a, b). Carbendazim degradation along with effects of environmental factors by strain *Bacillus pumilus* (NY97–1) has been detected by HPLC. Detected organic nitrogenous sources were found to have higher role in degradation of carbendazim than the inorganic nitrogenous sources which were showing negative impact (Zhang et al. 2009). *Azospirillum brasilense* and *Rhodococcus erythropolis* discovered were found capable of using carbendazim as a lone nitrogen or carbon source for growth (Lin et al. 2011). *Streptomyces* sp. M7 was isolated from organochlorine pesticide contaminated sediment and was capable of degrading lindane up to a concentration of 300 ug/ml showing increase in the growth as the pesticide concentration increased from 100 to 300 ug/ml. There is increased degradation activity when the strain is used in a consortia containing *Streptomyces* sp. A2-A5-M7-A11 (Fuentes et al. 2010). A novel carbendazim-degrading actinobacterium *Rhodococcus jialingiae* sp. nov. djl-6-2 was isolated from the sludge of a wastewater (containing carbendazim) treatment facility present in Jiangsu province, China (Wang et al. 2010). Wheat soil has been used for the isolation of a proficient carbendazim-degrading bacterium *Brevibacillus borstelensis*, which was found to degrade carbendazim effectively in

48 h and degradation products, 2-aminobenzimidazole and 2-hydroxybenzimidazole, were detected (Arya and Sharma 2014a, b). Bacterium identified as *Streptomyces albogriseolus* after biochemical and morphological analysis was found to degrade MBC in a time-dependent manner from the initial concentration of 29.12 µg/ml–2.86 µg/ml and 0.63 µg/ml in 24 h and 48 h, respectively. LCMS/MS analysis showed the presence of metabolite, 2-aminobenzimidazole, after 10 h of growth which eventually disappeared after 24 h of growth (Arya and Sharma 2014a, b). When both the above isolated strains were grown together, they were found to be more efficient in the removal of carbendazim, with nearly zero in 10–12 h of growth. LCMS/MS studies further confirmed the presence of various metabolites (Arya and Sharma 2016).

The degradation of various organophosphorous and carbamate pesticides including carbendazim in the tropical freshwater was studied and found that degradation rate was increased as the pesticide reached to sediment after leaching out from water in the post-monsoon water. The effect of pH and organic matter on the rate of degradation was also observed (Bhushan et al. 1997). Carbendazim transformation induced by hydroxyl radicals generated by the UV photolysis of H_2O_2 in dilute aqueous solution has also been investigated previously (Mazeilier et al. 2002). Adsorption of carbendazim was found to be inversely proportional to pH range in soil in a study carried out on determining the effect of pH (3–7) on adsorption of carbendazim in three mineral agricultural soils, namely, Hypereutric Camisol, Haplic Luvisol, and Hyperdystric Arenosol (Paszko 2012). The capacity of carbendazim for adsorption in peat, montmorillonite, and soil is dependent on the organic matter, nitrogen, and clay content, as well as on the cation exchange capacity (Cancela et al. 2006).

A study was carried out on the adsorption and biotransformation of the two pesticides, carbendazim and iprodione, singly and together, and it was observed that carbendazim leads to reduction in adsorption of iprodione by 70%. Carbendazim had negative effect on transformation of iprodione and reduced it by 26%, while iprodione had a very little effect on transformation of carbendazim (Leistra and Matser 2004). The effect of environmental factors on the degradation capability of a microbial consortium for degradation of fungicide, carbendazim, herbicide, and 2, 4-D was studied for 2 months in a continuous column reactor. The study has been investigated for different flow rates and consistent ability of the consortium for 6 months (Nagase et al. 2006).

The photodegradation of carbendazim was found to be enhanced with increase in pH and increase in dissolved O_2 concentration (Panades et al. 2000). The extraction of pesticides like dimethoate, malathion, methyl parathion, carbaryl, carbofuran, and carbendazim was evaluated by HPLC followed by their persistence and degradation studies. High Ca content, moderate moisture, and higher pH enhanced degradation and the presence of organic matter leading to increase in persistence of the pesticides (Thapar et al. 1995).

The effect of physical parameters like soil moisture, cadmium, and the microbes on the degradation profile of carbendazim in the paddy soil has been studied earlier under lab conditions (Xiao et al. 2012a, b). Half-life of carbendazim was found to be 12.6–13.8 times more in sterilized soils than in nonsterilized soils. It was found to decrease to 46.2–74% if soil moisture gets increased by 40–80% (Xiao et al. 2012a, b). Half-life of carbendazim was found to decrease by 32.1–52.4% in the presence of low levels of cadmium, while it decreased to nearly 34% in the presence of carbendazim-degrading strains along with cadmium (Xiao et al. 2012a, b). The absorption, desorption, and mobility of a pesticide is influenced by the coexistence of the other pesticides like carbendazim, imidacloprid, and atrazine in the soil (Jin et al. 2013).

The half-life of sulfosulfuron was detected to be 28 days in high pH soil and 11 days in low pH soil. After 120 days, 14% and 5% of the sulfosulfuron remained in high and low pH soils, respectively (Brar et al. 2006a, b). Investigations were done on the effects of pH on the hydrolysis pattern of some sulfonylurea herbicides in soil and aqueous solutions. Also functional relationships between pH versus hydrolysis rate constants, temperature, and the presence of minerals were analyzed (Sarmah and Sabadie 2002). The stability of sulfosulfuron was studied in a controlled environment of pH, temperature, solvent, and surface, as well as in alkaline and acidic conditions (Saha and Kulshrestha 2002). Sulfosulfuron was found to have a half-life of 93 days in unsterilized soil and 120 days in sterilized soil (Brar et al. 2006a, b). The photocatalytic degradation of five sulfonylurea herbicides, viz., chlorosulfuron, nicosulfuron, flazosulfuron, triasulfuron, and sulfosulfuron, was studied, and their degradation followed first-order kinetics and none of the pesticides were detected after 120 min. of illumination except chlorosulfuron (Fenoll et al. 2012).

An experiment done across Canadian Prairies has shown the long persistence of sulfonylurea herbicides in artificially created farm dugouts. These herbicides were found to be resistant to hydrolysis showing their slower microbial degradation (Cessana et al. 2006). The dissipation of sulfosulfuron in water along with its bioaccumulation in fish has been investigated. The dissipation rate followed first-order kinetics, and the metabolites, ethyl sulfone, aminopyrimidine, desmethyl sulfosulfuron, sulphonamide, guanidine, and rearranged amine were detected in water and fish samples by LCMS/MS analysis (Ramesh et al. 2007).

15.6 Pathways for Degradation of Pesticides

Reaction of dissolved oxygen in the environment with pesticides is called oxidation. Oxidation process can be accomplished by singlet oxygen, ozone, hydrogen, peroxide, and other hydroxyl radicals. Hydroxyl radicals are considered the primary agents that bring about chemical oxidation of pesticides in water or atmosphere. For example, DDT shows both reduction as well as oxidation reactions in the soil with the help of *Enterobacter aerogenes* under UV light in the presence or absence of iron catalyst to form DDE and DDD as well as dichlorobenzophenone. Carbendazim transformation by UV/H_2O_2 is a second-order reaction, and it was observed that hydroxyl radicals get quenched with the generation of carbonate radicals (Mazellier et al. 2003).

When a pesticide undergoes reduction in its oxidation state, the chemical reaction that persists is called reduction of pesticides. The reducing agents in the environment are usually H+ve. As an example malathion performs reduction in acidic/aquatic environment that continues by the replacement of any ethyl group with H^+ resulting in the construction of two functional isomeric molecules of malathion monoacid.

Acephate is degraded to methamidophos detected in HPLC and LCMS/MS studies by aerobic bacteria belonging to genus *Pseudomonas*, and no further degradation indicates the capability of bacteria to breakdown at initial steps only (Pinjari et al. 2012). A strain *Bacillus subtilis* was isolated by Xiao et al. (2015) capable of degrading beta-cypermethrin efficiently along with some other pesticides like deltamethrin, beta-cyfluthrin, and cypermethrin. Seven metabolites were detected in beta-cypermethrin degradation pathway.

Pseudomonas sp. RPT 52 discovered by Gupta et al. (2016) was capable of degrading imidacloprid, Coragen, and endosulfan in a time range of 40 h. Degradation kinetics studies showed first-order kinetics for imidacloprid and endosulfan, while zero-order kinetics for Coragen. Rotary drum and windrow composting of vegetable waste resulted in removal of pesticides, endosulfan, and aldrin by degradation into metabolites chlorendic acid and chloroendic anhydride by epoxidation reaction and oxygenation of carbon bridge of aldrin and the presence of endosulfan sulfate and dehydration reaction resulting in dieldrin and hydroxychlorodene formation (Ali et al. 2016).

The degradation of various organophosphorous and carbamate pesticides including carbendazim in the tropical freshwater was also studied and found that degradation rate was increased as the pesticide reached to sediment after leaching out from water in the post-monsoon water. The effect of pH and organic matter on the rate of degradation was also observed (Bhushan et al. 1997).

Photolysis of carbendazim along with degradation products, viz., 2-aminobenzimidazole and two unidentified compounds, were reported in a study carried out on phototransformation by UV photolysis, and kinetics of photodecomposition was studied using HPLC-diode array (Boudina et al. 2011). Carbendazim is hydrolyzed to 2-aminobenzimidazole and then changed to benzimidazole, 2-hydroxy benzimidazole, by a novel actinobacterial strain *R. jialingiae* djl-6-2 (Zhichun et al. 2010). Rajeswari and Kanmani (2009) proposed the mechanism of carbendazim degradation and deduced its pathway using TiO_2-based photocatalysis and ozonation process.

Arya and Sharma (2016) suggested the degradation of carbendazim by the isolated strains *Brevibacillus borstelensis* and *Streptomyces albogriseolus* together reduced carbendazim to benzimidazole and 2-hydroxybenzimidazole in 12 h of growth. Carbendazim could first be converted to 2-aminobenzimidazole as in the case of *Brevibacillus borstelensis*, which is very rapidly converted to benzimidazole or 2-hydroxybenzimidazole. 2-amino benzimidazole could also have acted as an intermediate. 2-hydoxybenzimidazole and benzimidazole could be converted very rapidly to catechol and then even to CO_2 after ring cleavage (Fig. 15.1).

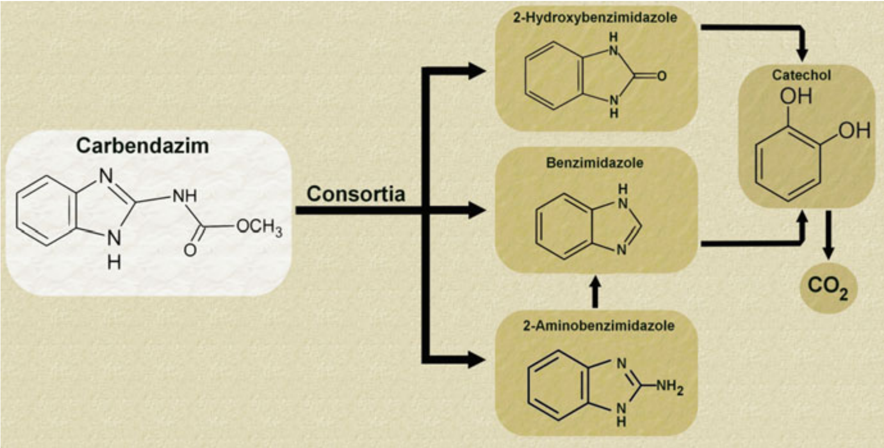

Fig. 15.1 Proposed pathway for degradation of carbendazim (Arya and Sharma 2016)

Sulfosulfuron [1-(2-ehtylsulfonylimidazo [1,2-a]pyridine-3-ylsufonyl)-3-(4,6-dimethoxypyramidin-2yl) urea] degrades in alkaline conditions to the metabolite, 1-(2-ethylsulfonylimidazo [1,2-a]pyridine)-3-(4,6-dimethoxypyramidin-2-yl) amine. However, in acidic conditions, the metabolites formed are 1-(2-ethylsulfonyl imidazo [1, 2-a] pyridine)-3-sulfonamide and 4, 6-dimethoxy-2-aminopyramidine. Metabolites formed by photodegradation are similar to acidic hydrolysis because of the cleavage of sulfonylurea bridge, while in alkaline conditions, contraction of bridge was found (Saha et al. 2003).

Ramesh et al. (2007) investigated the presence of metabolites, ethyl sulfone, aminopyrimidine, desmethyl sulfosulfuron, sulphonamide, guanidine, and a rearranged amine in water and fish samples by LCMS/MS analysis. A fungus *Trichoderma* was isolated from contaminated soil of wheat rhizosphere by Yadav and Choudhury (2014), which was able to degrade sulfosulfuron up to concentration of 2 g/l. In LCMS analysis, the authors observed presence of metabolites, 2-amino-4,6-dimethoxypyrimidine and 2-ethylsulfonyl imidazo{1,2-a} pyridine-3-sulfonamide-2-ethylsulfonyl imidazo{1,2-a} pyridine-3-sulfonamide, N-(4,6-dimethoxypyrimidin-2-yl)urea, N-(4,6-dimethoxypyrimidin-2-yl)-N-″-hydroxyurea (IV) and N, N″-bis(4,6-dimethoxypyrimidin-2-yl)urea. Carbendazim-degrading bacterial strains *Brevibacillus borstelensis* and *Streptomyces albogriseolus* isolated by Arya and Sharma (2016) has also been found to degrade sulfosulfuron to 2-aminopyrimidine and a rearranged amine in their growth individually as well as together with same effectiveness (unpublished work). Novel bacteria identified as *Pseudomonas* sp. has been isolated from carbendazim-contaminated soil which was found to decrease the degradation half-life of MBC to 3.06 days from 14.15 days. HPLC studies revealed the presence of 2 aminobenzimidazole, 2-hydoxybenzimidazole, and benzimidazole.

15.7 Genetic Studies

Bacteria, identified as *Brevibacillus borstelensis* AG1 on the basis of phenotypic, biochemical, and molecular characteristics (using 16S rRNA gene sequencing technique), were isolated from Marcha (fermentable local wine in Northeast India). This bacterium produces a bacteriocin-like inhibitory substance which has been tested against six food-borne/spoilage-causing pathogens, viz., *Listeria monocytogenes* MTCC 839, *Clostridium perfringens* MTCC 450, *Bacillus subtilis* MTCC 121, *Staphylococcus aureus*, *Lactobacillus plantarum*, and *Leuconostoc mesenteroides* MTCC 107 (Sharma et al. 2013).

In previous studies, it has been discovered that major pathways for degradation of aromatic compounds is to bring about by a number of enzymes converting to some of the intermediates normally leading to catechol and finally finding an entry to tricarboxylic acid cycle (Chaudhry and Chapalamadugu 1991; Clarke 1982; Commandeur and Parsons 1990; Fewson 1988; Reineke 1984; Reineke and Knackmuss 1988). The catabolic genes present on plasmid NAH7 codes for enzyme degrading naphthalene via an intermediate salicylic acid which are present on nah and sal operons. Toluene-degrading genes todF and todJ were discovered encoded by tod operon (Horn et al. 1991). Catechol-degrading *cat* genes and protocatechuate-degrading *pca* genes have been identified in different species showing varied patterns (Doten et al. 1987; Hughes et al. 1988; Ornston et al. 1990).

Bacterial species like *Pseudomonas putida*, *P. cepacia*, and *P. aeruginosa* are suggested to have a family of intradiol dioxygenases enzymes with subgroups of catechol dioxygenases, protocatechuate dioxygenases, and chlorocatechol dioxygenases (Aldrich et al. 1987; Ornston et al. 1990). *P. mendocina* KR1 contains toluene-4-monooxygenases enzyme complex which converts toluene to p-cresol (Yen et al. 1991). The main enzymes for transformation reactions of halogenated aliphatic compounds were hydrolytic dehalogenases normally classified in two categories, viz., haloalkane dehalogenases and 2-haloacid dehalogenases which were detected in *Pseudomonas* sp. and some other organisms as well (Schneider and Frank 1991).

15.8 Conclusions and Future Perspectives

Overall, it has been seen that the microbial flora has great impact on biodegradation of pesticides. Several scientific studies have demonstrated their potential to break-down the hazardous chemical moieties of pesticides. There are several health issues associated with the application of pesticides like chlorpyrifos, endosulfan, carbendazim, sulfosulfuron, etc. These moieties have been identified in a number of samples collected from different fields near to their application. This review emphasized the use of natural microbial flora involved in the remediation of these harmful pesticides and elucidated the mechanistic view of their degradation.

Microorganisms are involved in breakdown of a number of pesticides like carbendazim, chlorpyrifos, endosulfan, sulfosulfuron, etc. through their metabolic activities. The breakdown of pesticides in the soil depends on a number of living and nonliving factors like pH, temperature of soil, and availability of degrading microbial flora. Scientific studies have proven the pesticide-degrading capacity of *Brevibacillus borstelensis*, *Streptomyces albogriseolus*, and other microorganisms, which could easily break down the hazardous chemical moieties of pesticide.

These bioremediation of pesticides enables them to be an excellent natural biota for further investigating their microbial and molecular evolution. Moreover, the biochemical pathways attributed to these degradations should be clearly understood. The resolution of these metabolic pathways requires metabolite analysis of pesticide degradation. Most of these bioremediation carried out through the microbial enzymes by their catalytic activities. The enzymes itself is of biotechnological interest for growing their recombinant model to produce large-scale inoculums. This is of utmost importance to get acquatinted with their sequence, structure, and function associated with those genes involved in breakdown. Upstream coding sequences are of much relevance as the significant variance in operon sequences is of concern. Furthermore, these breakdowns of hazardous chemical moieties via nanoparticle formation should be evaluated, which further enhances the catalytic breakdown rate.

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