Chapter 4
Cyanoremediation: A Green-Clean Tool for Decontamination of Synthetic Pesticides from Agro- and Aquatic Ecosystems

Arun Kumar and Jay Shankar Singh

Abstract Immense use of synthetic chemicals in agriculture has deleterious effects on the environment even outside agro-ecosystem, microbial biodiversity, water bodies, and on life especially at the end of food chain, including humans. Therefore, there is a need to develop some viable and eco-friendly tools to remove these lethal chemicals from the environment. Bioremediation has been considered as a less-expensive alternative to physical and chemical means to decontaminate and degrade the pesticides from the contaminated sites. A number of microorganisms such as bacteria, fungi, actinomycetes, and cyanobacteria have been reported to degrade the pesticides. However, cyanobacteria (formally known as blue–green algae—BGA), the only known group of prokaryotes, capable of oxygenic photosynthesis and ubiquitous in distribution, have the remarkable ability to survive in harsh environments. Therefore, cyanobacteria could be a potential bioagent in degradation of noxious chemicals including pesticides. As a bioremediating agent, cyanobacteria have some advantages over other microbes in bioremediation, i.e., phototrophic nature makes them self-sufficient in growth, ability to fix nitrogen, and ease in biomass recovery. Some efficient and potential cyanobacterial genera such as *Anabaena, Leptolyngbya, Microcystis, Nostoc, Spirulina,* and *Synechocystis* have been found to tolerate and degrade various pesticides and herbicides. Biodegradation capabilities of cyanobacteria can be improved through genetic engineering, which can be exploited as cost-effective and eco-friendly remediation technology. This review focuses on the potential of cyanobacteria in the biodegradation of synthetic chemical residues from agro- and aquatic ecosystems.

Keywords Bioremediation • Cyanobacteria • Ecosystems • Insecticides • Synthetic Pesticides • Cell Immobilization

---

A. Kumar
Department of Environmental Microbiology, School for Environmental Sciences,
B.B. Ambedkar (Central) University, Raibarelly Road, Lucknow, Uttar Pradesh 226025, India

J.S. Singh (✉)
Department of Environmental Microbiology, Babashaeb Bhimrao Ambedkar (Central) University, Lucknow, Uttar Pradesh, India
e-mail: jayshankar_1@bbau.ac.in

J.S. Singh, G. Seneviratne (eds.), *Agro-Environmental Sustainability*,
DOI 10.1007/978-3-319-49727-3_4

4.1 Introduction

Synthetic pesticides are excessively applied in current agriculture practices to protect crops from various diseases and damages caused by fungi, insects, mites, and nematodes, to protect crops from abundant growth of weeds, and to control vectors responsible for certain diseases like malaria, dengue in human beings (Freedman 1995; Palanisami et al. 2009). These pesticides are known to be persistent in nature, causing toxicity and teratogenicity. They also cause deleterious side effects, not only in the cultivated soils where they are applied, but also can be accumulated into food crops; but also can be accumulated into food crops; and finally enter in food chain (El-Bestawy et al. 2007). In agro-ecosystems, they affect the growth of nontarget organisms such as beneficial microorganisms which play very crucial role in soil fertility and enhance plant growth (Araujo et al. 2003). Apart from this, they can enter into aquatic ecosystems by spraying, drifting, leaching, surface runoff, discharges from the pesticide manufacturing plants, and by accidental spills; this leads to the killings of fishes and aquatic invertebrates (Akhtar et al. 2009).

Bioremediation is an effective and eco-friendly approach for the decontamination of synthetic pesticides from agro- and aquatic ecosystems; it is a microorganism-mediated transformation or degradation of pollutants into nontoxic or less-toxic substances (Singh et al. 2011a, b, c). The application of various organisms like bacteria, actinomycetes, algae, methanotrophs (Singh and Gupta 2016), and cyanobacteria for efficient bioremediation of pesticide has been reported. Cyanobacteria are successively applied in wastewater treatment to remove nitrogen and phosphorus, textile dyes, and heavy metals (Palanisami et al. 2009; Singh et al. 2016). Cyanobacteria have been shown to be highly effective degraders of pesticides (Megharaj et al. 1994; Singh et al. 2011a, b, c).

Cyanobacteria, generally known as blue–green algae, are considered among the oldest photosynthetic organisms on planet Earth that existed since about 2.6–3.5 billion years ago (Hedges et al. 2001). They show diverse morphology including unicellular, filamentous, and colonial forms; benthic as well as planktonic (Whitton and Potts 2000; Burja et al. 2001). Cyanobacteria can flourish in a variety of habitats: from marine to freshwater and to terrestrial ecosystems; from arctic to Antarctica and to tropical deserts (Kulasooriya 2011). Some filamentous cyanobacteria have endowed with specialized cells known as heterocysts, known for the sites of nitrogen fixation (Capone et al. 2005).

This chapter gives us little information on synthetic pesticides and their fate and impact on agro- and aquatic ecosystems, but prime focus is on cyanobacteria-mediated bioremediation or cyanoremediation of synthetic pesticides and also focuses; how immobilization and genetically engineering enhance the capability to tolerate and degrade the synthetic pesticides.

4.2 Synthetic Pesticides

According to FAO (1989), "Pesticides are natural or synthetic substances or mixture of substances intended for preventing, destroying, or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies." Nowadays, the term "pesticide" is generally applied for synthetic chemicals used to prevent crop loss from various insects, fungi, bacteria, and nematodes; to suppress excess growth of weeds and other substances used for storage and transportation of agricultural commodities.

4.2.1 Classification of Synthetic Pesticides *(Based on Zacharia 2011; EPA 2012; Ortiz-Hernández et al. 2013)*

Synthetic pesticides could be classified according to their toxicity, chemical group, environmental persistence, target organism, or other features (Tables 4.1 and 4.2). According to their chemical nature, pesticides are divided into following groups:

4.2.1.1 Organochlorines

Organochlorine pesticides are organic compounds with five or more chlorine atoms, and they are widely used as insecticides for the control of a wide range of insects. Organochlorine pesticides also show long persistence in the environment. These pesticides (mostly insecticides) disrupt nervous system, leading to convulsions and paralysis of the insect and its eventual death. DDT, lindane, endosulfan, aldrin, dieldrin, and chlordane are the commonly used organochlorine pesticides.

4.2.1.2 Organophosphorous

Organophosphorous pesticides possess a phosphate group as their basic structure; this is defined by Schrader's formula:

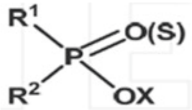


Table 4.1 Synthetic pesticides: types, mode of action and their examples

Types	Mode of action	Examples
Insecticides		
Organochlorines	Nervous system disruptors	Lindane, DDT, Heptachlor
Organophosphorous	Cholinesterase inhibitors, not specific	Malathion, Chloroprifos
Carbamates	Cholinesterase inhibitors, but specific	Carbendizm, Aldicarb
Pyrethroids	Synthetic analogues of the naturally occurring pyrethrins	Cypermethrin, Fenvalerate
Insect growth regulators	Inhibit endocrine or hormone system of insects	Azadirachtin, Methoprene
Nicotinic	Affect the central nervous system of insects	Imidacloprid, Acetamiprid
Pyrajole/Pyrrole	Inhibits mitochondrial electron transport	Chlorantrailiprole, Pyraclofos
Herbicides		
Phenoxics	Growth regulators	Bromofnoxim, 2,4,5-T
Trizines	Photosynthesis inhibitors(Photosystem II)	Trihydroxytrizine, Chlorazine
Benzoics	Growth regulators	Fenquinotrione
Sulfonylureas	ALS Inhibitors	Amidosulfuron
Bipyridilium	Photosynthesis inhibitors(Photosystem I)	Paraquat, diquat
Chloroacetamide	Shoot growth inhibitors	Acetochlor
Glycine	Aromatic amino acid synthesis inhibitors	Glyphosate
Dinitroaniline	Root growth inhibitors	Pendimethalin
Phenylpyrazoline	ACCase inhibitors	Fluazolate
Fungicides		
MBC	Inhibits tubulin formation in mitosis	Thiophanate-methyl
DMI	Sterol biosynthesis inhibition	Triforine, Tebuconazole
Phenylamide	Inhibits RNA synthesis	Mefenoxam
Anilopyrimidine	Methionine biosynthesis and hydrolytic enzymes	Cyprodinil, Pyrimethanil
QoI	Inhibits respiration (MET-III, cyto-bc1)	Azoxystrobin
Phenylpyrrole	Disrupts membrane integrity	Fludioxonil
Aromatic hydrocarbon	Thought to act on lipids	Dicloran, Etridiazole
Host plant defense inducers (SAR)	Activates plant's systemic acquired resistance (SAR)	Acibenzolar-*S*-methyl, Harpin

Note: *MBC* methyl benzimidazole carbamate; *DMI* demethylation inhibitor; *QoI* quinone outside inhibitor

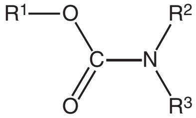
Table 4.2 Synthetic pesticides: classified according to their toxicity

Class	Toxicity
Ia	Extremely hazardous
Ib	Highly hazardous
II	Moderately hazardous
III	Slightly hazardous
IV	Product unlikely to present acute hazard in normal value

In this formula, R^1 and R^2 are usually methyl or ethyl groups; the O in the OX group can be replaced with S in some compounds, whereas the X group can take a wide diversity of forms. Organophosphorous insecticides are not persistent in the environment (Martin 1968) like organochlorine pesticides, but it is observed that they are more harmful for vertebrates and invertebrates due to cholinesterase inhibitors, leading to paralysis and death. Some of the widely used organophosphorous insecticides include parathion, malathion, diaznon, and glyphosate.

4.2.1.3 Carbamates

Carbamates are organic compounds which are derivatives of carbamic acid and defined through this formula:



Where R^1 is an alcohol group, R^2 is a methyl group, and R^3 is usually hydrogen. Carbamates (both aryl and oxime) are heavily toxic to insects and mammalians due to cholinesterase inhibitors. Although both carbamates and organophosphorous are cholinesterase inhibitors, the difference is in species specificity and reversibility (Drum 1980). Carbaryl, carbofuran, and aminocarb are the common example of carbamate pesticides.

4.2.1.4 Pyrethoids

Pyrethroids are synthetic equivalents of the naturally occurring pyrethrins extracted from flowers of *Chrysanthemum cinerariaefolium*. Pyrethroids are known to be very effective against insect pests, with minimal toxicity to mammals and easily biodegradable. The most widely used synthetic pyrethroids include permethrin, cypermethrin, and deltamethrin. Although less toxic and persistent than other groups of insecticides, they can still represent a problem. Pyrethroids display high affinity to Na+-channels and its binding to these channels causes a prolonged channel opening that may result in a complete depolarization of the cell membrane thus blocking neuronal activity.

Other groups of synthetic pesticides that are widely used in control of weeds include among others phenoxyacetic acid under which the herbicide 2,4-D belongs and bipyridyls under which the herbicides paraquat and diquat belong.

There is another group that includes the pesticides which can be applied for the control of fungal infections in crops. There are inorganic and organic fungicides. Inorganic fungicides include Bordeaux mixture, $Cu(OH)_2.CaSO_4$ and malachite, $Cu(HO)_2 \cdot CuCO_3$. Organic fungicides, on the other hand, include among others, benomyl and xine copper (Manahan 2001).

4.3 Fate of Synthetic Pesticides in Agro- and Aquatic Ecosystems

Synthetic pesticides are applied in agriculture through various ways like spraying, dusting or spreading. These pesticides are taken up by pests or crop plants that are converted into degradable products and bio accumulated into plant parts or animal tissues (Babu et al. 2003; Waliszewski et al. 2008). Some parts of the pesticides applied in agricultural fields are also removed upon crop harvesting. The remaining parts of the pesticides can be degraded through chemical reactions and microbial actions in the soil, can be mineralized through sorption onto soil organic matter and clay minerals, and can also be lost to atmosphere through volatilization. Some synthetic pesticides that are not degraded, immobilized, detoxified, or removed with the harvested crop are escaped from the applied sites. The major loss pathways of pesticides to the environment are volatilization into the atmosphere and aerial drift, runoff to surface water bodies in dissolved and particulate forms, and leaching into groundwater basins (Fig. 4.1). The fate and transfer pathways of pesticide applied to crop plants are complex, requiring some knowledge of their chemical properties, their transformations (breakdown), and the physical transport process. Transforms and transport are strongly influenced by site-specific conditions and management practices.

4.4 Impact of Pesticides

Synthetic pesticides help enhancing economic potential through increased production of agricultural commodities and prevention of vector-borne diseases (Igbedioh 1991; Forget 1993). This negative impact of pesticides is mainly due to the high toxicity, stable nature, less soluble active ingredients of pesticide.

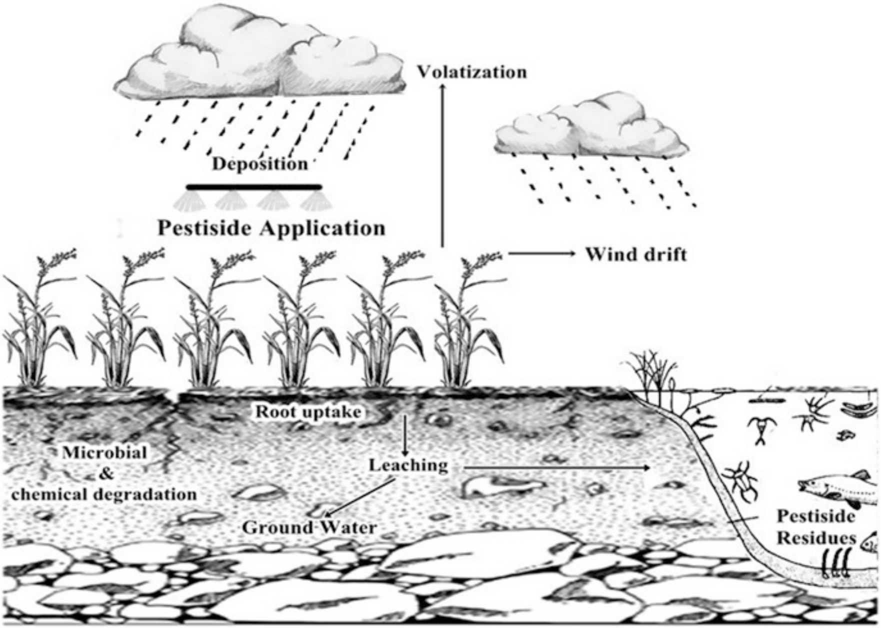


Fig. 4.1 Fate of synthetic pesticides in agro- and aquatic ecosystems

4.4.1 *Soil Contamination*

The major portion of the synthetic pesticides remains unused after application and is responsible for the contamination of the soil. In the soil, it can remain persistent, degraded, or transformed. Several researchers reported a variety of transformation products (TPs) from a wide range of pesticides (Barcelo and Hennion 1997; Roberts 1998; Roberts and Hutson 1999). The pesticides and their TPs are sorbed by soils to different degrees, depending on the interactions between soil and pesticide properties. The most influential soil characteristic is the organic matter content; larger the organic matter content, the greater the adsorption of pesticides and TPs (Akhtar et al. 2009).

4.4.2 *Surface and Groundwater Contamination*

From applied sites, pesticides can escape to surface water through runoff from treated plants and soil. Contamination of surface water by pesticides is a widespread problem. During a survey in India, 58 % of drinking water samples drawn from various hand pumps and wells around Bhopal were contaminated with organochlorine pesticides above the EPA standards (Kole and Bagchi 1995). Once ground water is polluted with toxic chemicals, it may take many years for the contamination to dissipate or be cleaned up. Cleanup may also be very costly and complex, if not impossible (Waskom 1994; O’Neil et al. 1998; US EPA 2001).

4.4.3 Effect on Soil Fertility

Due to indiscriminate use, pesticides have a negative impact on beneficial soil microorganisms. Elaine Ingham stated that if both bacteria and fungi populations are affected, then the soil starts to degrade. Overuse of chemical fertilizers and pesticides have the same side effects on the soil organisms that are similar to human overuse of antibiotics. Although after application of chemicals, it takes days, months, or years to be sort out or escape, but after a while, there aren't enough "beneficial soil organisms to hold onto the nutrients" (Savonen 1997). Soil microorganisms play a vital role in plants in terms of transformation of atmospheric nitrogen into nitrates, which plants can use, enhancing bioavailability on nutrients.

4.4.4 Nontarget Organisms

Nowadays, synthetic pesticides are found as common contaminants in soil, air, water, and our urban landscapes. They can also harm plants and animals ranging from nontarget insects, plants, fish, birds, and other wildlife. Synthetic pesticides are continuously applied and can be responsible for the extinction of useful organisms present in the agro- and aquatic ecosystems. Pesticide residues not only affect the soil features but also affect useful organisms like earthworms, bees, spiders, and plants (Singh et al. 2014).

4.4.5 Contamination of Vegetation

Pesticide application can directly affect nontarget vegetation or can drift or volatilize from the applied area and contaminate air, soil, and nontarget plants. Some pesticide drift occurs during every application, even from ground equipment (Glotfelty and Schomburg 1989). Pesticide drift can be responsible for a loss of 2–25 % of the pesticide being applied, which can spread over a distance of a few yards to several hundred miles and after few days of application, up to 80–90 % of an applied pesticide can be volatilized (Majewski and Capel 1995).

4.4.6 Human Health

Increase in the use of pesticides can result in various health and environmental problems like poisoning of farmers and farm workers, leading to cardiopulmonary, neurological, and skin disorders, fetal irregularities, miscarriages, lowering the sperm count of applicators, etc. These are categorized into acute and chronic poisoning: (a) Acute pesticide poisoning causes fatigue, headaches and body aches, skin discomfort, skin rashes, poor concentration, feelings of weakness, circulatory problems, dizziness, nausea, vomiting, excessive sweating, impaired vision, tremors, panic attacks, cramps, etc., and in severe cases, coma and death (Bödeker and Dümmler 1993; Alavanja et al. 2004); (b) Chronic poisoning due to pesticide use or due to long-term ingestion of small amounts of these substances include weakening of the immune system and effects on the reproductive system, which can lead to miscarriage, still birth, and premature birth or to low birth weight(WWF 2002; UNEP 2004; Terre Des Hommes 2011).

4.5 Bioremediation of Synthetic Pesticides

Conventionally, bioremediation of synthetic pesticides is attained through the use of microorganisms; but nowadays, several other gents such as plants, fungi, algae, or enzymes (obtained from organisms) are also used in bioremediation which extends the application of bioremediation in various aspects. Bioremediation of synthetic pesticides includes two terms, biodegradation and biotransformation, recognized similar to each other but they are quite different.

Biodegradation involves the biological reactions that modify the chemical structure of the compound so this implies a decrease in toxicity, while biotransformation reduces the pollutant concentration by either modification or translocation. Thus, biotransformation could end decreasing or increasing the undesirable effects. Their difference is clear in the case of pollutants translocation when biodegradation does not occur but biotransformation does. Biotransformation concept has been developed for biological detoxification systems (Alexander 1999; Parkinson 2001). When microorganisms are imported to a contaminated site to enhance degradation, the process is known as bioaugmentation (Murali et al. 2014).

4.6 Factors Affecting the Bioremediation of Synthetic Pesticides

The biodegradation or biotransformation of synthetic pesticides is a complex process, and it is influenced by several physical and chemical attributes such as structure and concentration of pesticide, environmental conditions (temperature, pH, moisture), salinity, and sustainable population of microorganisms.

4.6.1 Structure and Concentration of Pesticide

The structure of synthetic pesticides is an important attribute; pesticides have some of their own physical and chemical properties which varyfrom pesticide to pesticide. Cork and Krueger 1991 stated that in a pesticide polar group such as OH, COOH and NH_2^{+3} are available to the microbial system; it could be an easier site for attack but if the pesticide molecule is available as a substituent of halogen or alkyl, it makes it more resistant to biodegradation. The rate of degradation of pesticides can be influenced by minor difference in the arrangement or nature of substituent in pesticides of the same class (Topp et al. 1997). Beside the structure, the concentration of pesticide considerably affects the bioremediation of pesticides. The rate of degradation decreases generally quantitatively with the residual pesticide concentration (Topp et al. 1997).

4.6.2 Effect of Temperature, pH, and Moisture

Various environmental factors such as temperature, pH, and moisture also affect the process of biodegradation of synthetic pesticides. According to Alexander 1977, the entire process of biodegradation is carried out at mesophillic (30–37 °C with optimum temperature 35 °C) and thermophillic (50–60 °C with optimum temperature 55 °C) temperature ranges. The optimal temperature required for both the ranges is not invariably critical for the biodegradation.

Soil pH is a crucial factor for adsorption of pesticides for the abiotic and biotic degradation processes, and it also effects the adsorption behavior of pesticide molecules on clay and organic surfaces. This also affects the chemical speciation, mobility, and bioavailability (Burns 1975; Hicks et al. 1990). Racke et al. (1997) reported that degradation of a given pesticide depends mostly on the soil alkaline or acidic pH. In fact, the biodegradation of pesticides depends upon the susceptibility of the microorganism in the optimum pH of the medium. Moisture is another environmental factor which affects the rate of biodegradation; water facilitates as medium for the movement and diffusion of pesticides; it is necessary for microbial availability of pesticides.

Moisture maintains the osmotic pressure and pH of agro- and aquatic ecosystems; it also affects the exchange of respiratory gases in pore spaces of soil. Under saturated conditions, oxygen can be consumed faster than it is replenished in the soil space and the soil becomes anaerobic; this leads to slowing the rate of biodegradation and also changes metabolic activity of microorganisms to occur. Soil moisture content should be between 25 and 85 % of the water holding capacity (with optimum range of 50–80 %) for effective biodegradation of synthetic pesticides.

4.6.3 Effect of Salinity

There is not much information about the effects of salinity on the degradation of synthetic pesticides. Salinity is a big problem in many arid, semiarid, and coastal regions; it could affect the biodegradation of synthetic pesticides. Reddy and Sethunathan (1985) reported that parathion degradation is faster in nonsaline soils. It is also reported that the stability of pesticides in estuarine and sea water, varying degrees of salinity; high salt content in seawater may be barrier for biodegradation (Walker 1976) or inhibit biodegradation of pesticides (Weber 1976; Kodama and Kuwatsuka 1980).

4.6.4 Sustainable Population of Microorganisms

Although microorganisms are able to survive in subzero temperatures, extreme heat, desert conditions, in aerobic or anaerobic conditions, with the presence of hazardous compounds but for the effective biodegradation of synthetic pesticides, it is necessary to meet these variables such as availability of pesticide or metabolite to the microorganisms, physiological status of the microorganisms, survival and/or proliferation of pesticide degrading microorganisms at contaminated site and most important is sustainable population of these microorganisms (Singh 2008).

4.7 Cyanoremediation

Cyanoremediation is the use of cyanobacteria for the removal or degradation or transformation of pollutants including heavy metal, dyes, or pesticides from wastewater or contaminated soil. Figure 4.2 illustrates the advantages using cyanobacteria over other microbes for bioremediation of pesticide contamination. There are numerous examples of cyanobacterial genera which are successfully implemented for the bioremediation of synthetic pesticides (Table 4.3).

According to Hatzios (1991), pesticide degradation is a process involving three phases: (a) Phase I involves oxidation, reduction, or hydrolysis, which makes the pesticide more water soluble and less toxic pesticide metabolites. In this phase, oxygenation is the crucial step in the degradation of pesticides and many of oxygenation reactions are carried out by oxidative enzymes, e.g., cytochrome P_{450}s, peroxidases, and polyphenol oxidases. (b) Phase II involves conjugation of a pesticide or pesticide metabolites to a sugar, amino acid or glutathione, which enhances the water solubility and reduces the toxicity compared to parent pesticide compound. Generally, metabolites obtained from Phase II have little or no toxicity and may be stored in cellular organelles. In this phase, enzyme Glutathione S-transferase plays a great role which catalyzes the nucleophilic attack of the sulfur atom of GSH by the electrophilic center of the substrate (Armstrong 1994; Marrs 1996); (c) Phase III involves conversion of Phase II metabolites into secondary conjugates, which are also nontoxic.

In the degradation process, pesticides produce singlet oxygen and other active oxygen species at various sites of photosynthetic electron transport chain. These active oxygen species are scavenged by cellular systems through raising antioxidative machinery such as superoxide dismutase, catalase, and peroxidase (Palanisami et al. 2009).

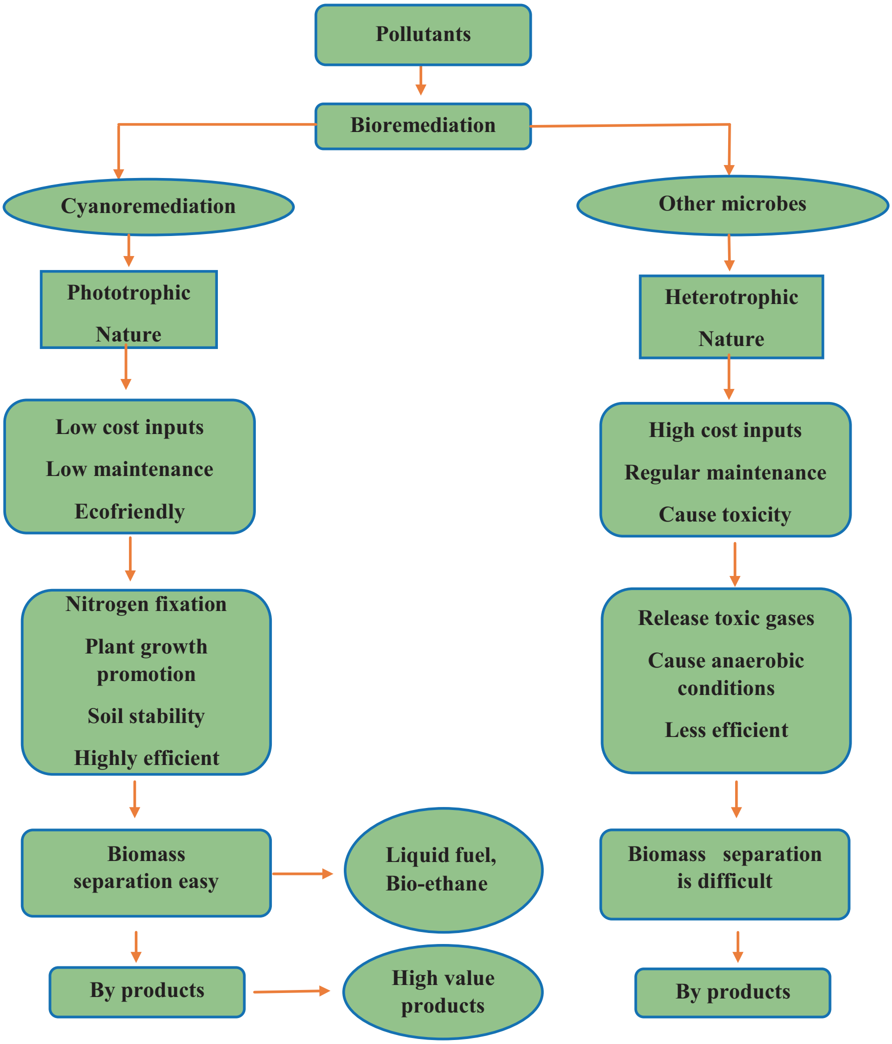


Fig. 4.2 Advantages of using Cyanobacteria over other microbes for bioremediation

4.7.1 Organochlorine Insecticides

Organochlorines are chlorinated hydrocarbon chemicals used to control various agricultural, horticultural, and public health pests (Lal et al. 2010). Their residues cause serious problems, not only in the cultivated soils where they are applied, but also in the crops that systematically retain part of these residues in nontarget organisms (El-Bestawy et al. 2007; González et al. 2012).

Table 4.3 Some synthetic pesticides and cyanobacteria species responsible for their degradation

Synthetic pesticides	Cyanobacteria	References
2,4-D (Dichlorophenoxyacetic acid)	*Anabaena fertilissima, Aulosira fertilissima, Westiellopsis prolifica*	Kumar et al. (2013)
2,4-DNP (Dinitrophenol)	*Anabaena variabilis* *A. cylindrica*	Hirooka et al. (2006)
Anilofos	*Synechocystis* sp. Strain PUPCCC 64	Singh et al. (2013)
Acetachlor	Cyanobacteria mat consisting *Phormidium and Oscillatoria*	El-Nahhal et al. (2013)
Carbaryl	*Calothrix berevissima*	Habib et al. (2011)
Carbendizm	*Oscillatoria* sp.	Ravindran et al. (2000)
Carbofuran	*Anabaena sphaerica, Nostoc hatei, Westiellopsis prolifica*	Jha and Mishra (2005)
Chlorpyrifos	*Phormidium valderianum, Spirulina platensis, Synechocystis* sp. *Strain PUPCCC64*	Palanisami et al. (2009)
Cypermethrin	*Oscillatoria*	Thengodkar and Sivakami (2010)
Endosulfan	*Anabaena* sp. PCC 7120 *A. flos-aquae* *Aulosira fertilissima*	Singh et al. (2011a, b, c) Ravindran et al. (2000) Lee et al. (2003)
Fenamiphos	*Nostoc muscorum, Anabaena* sp.	
Glyphosate	*S. platensis, N. punctiforme, M. aeroginosa, L. boryana*	Kumar et al. (2012); Caceres et al. (2008); Forlani et al. (2008); Lipok et al. (2009)
Isoproturon	*Anabaena inaequalis*	Arunakumara et al. (2013)
Lindane	*M. aeruginosa, Pseudoanabaena limnetica*	Mostafa and Helling (2001)
	Anabaena sp. *Strain PCC 7120* *Nostoc elliposporum*	González et al. (2012)
Malathion	*Anabaena oryzae, N. muscorum, S. platensis*	Kuritz and Wolk (1995)
	Anabaena sp. *Strain PCC 7120*	El-Bestawy et al. (2007)
Methyl parathion	*Anabaena fertilissima, Aulosira fertilissima, Westiellopsis prolifica*	Ibrahim et al. (2014)
Monocrotophos Penycuron		Barton et al. (2004) Kumar et al. (2013)

Among organochlorines, lindane (a common A-hexachlorocyclohexane (HCH) formulation) is a wisely applicable pesticide, mainly used for rice crop protection in rice-producing countries (Abdullah et al. 1997). Lindane persists in the environment (Alexander 1994) and can be noticed in the air, rain, and surface water at 90 % of sites long after its application (Majewski and Capel 1995). Singh (1973) reported that some cyanobacterial strains isolated from paddy fields, i.e., *Cylindrospermurn* sp., *Aulosira fertilissirna*, and *Plectonema boyanurn*, are able to tolerate commercial preparations of lindane in concentrations up to 80 pg/mL. Kuritz and Wolk (1995) also showed that two laboratory strains, *Anabaena* sp. PCC7120 and *Nostoc ellipsosporurn*, degraded A-HCH to a mixture of 1,2,3-and 1,2,4-trichlorobenzenes (and, possibly, beyond) via pentachlorocyclohexene as an intermediate. It is also observed that lindane did not affect the growth rates of these cyanobacteria at concentrations up to 20 pg/mL (Singh 1973).

It is reported that *Anabaena* sp. Strain PCC 7120 and *Anabaena flos-aquae* biotransformed endosulfan into endodiol, primary product and trace the amount of endosulfan sulfate (Lee et al. 2003). Endodiol is a nontoxic metabolite to fish and other organisms. But endosulfan sulfate has a similar toxicity compared to parent compound endosulfan, and it has a much longer tolerance into soil environment in comparison to endosulfan (Kennedy et al. 2001).

4.7.2 Organophosphorous Insecticides

Organophosphorous insecticides are esters of phosphoric acids and commonly known as organophosphates, which include aliphatic, phenyl, and heterocyclic derivatives and have one of the basic building blocks as a part of their much more complex chemical structure. They are applied for a variety of sucking, chewing, and boring insects, spiders and mites, aphids and pests attacking crops like cotton, sugarcane, peanuts, tobacco, vegetables, fruits, and ornamentals. Some of the main agricultural products are parathion, methyl parathion, chloropyrifos, malathion, monocrotofos, and dimethoate (Kanekar et al. 2004).

Organophosphorus pesticides are less environmentally persistent than organochlorine compounds; however, they still can be detected in air and water due to heavy use (Majewski and Capel 1995). In aquatic environments, nonenzymatic hydrolysis of organophosphates is responsible for their slow decomposition to more toxic and persistent para-nitrophenol (Megharaj et al. 1994). To overcome this problem, microalgae (including cyanobacteria)-mediated degradation could be an effective approach for their cleanup in the environment (Megharaj et al. 1994). Cyanobacteria are not so much affected by organophosphorus pesticides at working concentrations and concentrations present in wastewaters (Singh 1973; Doggett and Rhodes 1991; Megharaj et al. 1994; Subramanian et al. 1994). Pure cultures of *Nostoc*, *Oscillatoria*, and *Phomidium* isolated from methyl parathion-enriched soil, grew in media supplemented with methyl parathion or other organophosphorus pesticides as a sole source of organic phosphorus and nitrate (Megharaj et al. 1987; Orus and Marco 1991;

Megharaj et al. 1994; Subramanian et al. 1994) and utilized phosphorus from the pesticide for growth and development (Megharaj et al. 1994; Subramanian et al. 1994). Megharaj et al. (1994) stated that cyanobacteria are also able to oxidize the nitro group of para-nitrophenol accompanied by the release of nitrite into growth media, but enzymatic system which is involved in this process is not known. The metabolism/assimilation of the released nitrite is likely to depend on the activity of nitrite reductase encoded by the *nir operon*. Subramanian et al. (1994) also noted that the link between nitrogen metabolism and the effectiveness of phosphorus utilization from organophosphorus pesticides; however, the authors did not analyze possible effects of various sources of fixed nitrogen on biodegradation (Kuritz 1999).

Palanisami et al. (2009) reported that cyanobacterium *Phormidium valderianum* BDU 20041 tolerant to chloropyrifos exposure showed increased activity of oxidoreductase enzymes to degradation of chloropyrifos. *Sprirulina platensis* are able to grow in media containing up to 80 ppm choloropyrifos and converted to its primary metabolite TCP(3, 5, 6-trichloro-2-pyridinol) through the enzyme alkaline phosphatase (ALP) (Thengodkar and Sivakami 2010). Singh et al. (2011) concluded that cyanobacterium *Synechocystis* sp. Strain PUPCCC 64 is able to degrade the pesticide chloropyrifos. Three strains of cyanobacteria *Anabaena oryzae*, *Nostoc muscorum*, and *Spirulina platensis* are able to degrade and utilize malathion as a source of phosphorous. These strains grow under high concentration of malathion with enhancement of biomass carbohydrate and protein content (Ibrahim et al. 2014). It is also reported that cyanobacterium *Anabaena* sp. Strain PCC 7120 reduced the nitro group of methyl parathion to an amino group via a nitroso group intermediate under aerobic conditions (Barton et al. 2004).

4.7.3 Herbicides

Gimsing et al. (2004) reported that the degradation rate of pesticide is strongly correlated with the population size of soil microbes in case of *Pseudomonas* spp. Lipok et al. (2007) concluded that mixed culture of *Spirulina* sp. exhibited a remarkable ability to degrade glyphosate and the rate of glyphosate disappearance from the aqueous medium was independent of its initial concentration. They also suggested that the degradative pathway for glyphosate in *Spirulina* sp. might differ from those exhibited in other bacteria. In fact, Lipok et al. (2009) reconfirmed the ability of the cyanobacterium *S. platensis* and bacterium *Streptomyces lusitanus* to catalyze glyphosate metabolism. Four cyanobacterial strains (*Anabaena* sp., *L. boryana*, *M. aeruginosa*, and *N. punctiforme*) are able to use the glyphosate as the only source of phosphorus (Forlani et al. 2008). Dyhrman et al. (2006) also stated that marine cyanobacteria *Trichodesmium erythraeum* showed existence of phosphorous-dependent glyphosate transformation. However, reports on the utilization of glyphosate as a source of nitrogen by cyanobacteria are not yet available in the literature. Ravi and Balakumar (1998) reported that extracellular phosphatases are able to hydrolyze the C-P bond of glyphosate with working on cyanobacterium *A. variabilis*; however, this claim has not been reiterated so far by the other authors. Forlani et al. (2008) stated that extracellular phosphatases seem unlikely to contribute any substantial scale to glyphosate degradation. Cyanobacterial strains which possess the ability to use this phosphonate as a source of phosphorus is of practically significance because such strains could effectively be employed for the cleanup of pesticides (Arunakumara et al. 2013).

4.8 Cyanobacterial Immobilization

The concept of immobilization of microorganisms in matrix or material may enhance the current benefits from the mass culture of the microorganism by degrading a specific metabolite or removing pollutants (De-Bashan and Yoav Bashan 2010; Ortiz-Hernández et al. 2011, 2013). And it can be employed for the bioremediation of synthetic pesticides because it confers the possibility of maintaining catalytic activity over long periods of time (Martín et al. 2000; Richins et al. 2000; Chen and Georgiou 2002). There are many advantages of immobilization of microorganisms over free-living microorganisms, such as the maintaining high cell density, the minimum cell washout, even at high dilution rates, easy separation of cells from the reaction system, repeated use of cells, and better protection of cells from the toxic effects of hazardous compounds and harsh environments. Immobilization can increase the cells' survival and metabolic activity in bioremediation systems (Moslemy et al. 2002; Tao et al. 2009; Ha et al. 2008, 2009; Sun et al. 2010). Two types of immobilization are as follows:

4.8.1 Passive Immobilization

Some microorganisms (including some groups of microalgae/cyanobacteria) have a natural tendency to attach to surfaces and grow on them (Robinson et al. 1986). This characteristic can be exploited in order to immobilize cells on carriers of different types (Codd 1987). In passive immobilization, carriers (adsorbent materials) can be natural or synthetic, and this process is reversible (Cohen 2001; Moreno-Garrido 2008). The natural carrier loofa biomass is widely used and accepted for passive immobilization while synthetic materials, polyvinyl and polyurethane, are widely used in experiments involving passive immobilization (Urrutia et al. 1995).

4.8.2 Active Immobilization

For active immobilization, a variety of carriers such as flocculant agents, chemical attachment, and gel entrapment are currently in use. Among flocculants, chitosan has been the most widely employed. Chemical attachment is carried out through the chemical interaction (mainly due to covalent bonding, cross-linking) by common carriers such as glutaraldehyde, or cells. Apart from flocculant and chemical attachment, gel entrapment can be performed by the use of synthetic polymers (acrylamide, photocrosslinkable resins, polyurethanes), proteins (gelatine, collagen, or egg white), or natural polysaccharides (Taha et al. 2013).

Entrapment in natural polymeric gels has become the best suitable technique for the immobilization of cells (Mallick 2002); however, immobilized cells on supports have been used more frequently in xenobiotics biodegradation than for pesticides (Lusta et al. 1990). For cyanoremediation of synthetic pesticides, it is important to search for materials with favorable characteristics for the immobilization of cells, including aspects such as physical structure, ease of sterilization, and the possibility of using it repeatedly. Above all, the support must be affordable enough to allow its future use for pesticide degradation.

4.9 GE Cyanobacteria as Biopesticides

Gene manipulation offers a way of engineering microorganisms to deal with a pollutant, including pesticides that may be present in the contaminated sites. The simplest approach is to extend the degradative capabilities of existing metabolic pathways within an organism either by introducing additional enzymes from other organisms or by modifying the specificity of the catabolic genes already present. Cyanobacteria have long been studied as model organisms for photosynthesis (Vermaas 2001; Dong and Golden 2008); the engineering of cyanobacteria for applied purposes remains an underdeveloped field of interest. The potential of genetically modified cyanobacteria is still in the initial stages of exploration. Only a handful of cyanobacterial species have been investigated as host organisms for industrial and bioremediation purposes (Table 4.4). As new species are discovered and sequenced and new tools become available for genetic manipulation, the rich diversity of cyanobacterial phenotypes and genotypes can be exploited for new applications. Increased knowledge of native cyanobacterial genetics, metabolism, and regulatory systems will provide targets for increased production, enabling the synthesis of new products and improving the ability to predict the effects of targeted genetic manipulation.

Genetic engineering in filamentous N_2-fixing cyanobacteria usually involves *Anabaena* sp. PCC 7120 and several other non-aggregating species. Mass culture and harvest of such species are more energy consuming relative to aggregating species. To establish a gene transfer system for aggregating species, Qiong et al. (2010) tested many species of Anabaena and Nostoc and identified *Nostoc muscorum* FACHB244 as a species that can be genetically manipulated using conjugative gene transfer system. To promote biodegradation of organophosphorous pollutants in environments, they introduced a plasmid containing the organophosphorous degradation gene (opd) into *Anabaena* sp. PCC 7120 and *N. muscorum* FACHB244 by conjugation. The opd gene was driven by a story promoter, PpsbA. From both species, they obtained transgenic strains having organophosphorous degradation activities. The genetic manipulation of cyanobacteria could be utilized in the elimination of pollutants and large-scale production of valuable proteins or metabolites.

Table 4.4 Some GE cyanobacterial strains and their transformation methods

Cyanobacterial strains	Transformation methods	References
Anabaena & *Nostoc* sp. PCC 7120	Conjugation	Khasdan et al. (2003); Masukawa et al. (2007)
A.variabilis ATCC 29413	Conjugation	Roessler et al. (2009); Happe et al. (2000)
N. punctiforme ATCC 29133	Conjugation	Lindberg et al. 2002
Nostoc sp. PCC 7422	Conjugation	Yoshino et al. (2007)
Synechococcus elongatus PCC 7942	Natural	Niederholtmeyer et al. (2010); Kaczmarzyk and Fulda (2010);
	Natural	Takeshima et al. (1994)
Synechococcus sp. PCC 6301 *Synechococcus* sp. PCC 7002	Natural	McNeely et al. (2010); Reppas and Ridley (2010)
	Conjugation	Asada et al. (1999); Miyake et al. (2000)
Synechococcus sp. MA 19	Conjugation	Sode et al. (1998); Yu et al. (2000)
Synechococcus sp. NKBG15041c	Conjugation	Nobles and Brown (2008)
S. leopoliensis UTCC 100 *Synechococcus* sp. PCC 6803	Natural conjugation electroporation	Lindberg et al. (2010); Kaczmarzyk and Fulda (2010)

4.10 Conclusions

Although the use of chemical pesticides in agriculture is helpful in the increment of crop production, soil productivity, and products quality, it is also reflected in economic benefits, vector disease control, and in general, in public health. But approximately only 10 % of applied pesticides reach the target organism and rest of the applied pesticides is deposited into soil, water, and sediments which affects the nontarget organism in agro- and aquatic ecosystems besides affecting public health. For this reason, it is necessary to generate strategies for the removal of pesticide contamination from polluted sites, and the biological treatment is an important technology from an economical and environmental point of view for the cleanup of pesticide contamination.

The choice of the bioremediation strategy should be made on the basis of the type of pesticide, environment, and the target organisms present in the ecosystem. Since, the target organism is the only major concern and the information about features, advantages or disadvantages of target organisms can be helpful for better and successive bioremediation. Some parameters like pH, temperature, cell count, biomass growth rate, substrate bioavailability, and moisture, which are crucial for microbial population, can be addressed for bioremediation (Velázquez-Fernández et al. 2012). Moreover, it is important to understand the molecular mechanisms involved in enzymatic catalysis, which will be possible to design new alternatives and/or efficient tools for the treatment of pesticide residues or for the bioremediation of contaminated sites.

Use of cyanobacteria and microlage for the degradation of synthetic pesticides either by increasing the degradation capability of the cyanobacterial community to remove the pollutant is cost-effective and safe technology (Kumar and Singh 2016). Among the cyanobacterial genera, the high tolerance of some cyanobacterial genera toward synthetic pesticides resulted in colonized contaminated environments. It should also be kept in mind that cyanobacteria provide high product selectivity, simple catalyst preparation, and a recycling system.

Moreover, in implementing strategies to increase the efficiency of degradation, such as immobilization of cyanobacterial cells, we may have tools to decline the existence of obsolete pesticides and waste generated; it will reduce the danger of pesticides on the environment and health (Ortiz-Hernández et al. 2013). However, there is a suggestion that immobilization affects the cell's behavior, but many of the observations, particularly with respect to productivity are contradictory. It is therefore, there is a need to increase understanding on the effects of immobilization on cyanobacterial cell physiology and biochemistry. The leakage problem is one of the key concerns in cell immobilization since it obviates the primary purpose of delimiting viable cells in a confined matrix.

Despite the uncertainty regarding the development of GE algae as production strains, development of genetic tools is still imperative from a research standpoint. Understanding the basic biology that will inform such aspects as lateral gene transfer, potential for toxin production, potential for large-scale blooms and subsequent anoxic zone formation, and choice of cultivation methods in terms of organism containment, are very important.

References

Abdullah AR, Bajet CM, Matin MA, Nhan DD, Sulaiman AH (1997) Ecotoxicology of pesticides in the tropical paddy field system. Environ Toxicol Chem 16:59–70

Akhtar W, Sengupta D, Chowdhury A (2009) Impact of pesticide use in agriculture: their benefits and hazards. Interdiscip Toxicol 2(1):1–12

Alavanja MCR et al (2004) Health effects of chronic pesticide exposure – cancer and neurotoxicity. Annu Rev Public Health 25:155–197

Alexander M (1977) Introduction to soil microbiology, 2nd edn. Wiley Eastern Limited, New Delhi

Alexander M (1994) Biodegradation und bioremediation. Academic Press, San Diego, CA

Alexander M (1999) Biodegradation and bioremediation, 2nd edn. Academic Press, London

Araujo ASF, Monterio RTR, Abarkeli RB (2003) Effect of glyphosate on the microbial activity of two Brazilian soils. Chemosphere 52:799–804

Armstrong RN (1994) Glutathione S-transferases: structure and mechanism of an archetypical detoxication enzyme. Adv Enzymol Relat Areas Mol Biol 69:1–44

Arunakumara KKIU, Walpola BC, Yoon MH (2013) Metabolism and degradation of glyphosate in aquatic cyanobacteria: a review. Afr J Microbiol Res 7(32):4084–4090

Asada Y, Miyake M, Miyake J, Kurane R, Tokiwa Y (1999) Photosynthetic accumulation of poly-(hydroxybutyrate) by cyanobacteria-the metabolism and potential for CO2 recycling. Int J Biol Macromol 25:37–42

Babu GS, Farooq M, Ray RS, Joshi PC, Viswanathan PN, Hans RK (2003) DDT and HCH residues in basmati rice (*Oryza sativa*) cultivated in Dehradun (India). Water Air Soil Pollut 144:149–157

Barcelo D, Hennion MC (1997) Trace determination of pesticides and their degradation products in water. Elsevier, Amsterdam, The Netherlands, p. 3

Barton JW, Kurtiz T, O'Connor LE, Ma CY, Maskarinee MP, Davison BH (2004) Reductive transformation of methyl parathion by cyanobacterium *Anabaena* sp., strain PCC 7120. Appl Microbiol Biotechnol 65:330–335

Bödeker W, Dümmler C (1993) Pestizide und Gesundheit, 2nd edn. Verlag C.F Müller, Karlsruhe

Burja AM, Banaigs B, Abou-Mansour E, Grant Burgess J, Wright PC (2001) Marine cyanobacteria-a prolific source of natural products. Tetrahedron 57:9347–9377

Burns RG (1975) Factors affecting pesticides loss from soil. In: Paul E A, AD ML (eds) Soil biochemistry, vol 4. Marcel Dekker, Inc., New York, pp 103–141

Caceres TP, Megharaj M, Naidu R (2008) Biodegradation of the pesticide fenamiphos by ten different species of green algae and cyanobacteria. Curr Microbiol 57(6):643–646

Capone DG, Burns JA, Montoya JP et al (2005) Nitrogen fixation by *Trichodesmium* spp.: an important source of new nitrogen to the tropical and subtropical North Atlantic Ocean. Global Biogeochem Cycles 19(2):1–17

Chen W, Georgiou G (2002) Cell-surface display of heterologous proteins: from high throughput screening to environmental applications. Biotechnol Bioeng 5:496–503

Codd GA (1987) Immobilized micro-algae and cyanobacteria. Br Phycol Soc Newsl 24:1–5

Cohen Y (2001) Biofiltration-the treatment of fluids by microorganisms immobilized into the filter bedding material: a review. Bioresour Technol 77:257–274

Cork DJ, Krueger JP (1991) Microbial transformations of herbicides and pesticides. Adv Appl Microbiol 36:1–66

De-Bashan LE, Yoav Bashan Y (2010) Immobilized microalgae for removing pollutants: review of practical aspects. Bioresour Technol 101:1611–1627

Doggett SM, Rhodes RG (1991) Effects of a diazinon formulations on unialgal growth rates and phytoplankton diversity. Bull Environ Contam Toxicol 47:36–42

Dong G, Golden SS (2008) How a cyanobacterium tells time. Curr Opin Microbiol 11:541–546

Drum C (1980) Soil chemistry of pesticides. PPG Industries, Inc., Pittsburgh, PA

Dyhrman ST, Chapell PD, Haley ST, Moffett JW, Orchard ED, Waterbury JB (2006) Phosphonate utilization by the globally important marine diazotroph *Trichodesmium*. Nature 439:68–71

El-Bestawy EA, Abd El-Salam AZ, Mansy AERH (2007) Potential use of environmental cyanobacterial species in bioremediation on lindane-contaminated effluents. Int Biodeter Biodegr 59:180–192

El-Nahhal Y, Awad Y, Safi J (2013) Bioremediation of acetochlor in soil and water systems by cyanobacterial Mat. Int J Geosci 4:880–890

EPA, 2012. What is a pesticide? http://www.epa.gov/opp00001/about/.

FAO (1989) International code of conduct on the distribution and use of pesticides, Rome.

Forget G (1993) Balancing the need for pesticides with the risk to human health. In: Forget G, Goodman T, de Villiers A (eds) Impact of pesticide use on health in developing countries. IDRC, Ottawa, p 2

Forlani G, Pavan M, Gramek M, Kafarski P, Lipok J (2008) Biochemical basis for a wide spread tolerance of cyanobacteria to the phosphonate herbicide glyphosate. Plant Cell Physiol 49:443–456

Freedman B (1995) Environmental ecology. Academic Press, New York

Gimsing AL, Borggaard OK, Jacobsen OS, Sørensen AJ (2004) Chemical and microbiological soil characteristics controlling glyphosate mineralization in Danish surface soils. Appl Soil Ecol 27:233–242

Glotfelty DE, Schomburg CJ (1989) Volatilization of pesticides from soil. In: Sawhney BL, Brown K, Madison WI (eds) Reactions and movements of organic chemicals in soil. Soil Science Society of America Special Publication, Madison, WI, p 181

González R, García-Balboa C, Rouco M, Lopez-Rodas V, Costas E (2012) Adaptation of microalgae to lindane: a new approach for bioremediation. Aquat Toxicol 109:25–32

Ha J, Engler CR, Lee SJ (2008) Determination of diffusion coefficients and diffusion characteristics for chlorferon and diethylthiophosphate in Ca-alginate gel beads. Biotechnol Bioeng 100(4):698–706

Ha J, Engler CR, Wild J (2009) Biodegradation of coumaphos, chlorferon, and diethylthiophosphate using bacteria immobilized in Ca-alginate gel beads. Bioresour Technol 100:1138–1142

Habib K, Kumar S, Manikar N, Zutshi S, Fatma T (2011) Biochemical effect of carbaryl on oxidative stress, antioxidant enzymes and osmolytes of cyanobacterium *Calothrix brevissima*. Bull Environ Contam Toxicol 87:615–620

Happe T, Schutz K, Bohme H (2000) Transcriptional and mutational analysis of the uptake hydrogenase of the filamentous cyanobacterium *Anabaena variabilis* ATCC 29413. J Bacteriol 182:1624–1631

Hatzios KK (1991) Biotransformation of herbicides in higher plants. In: Grover R, Cessna AJ (eds) Environmental chemistry of herbicides. CRC Press, Boca Raton, FL, pp 141–185

Hedges SB, Chen H, Kumar S, Wang DY, Thompson AS, Watanabe H (2001) A genomic timescale for the origin of eukaryotes. BMC Evol Biol 1(4):1–10

Hicks RJ, Stotzky G, Voris PV (1990) Review and evaluation of the effects of xenobiotic chemical on microorganisms in soil. Adv Appl Microbiol 35:195–253

Hirooka T, Nagase H, Hirata K, Miyamoto K (2006) Degradation of 2,4-dinitrophenol by a mixed culture of photoautotrophic microorganisms. Biochem Eng J 29:157–162

Ibrahim WM, Karam MA, El-Shahat RM, Adway AA (2014) Biodegradation and utilization of organophosphorus pesticide malathion by cyanobacteria. Biomed Res Int. Article ID 392682

Igbedioh SO (1991) Effects of agricultural pesticides on humans, animals and higher plants in developing countries. Arch Environ Health 46:218

Jha MN, Mishra SK (2005) Biological responses of cyanobacteria to insecticides and their insecticide degrading potential. Bull Environ Contam Toxicol 75(2):374–381

Kaczmarzyk D, Fulda M (2010) Fatty acid activation in cyanobacteria mediated by acyl-acyl carrier protein synthetase enables fatty acid recycling. Plant Physiol 152:1598–1610

Kanekar PP, Bhadbhade BJ, Deshpande NM, Sarnaik SS (2004) Biodegradation of organophosphorous pesticides. Proc Indian Natl Sci Acad B 70(1):57–70

Kennedy IR, Sanchez-Bayo F, Kimber SW, Hugo L, Ahmad N (2001) Off-site movement of endosulfan from irrigated cotton in New South Wales. J Environ Qual 30:683–696

Khasdan V, Ben-Dov E, Manasherob R, Boussiba S, Zaritsky A (2003) Mosquito larvicidal activity of transgenic *Anabaena* PCC 7120 expressing toxin genes from *Bacillus thuringiensis* subsp. *israelensis*. FEMS Microbiol Lett 227:189–195

Kodama T, Kuwatsuka S (1980) Factors for the persistence of parathion, methyl parathion and fenitrothion in seawater. J Pestic Sci 5:351–355

Kole RK, Bagchi MM (1995) Pesticide residues in the aquatic environment and their possible ecological hazards. J Inland Fish Soc India 27(2):79–89

Kulasooriya SA (2011) Cyanobacteria: pioneers of planet earth. Ceylon J Sci (Bio Sci) 40(2):71–88

Kumar A, Singh JS (2016) Microalgae and cyanobacteria biofuels: a sustainable alternate to crop-based fuels. In: Singh JS, Singh DP (eds) Microbes and environmental management. Studium Press Pvt. Ltd., New Delhi, pp 1–20

Kumar N, Bora A, Kumar R, Amb MK (2012) Differential effects of agricultural pesticides endosulfan and tebuconazole on photosynthetic pigments, metabolism and assimilating enzymes of three heterotrophic, filamentous cyanobacteria. J Biol Environ Sci 6(16):67–75

Kumar NJI, Amb MK, Kumar RN, Bora A, Khan SR (2013) Studies on biodegradation and molecular characterization of 2,4-D ethyl ester and pencycuron induced cyanobacteria by using GC-MS and 16S r DNA sequencing. Proc Int Acad Ecol Environ Sci 3(1):1–24

Kuritz T (1999) Cyanobacteria as agents for the control of pollution by pesticides and chlorinated organic compounds. J Appl Microbiol Symp Supplement 85:186S–192S

Kuritz T, Wolk CP (1995) Use of filamentous cyanobacteria for biodegradation of organic pollutants. Appl Environ Microbiol 61:234–238

Lal R, Pandey G, Sharma P, Kumari K, Malhotra S, Pandey R, Raina V, Kohler HPE, Holliger C, Jackson C, Oakeshott JG (2010) Biochemistry of microbial degradation of hexachlorocyclohexane and prospects for bioremediation. Microbiol Mol Biol Rev 74:58–80

Lee SE, Kim JS, Kennedy IR, Park JW, Kwon GS, Koh SC, Kim JE (2003) Biotransformation of an organochlorine insecticide, endosulfan, by *Anabaena* Species. J Agric Food Chem 51:1336–1340

Lindberg P, Schütz K, Happe T, Lindblad P (2002) A hydrogen-producing, hydrogenase-free mutant strain of *Nostoc punctiforme* ATCC 29133. Int J Hydrogen Energy 27:1291–1296

Lindberg P, Park S, Melis A (2010) Engineering a platform for photosynthetic isoprene production in cyanobacteria, using *Synechocystis* as the model organism. Metab Eng 12:70–79

Lipok J, Owsiak T, Młynarz P, Forlani G, Kafarski P (2007) Phosphorus NMR as a tool to study mineralization of organophosphonates-The ability of *Spirulina* spp. to degrade glyphosate. Enzyme Microb Technol 41:286–291

Lipok J, Wieczorek D, Jewginski M, Kafarski P (2009) Prospects of in vivo 31P NMR method in glyphosate degradation studies in whole cell system. Enzyme Microb Technol 44:11–16

Lusta KA, Starostina NG, Fikhte BA (1990) Immobilization of microorganisms: cytophysiological aspects. In: De Bont JAM, Visser J, Mattiasson B, Tramper J (eds) Proceedings of an international symposium: physiology of immmobilized cells. Elsevier, Amsterdam, The Netherlands

Majewski MS, Capel PD (1995) Pesticides in the atmosphere: distribution, trends, and governing factors, Pesticides in the hydrologic system, vol Vol 1. Ann Arbor Press Inc, Ann Arbor, MI, p. 118

Mallick N (2002) Biotechnological potential of immobilized algae for wastewater N, P and metal removal: a review. Biometals 15:377–390

Manahan SE (2001) Fundamentals of environmental chemistry, 2nd edn. CRC Press LLC, Boca Raton

Marrs KA (1996) The functions and regulation of glutathione S-transferases in plants. Annu Rev Plant Physiol Plant Mol Biol 47:127–158

Martin H (1968) Pesticides manual. British Crop Protection Council, London

Martín M, Mengs G, Plaza E, Garbi C, Sánchez M, Gibello A, Gutiérrez F, Ferrer E (2000) Propachlor removal by *Pseudomonas* strain GCH1 in a immobilized-cell system. Appl Environ Microbiol 66(3):1190–1194

Masukawa H, Inoue K, Sakurai H (2007) Effects of disruption of homocitrate synthase genes on *Nostoc* sp. Strain PCC 7120 photobiological hydrogen production and nitrogenase. Appl Environ Microbiol 73:7562–7570

McNeely K, Xu Y, Bennette N, Bryant DA, Dismukes GC (2010) Redirecting reductant flux into hydrogen production via metabolic engineering of fermentative carbon metabolism in a cyanobacterium. Appl Environ Microbiol 76:5032–5038

Megharaj M, Venkateswarlu K, Rao AS (1987) Metabolism of monocrotophos and quinalphos by algae isolated from soil. Bull Environ Contam Toxicol 39:251–256

Megharaj M, Madhavi DR, Sreenivasulu C, Umamaheswari A, Venkateswarlu K (1994) Biodegradation of methyl parathion by soil isolates of microalgae and cyanobacteria. Bull Environ Contam Toxicol 53:292–297

Miyake M, Takase K, Narato M, Khatipov E, Schnackenberg J, Shirai M et al (2000) Polyhydroxybutyrate production from carbon dioxide by cyanobacteria. Appl Biochem Biotechnol 84:991–1002

Moreno-Garrido I (2008) Microalgae immobilization: current techniques and uses. Bioresour Technol 99:3949–3964

Moslemy P, Guiot SR, Neufeld RJ (2002) Production of size-controlled gellan gum microbeads encapsulating gasoline-degrading bacteria. Enzyme Microb Technol 30:10–18

Mostafa FIY, Helling CS (2001) Isoproturon degradation as affected by the growth of two algal species at different concentrations and pH values. J Environ Sci Health B 36(6):709–727

Murali O, Shaik G, Mehar SK (2014) Assessment of bioremediation of Cobalt and Chromium using cyanobacteria. Ind J Fund Appl Life Sci 4(1):252–255

Niederholtmeyer H, Wolfstadter BT, Savage DF, Silver PA, Way JC (2010) Engineering cyanobacteria to synthesize and export hydrophilic products. Appl Environ Microbiol 76:3462–3466

Nobles D, Brown R (2008) Transgenic expression of *Gluconacetobacter xylinus* strain ATCC 53582 cellulose synthase genes in the cyanobacterium *Synechococcus leopoliensis* strain UTCC 100. Cellul 15:691–701

O'Neil W, Raucher R, Wayzata MN (1998) Groundwater Policy Education Project, Groundwater public policy leaflet series #4: the costs of groundwater contamination.

Ortiz-Hernández ML, Sánchez-Salinas E, Olvera-Velona A, Folch-Mallol JL (2011) Pesticides in the environment: impacts and its biodegradation as a strategy for residues treatment. In: Stoytcheva M (ed) Pesticides - formulations, effects, fate. InTech, Rijeka, pp 551–574

Ortiz-Hernández ML, Sánchez-Salinas E, Dantán-González E, Castrejón-Godínez ML (2013) Pesticide biodegradation: mechanisms, genetics and strategies to enhance the process. In: Chamy R, Rosenkranz F (eds) Biodegradation - life of science. InTech, Rijeka

Orus MI, Marco E (1991) Disappearance of trichlorophon from cultures with different cyanobacteria. Bull Environ Contam Toxicol 47:392–397

Palanisami S, Prabaharan D, Uma L (2009) Fate of few pesticide metabolizing enzymes in marine cyanobacterium *Phormidium valderianum* BDU 20041 in perspective with chlorpyifos exposure. Pestic Biochem Physiol 94:68–72

Parkinson A (2001) Biotransformation of xenobiotics. In: Klaassen CD (ed) Casarett and Doull's toxicology: the basic science of poisons, 6th edn. McGraw-Hill, New York, NY, pp 133–224

Qiong LI, Qing T, Xudong XU, Hong GAO (2010) Expression of organophosphorous-degradation gene (opd) in aggregating and non-aggregating filamentous nitrogen-fixing cyanobacteria. Chinese J Oceanol Limnol 28:1248–1253

Racke KD, Skidmore MW, Hamilton DJ, Unsworth JB, Miyamoto J, Cohen SZ (1997) Pesticide fate in tropical soils. Pure Appl Chem 69:1349–1371

Ravi V, Balakumar H (1998) Biodegradation of the C-P bond in glyphosate by the cyanobacterium *Anabaena variabilis* L. J Sci Ind Res India 57:790–794

Ravindran CRM, Suguna S, Shanmugasundaram S (2000) Tolerance of oscillatoria isolates to agrochemicals and pyrethroid components. Indian J Exp Biol 38:402–404

Reddy BR, Sethunathan N (1985) Salinity and the persistence of parathion in flooded soil. Soil Biol Biochem 17:235–239

Reppas NB, Ridley CP (2010) Methods and compositions for the recombinant biosynthesis of n-alkanes. Patent US 7794969, Joule Unlimited, Inc., Washington, DC

Richins R, Mulchandani A, Chen W (2000) Expression, immobilization, and enzymatic characterization of cellulose-binding domain-organophosphorus hydrolase fusion enzymes. Biotechnol Bioeng 69:591–596

Roberts TR (1998) Metabolic pathways of agrochemicals-part 1: herbicides and plant growth regulators. The Royal Society of Chemistry, Cambridge, pp. 396–399

Roberts TR, Hutson DH (1999) Acephate: metabolic pathways of agrochemicals - part 2: insecticides and fungicides. The Royal Society of Chemistry, Cambridge, pp. 201–204

Robinson PK, Mak AL, Trevan MD (1986) Immobilized algae: a review. Process Biochem 21:122–126

Roessler PG, Chen Y, Liu B, Dodge CN (2009) Secretion of fatty acids by photosynthetic microorganisms in Patent US, Ed. Synthetic Genomics, United States

Savonen C (1997) Soil microorganisms object of new OSU service. Good Fruit Grower. http://www.goodfruit.com/archive/1995/6other.html

Singh PK (1973) Effect of pesticides on blue-green algae. Arch Microbiol 89:317–320

Singh DK (2008) Biodegradation and bioremediation of pesticide in soil: concept, method and recent developments. Indian J Microbiol 48(1):35–40

Singh JS, Gupta VK (2016) Degraded land restoration in reinstating CH_4 sink. Front Microbiol 7(923):1–5

Singh JS, Abhilash PC, Singh HB, Singh RP, Singh DP (2011a) Genetically engineered bacteria: An emerging tool for environmental remediation and future research perspectives. Gene 480:1–9

Singh DP, Khattar JIS, Nadda J, Singh Y, Garg A, Kaur N, Gulati A (2011b) Chlorpyrifos degradation by the cyanobacterium *Synechocystis* sp. strain PUPCCC 64. Environ Sci Pollut Res 18:1351–1359

Singh JS, Singh DP, Dixit S (2011c) Cyanobacteria: an agent of heavy metal removal. In: Maheshwari DK, Dubey RC (eds) Bioremediation of pollutants. IK International Publisher Co., New Delhi, pp 223–243

Singh DP, Khattar JIS, Kaur M, Kaur G, Gupta M et al (2013) Anilofos tolerance and its mineralization by the Cyanobacterium *Synechocystis* sp. strain PUPCCC 64. PLoS One 8(1):e53445

Singh R, Singh P, Sharma R (2014) Microorganism as a tool of bioremediation technology for cleaning environment: a review. Proc Int Acad Ecol Environ Sci 4(1):1–6

Singh JS, Kumar A, Rai AN, Singh DP (2016) Cyanobacteria: a precious bio-resource in agriculture, ecosystem, and environmental sustainability. Front Microbiol 7(529):1–19

Sode K, Yamamoto Y, Hatano N (1998) Construction of a marine cyanobacterial strain with increased heavy metal ion tolerance by introducing exogenic metallothioneins gene. J Mar Biotechnol 6:174–177

Subramanian G, Sekar S, Sampoornam S (1994) Biodegradation and utilization of organophosphorus pesticides by cyanobacteria. Int Biodegrad Biodetertor 33:129–143

Sun W, Chen Y, Liu L, Tang J, Chen J, Liu P (2010) Conidia immobilization of T-DNA inserted *Trichoderma atroviride* mutant AMT-28 with dichlorvos degradation ability and exploration of biodegradation mechanism. Bioresour Technol 101:9197–9203

Taha TH, Taha Alamri SA, Mahdy HM, Hafez EE (2013) The effects of various immobilization matrices on biosurfactant production using hydrocarbon (HC)-degrading marine bacteria via the entrapment technique. J Biol Sci 13:48–57

Takeshima Y, Takatsugu N, Sugiura M, Hagiwara H (1994) High-level expression of human superoxide dismutase in the cyanobacterium *Anacystis nidulans* 6301. Proc Natl Acad Sci U S A 91:9685–9689

Tao XQ, Lu GN, Liu JP, Li T, Yang LN (2009) Rapid degradation of phenanthrene by using Sphingomonas sp. GY2B immobilized in calcium alginate gel beads. Int J Environ Res Public Health 6:2470–2480

Terre Des Hommes (2011) Pestizide und Kinder. PAN Germany, Osnabrück

Thengodkar RRM, Sivakami S (2010) Degradation of Chlorpyrifos by an alkaline phosphatase from the cyanobacterium *Spirulina platensis*. Biodegradation 21:637–644

Topp E, Vallaeys T, Soulas G (1997) Pesticides microbial degradation and effect on microorganisms. In: Van Elsas JD, Trevors JT, Wellington EMH (eds) Modern soil microbiology. Mercel Dekker Inc., New York, pp 547–575

UNEP (2004) Childhood pesticide poisoning, Châtelaine

Urrutia I, Serra JL, Llama MJ (1995) Nitrate removal from water by *Scenedesmus obliquus* immobilized in polymeric foams. Enzyme Microb Technol 17:200–205

US EPA (2001) Source water protection practices bulletin: Managing small-scale application of pesticides to prevent contamination of drinking water. Office of Water, Washington, DC EPA 816-F-01-031

Velázquez-Fernández JB, Martínez-Rizo AB, Ramírez-Sandoval M, Domínguez-Ojeda D (2012) Biodegradation and bioremediation of organic pesticides. In: Soundarajan RP (ed) Pesticides – recent trends in pesticide residue assay. InTech, Rijeka

Vermaas WFJ (2001) Photosynthesis and respiration in cyanobacteria. Wiley, New York

Waliszewski SM, Carvajal O, Gomez-Arroyo S, Amador-Munoz O, Villalobos-Pietrini R, Hayward-Jones PM, Valencia-Quintana R (2008) DDT and HCH isomer levels in soils, carrot root and carrot leaf samples. Bull Environ Contam Toxicol 81:343–347

Walker WW (1976) Chemical and microbiological degradation of malathion and in an estuarine environment. J Environ Qual 5:210–216

Waskom R (1994) Best management practices for private well protection. Colorado State Univ. Cooperative Extension. http://hermes.ecn.purdue.edu:8001/cgi/convertwq?7488

Weber K (1976) Degradation of parathion in seawater. Water Res 10:237–241

Whitton BA, Potts M (2000) Introduction to the cyanobacteria. In: Whitton BA, Potts M (eds) The ecology of cyanobacteria: their diversity in time and space. Kluwer Academic, Dordrecht, The Netherlands, pp 1–11

WWF (2002) Gefahr durch hormonell wirksame Pestizide und Biozide, Schadstoffe in Lebensmitteln, Garten und Haus. WWF-Fachbereich Meere und Küsten, Bremen

Yoshino F, Ikeda H, Masukawa H, Sakurai H (2007) High photobiological hydrogen production activity of a *Nostoc* sp. PCC 7422 uptake hydrogenase-deficient mutant with high nitrogenase activity. Marine Biotechnol 9:101–112

Yu R, Yamada A, Watanabe K, Yazawa K, Takeyama H, Matsunaga T et al (2000) Production of eicosapentaenoic acid by a recombinant marine cyanobacterium, *Synechococcus* sp. Lipids 35:1061–1064

Zacharia JT (2011) Identity, physical and chemical properties of pesticides. In: Stoytcheva M (ed) Pesticides in the modern world - trends in pesticides analysis. InTech, Rijeka