Effective pesticide nano formulations and their bacterial degradation

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Effective pesticide nano formulations and their bacterial degradation

M Ramadass and P Thiagarajan
School of Biosciences and Technology, VIT University, Vellore, India

E.mail:padmadk4@gmail.com

Abstract. The use of chemical pesticides for agricultural pest control and the consequent damage to the ecosystem at air, water and soil levels has become a factor of common knowledge. This alarming trend has led to research and development in the area of nanoformulations to achieve the end use of pest control with very low concentrations of pesticides. Such formulations are being proven to be as effective as traditional formulations due to their inherent ability to achieve controlled delivery of their respective active ingredients. The end result is a successful pest control with minimum environmental damage. Despite this, certain organic groups, that form the essential structural constituents of these pesticides, are not readily degraded due to their complex nature. They continue to persist, accumulate and biomagnify in the environment leading to short and long term hazards. In this context, it has been noted that certain common genera of bacteria such as *Bacillus*, *Pseudomonas*, *Flavobacterium*, *Sphingomonas*, *Brevibacterium*, *Burkholderia*, etc possess the inherent ability to utilise specific chemical groups in the pesticides as their sole source of either carbon and / or nitrogen and consequently achieve their conversion into non-toxic end products. A potential bioremediation process is thus slowly gaining popularity and being implemented on a pilot scale. However, large scale successful pesticide microbial remediation will involve experimentation with several combinations of a variety of nano pesticide formulations with different genera of bacteria under optimised conditions. Such studies will throw light on the precise genus and species of bacteria that may degrade the required groups of pesticides, for environmental damage control in the long run.

1.Introduction

Pesticides are vital in agriculture to control insects and increase the crop yields. Generally, they are used to improve crop production and act as protective agents against plant pathogens. In addition, they also stimulate plant growth leading to high yield of desired products. Pesticides applied directly to the soil pose a risk of being washed off and thus causing environmental pollution [1]. They comprise of toxic compounds that affect non-target population including humans, animals and birds and thus altering the normal ecosystem. Their toxicity profile varies based on the group and percentage of active ingredients [2]. Pesticide exposure can cause serious health problems such as nausea, diarrhoea, weakness, fatigue, respiratory distress, lung impairment, asthma, chronic bronchitis, lung cancer, hormonal imbalance, reproductive problems, and hypersensitivity in humans [3-5]. Different formulations such as wettable powders, water dispersible granules, suspension concentrates, soluble concentrates, emulsifiable concentrates, microemulsions, and oil dispersions are used as pesticides. Microbes play a major role in biodegradation of environmental pollutants. The bacteria involved in bioremediation utilize the toxic chemicals in the pesticides for their growth by converting them into

non-toxic end products that stimulate the soil biota [6, 7]. *Bacillus* and *Pseudomonas* are the most common groups of bacteria involved in bioremediation processes [8, 9]. Such microbes when collected from contaminated sites have a better ability to degrade and utilize pesticides.

Nano emulsions can be the oil in water or water in oil types with droplet sizes of 20-200nm. The characteristic features of nano emulsion formulations are low viscosity, good stability, dispersity, and transparent properties that make them beneficial in numerous fields like cosmetic, pharma and food industries and as agrochemical formulations [10-12]. Certain pesticides are water insoluble, so organic solvents are used to formulate them. Nanoemulsion formulations act by permitting the delivery of pesticides with low surfactant concentrations, in addition to preventing the premature degradation of the active ingredient [13, 14]. It is also able to achieve its target with low concentrations of active ingredients by adopting a controlled release strategy. Toxicity towards non-target organisms is thus decreased [15, 16].

2. Classification of pesticides

These include insecticides, herbicides, nematicides, acaricides, rodenticides, termiticides, fungicides, bactericides, virucides, chemosterilants, molluscicides, plant growth regulator, plant activators, antifeedants, and avicides. Depending on their chemical nature they are classified into organophosphates, organochlorines, carbamates and pyrethroids. The most commonly used group of pesticides worldwide are organophosphates and carbamates [4, 17, 18]**.**

2.1. Insecticide formulations

Beta-cypermethrin belongs to a hydrophobic pyrethroids group of insecticide that can be incorporated into nano emulsions and shows uniform distribution and stability. There no difference in the droplet size of the emulsion with and without the pesticide. The extent of pesticide solubility is very important in diluted forms of emulsions [19].When compared to commercial formulations; it shows good dispersion in the nano emulsion formulations [20].

Insecticide imidacloprid formulation shows good bio efficacy and is able to achieve controlled release of the insecticide. It controls the soybean pest and it also increases plant yield [21]. The formulation with imidacloprid and carbofuran controls widely distributed insects such as *Aphis gossypii* that affects almost all kind of agricultural crops like citrus, cucumber, pumpkin, cotton, watermelons, pepper etc. The formulation shows better control and is of superior choice than the commercial one [22, 23]. Etofenprox is a pyrethroid group of insecticide that is toxic to the aquatic environment. Nano formulation of controlled release etofenprox controls *Spodoptera litura* as it increases the availability of active ingredient and prevents the loss of insecticide [24].

Pyridalyl nano formulation controls *Helicoverpa armigera,* commonly known as cotton bollworm that affects agricultural crops. When compared with the commercial formulation Sumipleo R 10% EC it shows 12-13 % more effectivity then the commercial product. An active ingredient of lower activity has an ability to control the pest than the commercial product with an active ingredient of higher activity [25, 26]. Insect growth regulator Novaluron is a chemical that belongs to the insecticide class. It is of low toxicity to the non-target organisms and environment. It also reduces the use of other groups of toxic pesticides. Novaluron added to the micro emulsion has an ability to control the pests like other commercial formulations and it possesses an additional advantage of being an organic solvent free formulation [27].

The organophosphate group in Triazofos acts as a nematicide, acaricide and insecticide. It is highly flammable and toxic. Usually, it is used in a micro emulsion system due to its poor solubility in water. As a basic solution, the pesticide has an ability to hydrolyse easily and it is very important to protect the active ingredient from hydrolysis. It can be overcome by incorporation of triazofos in the nano emulsion system and the concentration of 20% and 25% triazofos formulation shows typical particle size even in an 800 fold dilution. In the nanoemulsion form, it inhibits the hydrolysis of pesticide in an alkaline condition and this is more excellent than in the acidic condition [28, 29].

2.2. Herbicide formulations

Glyphosate is a hydrophilic organo phosphorous group of herbicide. Glyphosate isopropyl amine is added to the emulsion formulation and is diluted to form a nano formulation. An emulsion with low hydrophilicity is of low stability at a high temperature but in a nano formulated pre emulsion form; it has a long shelf life and a potent ability to deliver the glyphosate isopropyl amine to control the weeds, *viz., Eleusine indica that* is commonly known as Indian goose grass [30]. Lower amounts of surfactant, as compared to commercial pesticide formulations, are sufficient in this case, and in turn, this reduces the environment toxicity [30, 31].

The herbicide pretilachlor has been incorporated in micro emulsions and used as encapsulated monolithic dispersions to control the weed *Echinochloa crus-galli*. Two of such formulations are better than the commercial pretilachlor Rifit® 50EC. The emulsion is much better due to its low particle size. Even after further dilution of the emulsion formulation, the particle size is maintained in the nanoscale range. Due to its low droplet size, it shows a long shelf life for more than a year [32, 33]. Metribuzin is a most commonly used herbicide that is highly soluble in water. This results in groundwater contamination. Sepiolite gel is able to entrap the metribuzin and ensure controlled release of the herbicide [34].

2.3. Fungicide formulations

Mancozeb has been entrapped using polyethylene glycol to form a nano pesticide formulation. It is a non-systemic fungicide under the sub-class of carbamate group. It possesses both antibacterial and antifungal activities against *Staphylococcus aureus* and *Candida albicans* respectively [35].

Carbendazim is a systemic benzimidazole fungicide and controlled release of this fungicide formulation has been achieved using amphiphilic based co-polymers. Slow release of active ingredients compared to commercial 50% WP is a highlight here and it reduces the need for further applications. It effectively controls *Rhizoctonia solani*, the pathogen that affects the rice plant [36]. Encapsulation of carbendazim at a lower concentration of 0.5 and 1ppm controls the plant pathogen *Fusarium oxysporum* and *Aspergillus parasiticus*. Complete inhibition of target pathogens and non-toxicity to non-target organisms such as bacteria is an additional advantage [37, 38].

3. Microbial degradation of pesticides

Biodegradation of pesticides is very important to remove the toxic compounds from the natural ecosystem. Microbes play a major and important role in biodegradation. They utilize the toxic compounds from the pesticides and produce non-toxic end products. The process of bioremediation depends upon various environmental parameters, the type of microbes and the presence of degradative enzymes [39,40]. Bacteria such as *Bacillus*, *Pseudomonas*, and *Flavobacterium* have the ability to degrade the pesticides [41-43].

3.1. Insecticide degradation

3.1.1. Beta-cypermethrin

Beta-cypermethrin is utilized by *Serratia sp.,* strain JC1 and JCN13 in the range of 25 - 1000ppm. Rapid degradation has been reported by the strain JCN13 followed by the strain JC1 in 4 and 10days of incubation with the removal of 89% and 92% respectively. The rapid degradation by strain JCN13 is due to the presence of high hydrophobicity as compared to the strain JC1 [44]. *Ochrobactrum lupini* utilizes beta-cypermethrin and its metabolite 3-phenoxybenzoic acid completely. It is able to utilize 50-400ppm concentration. Other pyrethroid groups of pesticides are also utilized by the bacterium such as beta-cyfluthrin, deltamethrin, cyhalothrin, and fenpropathrin [45]. *Pseudomonas aeruginosa* utilizes beta-cypermethrin supplemented 67% in Minimal salt medium (MSM) with 100ppm of pesticide, within four days of incubation and it had an ability to produce biosurfactant Rhamnolipid that enhances the degradation process [46]. Around 90% degradation has been reported for *Bacillus*

subtilis at 50ppm in 7days. Cypermethrin was completely utilized by a coculture of *Streptomyces aureus* and *Bacillus cereus*. 50ppm was utilized in 72hours of incubation. It was able to tolerate about 500ppm of concentration. All the isolates reported above for the degradation of cypermethrin have been isolated from the activated sludge of pesticide manufacturing industries [47,48]. *Pseudomonas sp* has an ability to utilize cypermethrin; around 20ppm could be been effectively utilized by the bacteria within two days [49].

3.1.2. Imidacloprid, triazophos and methyl parathion

Klebsiella pneumoniae showed 78% removal of imidacloprid 50 ppm in 7 days [50]. It has been reported that bacteria such as *Rhizobium sp*., *Bacillus sp*., *Brevibacterium sp*., and *Pseudomonas putida* utilise imidacloprid [51-53]. *Bacillus sp* isolated from the sewage sludge degraded 100ppm of triazophos in 5 days, to an extent of 98.5%. The intracellular enzyme has been held responsible for the degradation of triazophos [54]. Pesticide contaminated field isolate *Pseudomonas aeruginosa* mpd strain degraded 1000ppm of methyl parathion effectively. Optimal conditions for bacteria enhance the degradation process. In an incubation period of 96 hours, around 95% of pesticide could be degraded in synthetic waste water [55]. *Pseudomonas diminuta, pseudomonas putida, Burkholderia cepacia, Ochrobactrum anthropi, Bacillus pumilus, Serratia sp, Achromobacter sp* and *Flavobacterium sp* have been reported for the degradation of methyl parathion [56-58].

3.1.3. Diazinon

It is a moderately toxic contact insecticide. The bacteria *Serratia marcescens* isolated from the soil source has an ability to utilize diazinon as a carbon source and the degradation could be carried out using MSM supplemented with 50 ppm of diazinon with a cell concentration of 10^6 cfu/ml. The complete degradation of diazinon was achieved upon 11days of incubation. The time period required for removal of a pesticide depends on the inoculum concentration and at high pesticide concentration, the rate of degradation is lower. The bacterium also has an ability to degrade another organophosphate group of pesticides such as parathion, chlorpyifos, isazofos and coumaphos [59]. *Ralstonia sp*. has been reported to degrade a wide and complex range of environmental pollutants and it has an ability to adapt to different environmental conditions. The bacteria possess an ability to degrade diazinon at a concentration of 100ppm at 60hours of incubation [60]. Bacteria such as *Flavobacterium sp*., *Brevundimonas sp*., *Pseudomonas sp*., *Arthrobacter sp*., *Burkholderia sp*., *Agrobacterium* have an ability to degrade diazinon insecticide [61, 62].

3.1.4. Chlorpyrifos

Bacillus pumilus C2A1 strain effectively degrades chlorpyrifos and 3, 5, 6-trichloro-2-pyridinol, which is the first hydrolysis metabolite of chlorpyrifos. It has an ability to degrade 90% of the metabolite in 8 days of incubation (300mg/L). An alkaline condition supports maximum degradation and the bacteria are able to tolerate till 1000ppm of chlorpyrifos [63]. The strain *Bacillus pumilus* with ryegrass mediated soil remediation, showed that 97% of pesticide could be degraded within 45 days. Ryegrass promotes the growth of bacteria and degrades the metabolite of chlorpyrifos. The bacteria increase plant growth and pesticide remediation process [64]. *Enterobacter sp*. has an ability to degrade 250ppm in a short incubation period of fewer than 2 days. There is no difference in the bacterial growth of *Enterobacter* in the presence of primary metabolite [65]. *Pseudomonas sp*. has an ability to degrade chlorpyrifos metabolite [66].

Alcaligenes faecalis, isolated from the chemical factory contaminated soil, degrades both chlorpyrifos and their metabolites. A study reported that the soil mediated degradation improves in the presence of cabbage cultivation. In liquid culture, the bacterial degradation was 93.5% of chlorpyrifos and 100% of its metabolite with 10days of incubation. Growth and degradation are not affected with even more than 800ppm of metabolite 3, 5, 6-trichloro-2-pyridinol. The bacterium additionally utilizes diazinon and parathion [67]. Soil isolate *Providencia stuartii* utilizes chlorpyifos at the concentration of 50-200 ppm and it is able to survive in the concentration of 400-700ppm [68]. Intestinal microbes like

Escherichia coli, *Lactobacillus lactis*, and *Lactobacillus fermentum* have an ability to tolerate chlorpyrifos at more than 1400ppm. *L. lactis* and *L. fermentum* degrade more effectively than *E.coli* [69].

3.1.5. Monocrotophos

Soil isolate *Bacillus subtilis* degraded 1000ppm of monocrotophos within 72 hours of incubation. 94.2% degradation was reported using 2ml of culture. The gene responsible for the effective degradation was opdA that is expressed 1.5 fold more during the process of degradation [70]. Pesticide contaminated soil isolates *Bacillus licheniforms*, *Bacillus subtilis*, *Pseudomonas stutzeri*, *Rhodococcus phenolicus* and *Rhococcus ruber* effectively degraded monocrotophos [71, 72]. *Paracoccus sp*., isolated from the sludge degrades monocrotophos rapidly and around 80% is removed after 6 hours of incubation. It also degrades the amide group of herbicides [73]. *Clavibacter michiganense subsp insidiosum* and *Pseudomonas aeruginosa* effectively degraded 86% and 98% of monocrotophos respectively within 24 hours of incubation [74].

3.2. Herbicide degradation

An *Enterobacter cloaca* has been reported to utilize organophosphate herbicide glyphosate. It has been isolated from the roots of *Helianthus tuberosus L* (sunflower). The strain utilizes and converts it into nontoxic end product such as sarcosine which is it further oxidized to glycine. In association with sugar sorghum and sunflower, bacteria enhance plant growth and promote the root surface bacteria to survive under stress conditions [75]. Glyphosate concentration of around 10,000ppm and 7200 ppm was tolerated by the bacterium *Pseudomonas fluorescens* and *Acetobacter sp*. that was isolated from the rice field soil [76]. Halophilic bacteria *Salinicoccus sp*. promotes the degradation of glyphosate till 2250ppm. *Flavobacterium sp* has been reported in the degradation of glyphosate [77].

Metribuzin is a triazinone group of herbicide and *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* from paddy fields degraded metribuzin at 25ppm as well as the insecticide profenofos [78]. *Gulosibacter molinativorax* mineralizes molinate that is a thiocarbamate herbicide [79]. Oxyfluorfen herbicide can be utilized by the bacterium genera *Arthrobacter*, *Pseudomonas*, and *Bacillus* to an extent of around 83- 96% [80]. Atrazine is a major group of herbicide that affects the water and soil. It has an s-triazine ring structure. *Arthrobacter sp*., isolated from the atrazine resistant plant (rhizospheric soil) utilizes atrazine as a nitrogen source. It converts atrazine into cyanuric acid and then to biuret. The bacteria *Arthrobacter sp*., utilizes the cyanuric acid and converts it into biuret that can be utilized by soil biota. Due to the presence of an atzD gene, it has a capacity to utilize cyanuric acid and it is able to degrade other triazine herbicides. Bacterial genera such as *Pseudomonas, Acinetobacter, Micrococcus, Bacillus, Delftia,* and *Agrobacterium* utilize atrazine [43, 81].

Complete mineralization of 100ppm acetochlor within 6 days was achieved by a bacterial consortium of *Rhodococcus sp, Delftia sp,* and *Sphingobium sp*. The bacteria *Rhodococcus sp* utilizes the herbicide acetochlor and converts it in to 2-methyl-6-ethyl-2-chloroacetanilide and it can be utilized by *Delftia sp* that results in the formation of the end product 2-methy-6-ethyl aniline. Further it can be degraded by *Sphingobium sp* [82]. *Pseudomonas oleovorans*, *Achromobacter* and *Ensifer adhaerens* are the reported bacteria for the degradation of acetochlor [83, 84]. Bacterial consortium of *Alcaligenes sp*., *Pseudomonas putida*, *Providencia rustigianii* and *Pseudomonas marginalis* have been reported for the degradation of alachlor and atrazine herbicides [85]. Butachlor is a chloroacetamide group of herbicide and 50ppm of it was degraded to an extent of 81.2% in 84hours by the novel strain *Catellibacterium caeni sp*. Effective degradation was reported across a broad range of pH and temperature [86]. Rice field soil isolate *Paracoccus sp*. has an ability to utilize chloroacetamide herbicides such as pretilachlor, butachlor, alachlor, propisochlor, acetochlor and metolachlor. *Pseudomonas aeruginosa* degraded 50ppm within 4days of incubation [46]. Bacteria such as *Klebsiella sp*., *Pseudomonas sp*., and *Enterobacter sp*., have been reported to degrade of S-metolachlor. In conventional plantation soil, *Klebsiella pneumoniae* strain showed effective

degradation of around 99%. They are isolated from humus (Ascomycota) [87]. Bacteria like *Ralstonia pickettii*, *Methylobacterium radiotolerans* and *Rhizobium radiobacter* are able to utilize and tolerate high concentrations (even 10 fold higher than the field application of herbicide sulfentrazone [88].
2, 4-dichlorophenoxyacetic acid is a phenoxy group of herbicides and it has been effectively degraded by *Achromobacter sp*., at the concentration of 200ppm with in 36hours. Around 90 and 75% of degradation was reported in the soil at a concentration of 50 and 100 respectively [89]. The other bacteria reported for degradation include *Acinetobacter sp*., *Flavobacterium sp, Serratia marcescens*, *Sphingomonas herbicidovorans*, *Stenothrophomonas maltophilia*, and *Pseudomonas putida*. Rapid degradation was reported in case of isolates *Delftia* and *Burkholderia cepacia* within 28 hours at the concentration of 200 and 500ppm respectively [90,91].

3.3. Fungicide degradation
Bacillus subtilis strains have an ability to degrade carbendazim in both liquid culture and soil slurry. They utilize fungicide rapidly in initial days and the growth is slow when the fungicide carbendazim is in lower concentration. For five days, the exponential phase increases rapidly and slows down on the 25th day. *Bacillus subtilis* can tolerate carbendazim up to a concentration of 50000 ppm[92]. *Pseudomonas sp* utilizes carbendazim and its metabolites completely. Within 3 days, the 10ppm concentration of fungicide is utilized by the isolate and converted into carbon-di-oxide [93]**.** The pesticide contaminated soil isolate *Rhodococcus erythropolis* effectively degrades around 99% of 1000ppm carbendazim within three days. *Rhodococcus sp*, utilizes and converts it into benzimidazole and 2-aminobenzimidazole[94]. The bacteria *Ralstonia sp* degrades carbendazim effectively in the presence of yeast extract. It stimulates the degradation process by around 95% at the concentration of 500ppm. Some other bacteria reported for carbendazim degradation are *Bacillus pumilus, Burkholderia cepacia, Pseudomonas fluorescens, Sphingomonas paucimobilis, Aeromonas hydrophila* [95-97].

Bacillus subtilis and *Pseudomonas fluorescens* are able to tolerate mancozeb up to 600 and 1600ppm respectively. They are also able to tolerate other fungicides such as captan, carbendazim, and thiram [98]. Thiophanate methyl is a benzimidazole fungicide that can be effectively utilized by the strain *Bacillus sp*, and *Enterobacter sp*. They utilize around 77 and 60% within 16days of incubation at the concentration of 50ppm respectively [99].
Triazole group of fungicide propiconazole has been degraded by the field isolate *Pseudomonas aeruginosa*. 8 μg/L of fungicide was utilized as a sole carbon source and the gene responsible for the degradation process were identified has CYP450 [100]. 88% of propiconazole degradation was reported by the bacterium *Burkholderia sp* within 4 days of incubation [101].

Phthalimide class of fungicide, captan, was degraded by polyurethane-foam immobilized cells of *Bacillus circulans*. Complete degradation of 0.2% captan was achieved within three days of incubation and it has an ability to degrade captan at a wide environmental range. The field isolate *Bacillus circulans* utilize captan has a sole carbon source and without losing the degradation ability, it has been significantly stable to degrade the fungicide in around 120days. When compared to freely suspended cells, the immobilized cells showed rapid degradation of captan even at higher concentrations [102]. *Bacillus circulans* completely mineralized 1g/L of captan and it has been reported that the bacteria is able to utilize other compounds produced during the degradation process. Complete utilization of metabolites was reported within 6 days of incubation [103].

4. Conclusion
Nano formulations are assuming importance as excellent agrochemicals. They are able to achieve effective pest control with lower concentrations of low activity ingredients than traditional formulations. They prevent pre-mature degradation of such ingredients and can deliver solvent free pesticides. They improve the bio efficacy of pesticides and have a good shelf life. Simultaneously, specific bacterial species are able to degrade the unspent active ingredients in the environment by using them as energy sources and facilitate bioremediation for environmental protection.

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