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ON

Application of Nanomaterials in Plant Protection

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ABSTRACT

Pesticides are biological or chemical agents that protect plants from various pests including insects and phytopathogens. But due to poor dispensability and application drift, most of the pesticides do not control their projected target. Excessive use of plant protection agents incurs more cost for crop production and responsible for environmental pollution. Various nanoformulations that have higher insecticidal activity, controlled released as well as targeted delivery properties were discussed in this review. Herein, bioefficacy of nano-based insecticide and its bulk commercial formulation against destructive crop pests were reviewed. In case of nano-based deltamethrin, at the recommended commercial formulation concentration, mean mortality percentage of *Trialeurodes vaporariorum* (a greenhouse whitefly) was found more than double compared to the mean mortality obtained from its commercial analogue. The result indicated higher insecticidal activity of nano based formulation. Additionally, the photocatalytic property played a vital role for degradation of pesticide residue following controlled delivery and target oriented manner. As per findings from the reviewed articles, nano-carrier enhanced >35 % larval mortality due to its drift resistance and targeted release property. Furthermore, nanoparticles enhanced solubility as well as dispersion stability that exhibited higher pest controls efficiency than bulk formulations. However, sustainable and constant release as well as prolonged persistence time of nanomaterials is considered as vital importance for its practical application. Finally, considering its lower dose, optimized release capability, targeted delivery and enhanced bioactivity, it is expected that nanopesticides would be considered as environmentally sustainable and brilliant pest control agent for green agriculture in future.

Key words: Nanoformulations, Nanopesticides, Controlled release, Bioefficacy, Targeted delivery

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CHAPTER I

INTRODUCTION

World population is growing rapidly and it has increased a momentum over time with a plenty of public funding and government policies to ensure food as well as nutritional security for the world community. In field condition, crops are attacked by diversified enemies including insects, weeds, nematodes and phytopathogens (Kitherian, 2017). Pesticides are considering as an important inputs for increasing crop productivity and protection crops from biological disasters (Zhao *et al.,* 2017). According to the statistics of FAO (Food and Agriculture Organization of the United Nations), approximately 30% of total output of agricultural products all over the world has restored by controlling pests and pathogens (FAO, 2007; Lamberth *et al.,* 2013). As a plant protection input, the annual use of pesticides have reached 4.6 million tons worldwide. About 90% of the pesticide run off into the environment and residue in agricultural products as well as reallocate in ecological cycle during application (Malaj *et al.,* 2014; Köhler and Triebskorn, 2013). Inefficient use of pesticides poses a series of ecological problems, such as development of pesticide resistance, non-point pollution, water eutrophication, degradation of soil, bioaccumulation in food chain and a huge loss of biodiversity (Zhao *et al.,* 2017). Most of the active ingredients (AIs) of pesticide are water insoluble organic compounds which are added with carrier material such as solvent, emulsifier, dispersant and other auxiliary ingredients as well as processed into a suitable formulation in order to facilitate the spray application at the field level (Ghormade *et al.,* 2011). The loss and decomposition rate of pesticide on crop foliar is typically more than 99% which are caused by run-off, spray drift and rolling down at the time of field application (Nuruzzaman *et al.,* 2016; Song *et al.,* 2017; Zhao *et al.,* 2017).

The nanotechnology has been emerged as a promising high efficient technology to control pest and diseases in crop production. Over the years, numerous scientific reports and patents have been published in the field of nanotechnology in agriculture (Parisi *et al.,* 2015). Nontechnology deals with the matter at nano scale (1-100 nm) dimensions. These materials when reduced to the nano scale show some properties which are different from bulk materials, enabling unique applications (Elizabath *et al.,* 2019). However, the simultaneously colloidal particulate at nano size dimensions of (10 to 1000 nm) can be considered as nanoparticles for application in agriculture and related disciplines (Nakache *et al,.* 1999; US Department of Agriculture, 2002). In this case, nanopesticides represent an advanced and alternative method to overcome the limitations of currently used chemical pesticides. Pesticides developed according to nano based formulation technique are called nanopesticides. Nanopesticides are prepared either by very small particles of pesticidal active ingredients or some other nanostructured molecules with pesticidal properties. Nanopesticides can enhance the dispersion and wettability of agricultural formulations (i.e., reduction in organic solvent runoff) and unwanted pesticide movement (Bhattacharyya *et al.,* 2016). However, nano pesticides tend to show amazing pesticidal activities and are required in lower quantities for effective pest management thereby, reducing pesticide load on the environment (Kumar *et al.,* 2015; Saini *et al.*, 2014). According to Athanassiou *et al.* (2018), nanoformulations are like other common pesticide formulations, they aid in increasing the apparent solubility of a poorly soluble active ingredient or in releasing the active ingredient in a slow or targeted manner, thus protecting the active ingredient against premature degradation. Silver as a bulk material don't possess such antimicrobial properties but nano forms of silver serve as powerful antimicrobial agents. When combined with fluconazole disks and ketoconazole disks, silver nanoparticles show synergistic activity against various destructive phytopathogenic fungi such as *Phoma glomerata*, *Trichoderma* sp., *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus tamarii*, *Aspergillus versicolor*, *Macrophomina phaseolina* and *Penicillium* sp. (Jogee *et al.,* 2017). A large body of literature describes the beneficial effects of nanopesticides over traditional synthetic chemical pesticides. This study aimed to review current knowledge of nanopesticides and updates our understanding the potentials of this new technology in agriculture. The specific objectives of this seminar paper are as follows:

i) To describe the concept and properties of nanomaterials as pesticides;

ii) To illustrate the higher efficacies of the nanopesticides over synthetic chemical pesticides;

iii) To discuss action mechanisms of nanopesticides such as controlled release, higher affinity to the targeted plants and pests; and

iv) To demonstrate the maintenance of environmental sustainability by the application of nanopesticides in agriculture.

CHAPTER II

MATERIALS AND METHODS

This paper is absolutely a review paper and all of the information has been collected from the secondary sources. During the preparation of the manuscript, a systematic search was carried out from Google Scholar, Google Web Browser and Scopus by using key words “nanomaterials”, “nano based pesticide”, “ environmental sustainability”, “applications of nanomaterials in crop protection” and “nano-encapsulation” with no filters. According to their contents and year of publication, found literatures against these searches were further screened for inclusion. Mostly scholarly articles published during 2000-2020 were incorporated in this review study. In this study, 62 peer reviewed research articles were selected. After collecting all the available information, it has been presented as per the objectives of this review.

CHAPTER III

REVIEW OF FINDINGS

3.1 The concept and properties of nanomaterials as pesticides

Nanotechnology includes manufacture, manipulation and application of ultra-structured materials that have at least one size dimension started from 1-100 nm (Auffan *et al.*, 2009) and within this length scale it possess some unique characteristics such as qualities that dependent on size, unique optical properties as well as high surface-to-volume ratio (Ghormade *et al.*, 2011). However, as a broader definition, particles with size dimension smaller than 500 nm that exhibit novel properties is accepted as nano-based pesticide formulations (Kah and Hofmann, 2014). A broad variety of natural or synthesized materials such as metal, metal oxides, non-metal oxides, carbon, silicates, ceramics, clays, layered double hydroxides, polymers, lipids, dendrimers, proteins, quantum dots, and so on have been used for production of pesticide nanoformulations, (Niemeyer *et al.*, 2001; Oskam, 2006; Perez-de-Luque and Rubiales, 2009; Gogos *et al.*, 2012; Khot *et al.*, 2012). Some nano materials which have been formulated for plant protection are described in (Table 1). Nano-pesticides are usually developed by two pathways, 1) directly processing into nanoparticles (nanosized pesticides), and 2) loading pesticides with nano-carriers in delivery systems (Ghormade *et al.*, 2011). In nano-carrier systems, pesticides are loaded through encapsulation inside the nanoparticulate polymeric shell, absorption onto the nanoparticle surface, attachment on the nanoparticle core via ligands, or entrapment within the polymeric matrix (Figure 1).

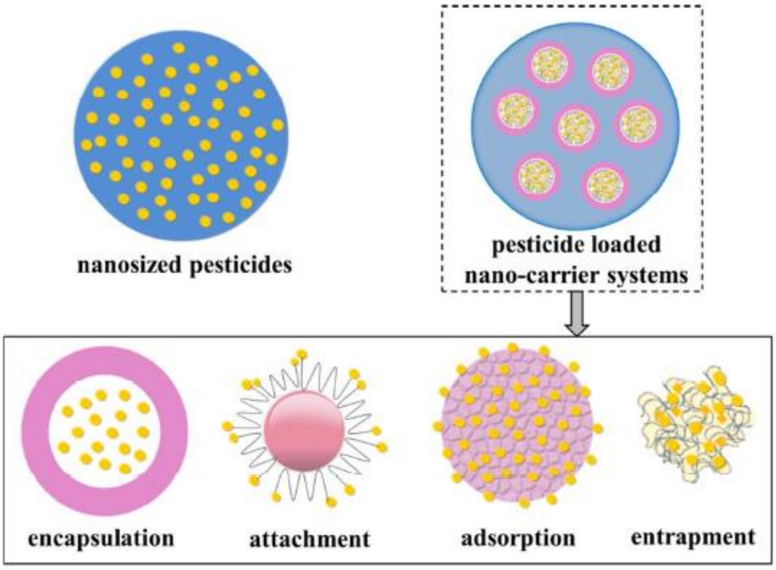


Figure 1. Schematic diagram of nano-based pesticide formulation (Zhao *et al.*, 2017).

Table 1. Some nanoparticles that show pesticidal effects for plant protection

Sl No.	**Nanomaterials**	**Use**	**Concentration**	**Size of nano particle**	**Action/Outcome**	**References**
1.	Ag NPs	Fungicide	400 µg/ml	10 nm to 32 nm	Potent antifungal activities against plant pathogenic fungi *Macrophomina phaseolina* (Charcoal rot), *Alternaria alternate* (Leaf spot) and *Fusarium oxysporum* (Fusarium wilt)	Bahrami-Teimoori *et al.*, 2017
2.	AgNPs	Fungicide	-	53 ± 20 nm (average diameter)	Ag-Dopa-CP samples showed excellent inhibition against the growth of the Wheat blast fungi as well. In addition, it has no visible phytotoxic effects on wheat plant.	Islam *et al.*, 2018
3.	Cu NPs	Fungicide	10 mg/L	13 nm (average)	$Cu_3(PO_4)_2 \cdot 3H_2O$ nanosheets significantly suppressed root fungal disease (58%) and increased yield of watermelon	Borgatta *et al.*, 2018
4.	ZnO/Nanocopper composite (ZnO-nCuSi)	Fungicide	0.22 kg/ha	ZnO (600-1100 nm); ZnO-nCuSi (irregular)	ZnO-nCuSi demonstrated strong in vitro antimicrobial properties against citrus phytopathogens and it was found effective in controlling citrus canker disease.	Young *et al.*, 2017
5.	Chitosan NPs	Fungicide	1000 ppm	180.9 nm (average)	Inhibited mycelia growth of *Fusarium graminearum*, a head blight pathogen of wheat.	Kheiri *et al.*, 2016
6.	Ag-doped hollow TiO_2	Fungicide	0.43 and 0.75 mg/plate respectively	-	Enhanced fungicidal activity under visible light exposure against *Fusarium solani* and *Venturia inaequalis.*	Boxi *et al.*, 2016
7.	Nano-Silicon (NSi)	Fungicide	1.5 and 3 mM	249 nm	NSi application increased the resistance of *Vicia faba* L. plants against *Botrytis fabae* infection through increasing the defensive compounds (such as proline and phenols) and enhancing the activity of defense enzymes.	Hasan *et al.*, 2020
8.	MgO NPs	Fungicide	100 ppm	-	MgO NPs showed potent antifungal activity against phytopathogenic *F. oxysporum, Sclerotium*	El-Argawy *et al.*, 2017

					rolfsii and *R. solani*	
Sl No.	**Nanomaterials**	**Use**	**Concentra-tion**	**Size of nano particle**	**Action/Outcome**	**References**
9.	Nitrogen-doped carbon nanohorn (NCNH)	Fungicide	100 µg/mL	50–60 nm	The growth of the phytopathogen *Rhizoctonia solani* was suppressed significantly.	Dharni *et al.*, 2015
10..	Silica nanoparticles	Insecticide	500 and 1000 ppm	12 nm	The SNPs reduced infestation of stored pulse beetle, *Callosobruchus maculatus* on seeds of *Cajanus cajan*, *Macrotyloma uniflorum*, *Vigna mungo*, *Vigna radiata*, *Cicer arietinum*, and *Vigna unguiculata*.	Arumugam *et al.*, 2016
11.	Citrus peel essential oil nanoformulations	Insecticide	23.10 mg/mL	50 nm	The nanoformulation of these natural compounds successfully used in integrated pest management programs for controlling *Tuta absoluta.*	Campolo *et al.*, 2017
12.	Camphor essential oil (EO) nanoemulsion	Insecticide	181.49 µg/g	-	The camphor EO nanoemulsion protected grains against *Sitophilus granarius* and other insects.	Mossa *et al.*, 2017
13.	Silver—*Avicennia marina*	Insecticide	50mg/ml	15-25 nm	Biosynthesized silver and lead nanoparticles using aqueous extract of *Avicennia marina* showed potent antibacterial activity against various bacterial phytopathogens.	Sankar and Abideen, 2015
14.	Mesoporous silica nanoparticles	Herbicide	-	423 nm (average)	The mesoporous silica nanoparticles had high herbicide (2,4-dichlorophenoxy acetic acid) loading and good bioactivity on targeted plant without any adverse effects on nontargeted plants.	Cao *et al.*, 2017
15.	Isocyanate-functionalized silica cross-linked PEI	Herbicide	-	-	It showed good pendimethalin herbicide loading efficiency (~30% w/w), protection against photo- and thermal degradation, and urease-controlled drug release profile.	Liang *et al.*, 2017

NPs: Nanoparticles; Ag NPs: Silver nanoparticles; NSi; Nano-silicon; SNPs: Silica nanoparticles; PEI: Polyethylenimine

3.2 The higher efficacy of the nanopesticides over synthetic chemical pesticides

Smaller pesticide particles can significantly increase their water-dispersion, targeting exposure and insecticidal action due to reduced particle size and higher surface area. Moreover, pesticide nanoformulations increase adhesion and deposition of droplets on the leaves through modifying the leaf-affinity (as shown in Figure 2) (Zhao *et al.*, 2017)

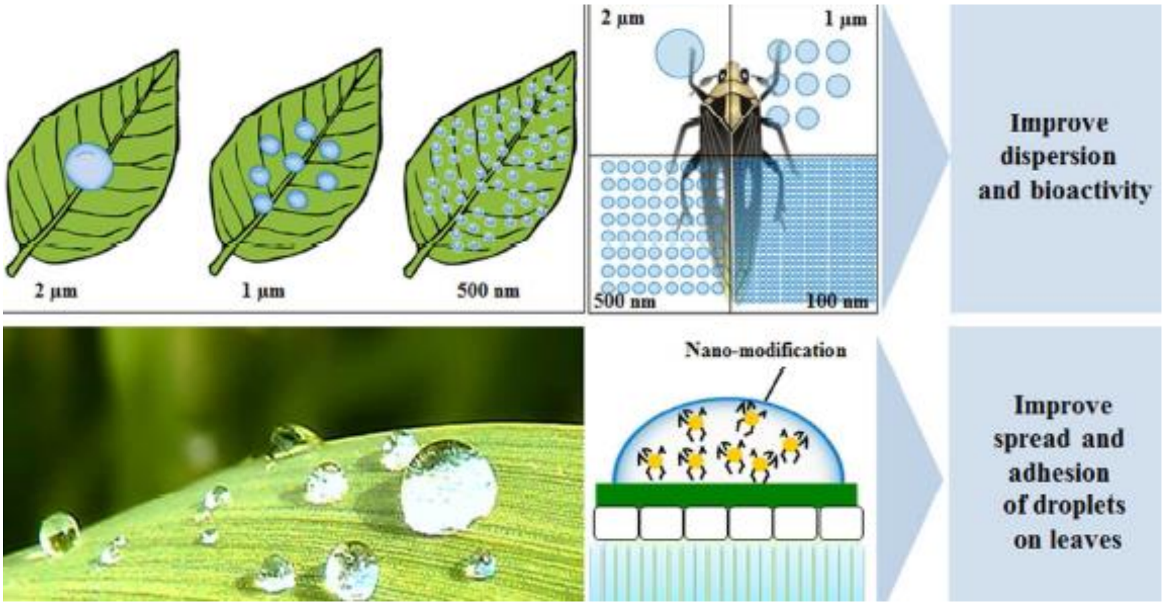


Figure 2. Size-down of pesticides increase bioavailability and efficiency (Zhao *et al.*, 2017).

A number of nano based formulations of pesticides have been developed for plant protection like imidacloprid (Chhipa, 2017), thiamethoxam (Wibowo *et al.*, 2014) and thiram (Fraceto *et al.*, 2016). The potential of nano-pesticides is the reduction of toxic impact of a conventional chemical formulation by reducing the rate of pesticide use (Nuruzzaman *et al*., 2016). For instance, an experiment was conducted by Shifa *et al.* (2019) to evaluate the bioefficacy of nano-formulation of deltamethrin (average particle size of 90 nm) and its conventional commercial analogue under *in vitro* conditions against greenhouse whitefly, *Trialeurodes vaporariorum* through contact or residual bioassay. Both the insecticide treatments were tested at a range of dose concentrations starting from the recommended concentration of the commercial formulation (0.01%) The bioassay of commercial and nano-formulation of deltamethrin revealed the mortalities in both cases and this mortality data was transformed to percent mortality which was afterwards changed to corrected percent mortality (Table 2).

Table 2. Comparison of the corrected percent mortality of *Trialeurodes vaporariorum* caused by commercial formulation and nano-formulation of deltamethrin at 0.01 percent dose concentration (Reconstructed from Shifa *et al.*, 2019)

Chemical	**Concentration (%)**	**Treatment code**	**Corrected percent mortality**	**Relative fold (in terms of mortality)**
Deltamethrin- Commercial formulation (D)	0.01 (Recommended)	D1	38.77*	1
Nano-deltamethrin (ND)	0.01	ND1	82.95*	2.13

* Each figure indicates a mean of five replications.

The corrected percent mortalities were compared and the comparisons have been shown in the Table 2. It was established that the nano-formulation of deltamethrin caused two times more mortality than the commercial formulation of deltamethrin at the same concentration of 0.01 percent. So, nano-deltamethrin to be more potent than the commercial formulation at the dose of 0.01 percent. Besides, bioassay with lower doses of nano-deltamethrin put forward the corrected mortality percentages which are plotted in Figure 3. Nine lower dose concentrations were tested (0.009, 0.008, 0.007, 0.006, 0.005, 0.004, 0.003, 0.002 and 0.001) which caused 77.32%, 72.00%, 64.01%, 58.32%, 55.68%, 49.36%, 44.21%, 39.87% and 37.20% mean mortality respectively.

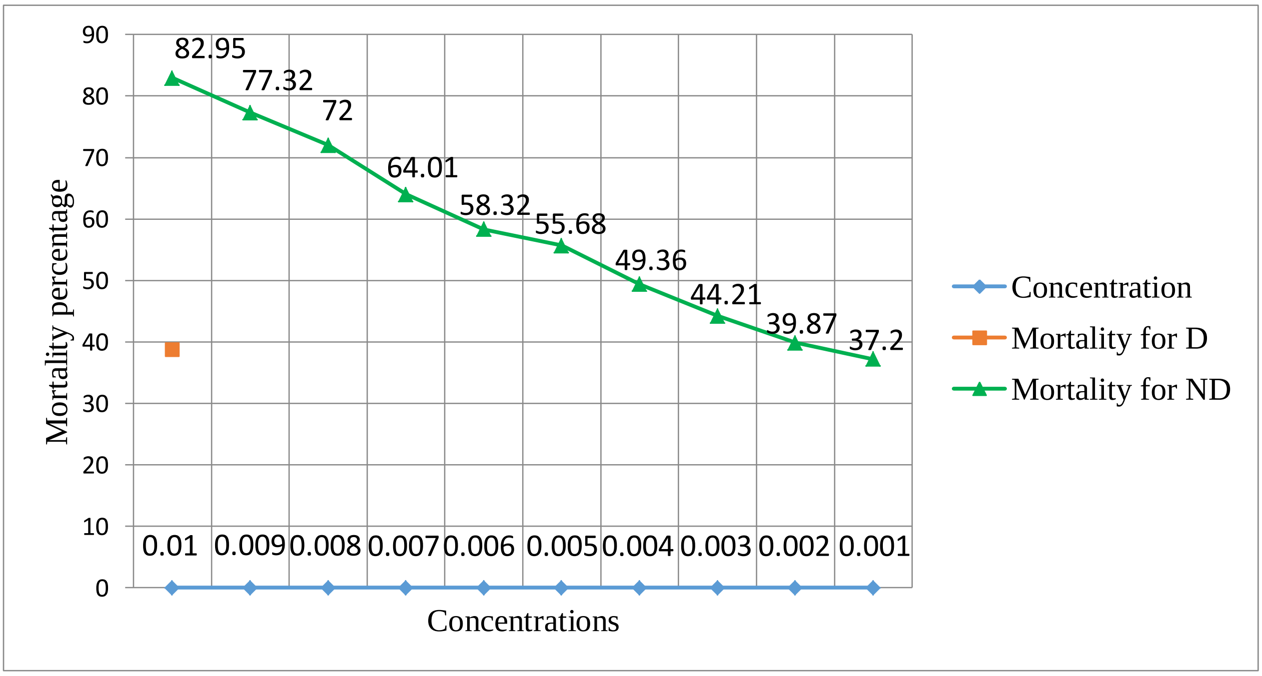


Figure 3. Comparison of the corrected percent mortalities of nano-deltamethrin (ND) and commercial deltamethrin (D) @ 0.01 percent (Redrawn from Shifa *et al.*, 2019).

It was thus established that the corrected mortality percentage of 38.77% caused by the commercial formulation of deltamethrin at the recommended dose (0.01%) was equated by the equivalent mortality response range of 37.20% to 39.87% in case of nano-deltamethrin, caused at very low concentrations of 0.001% to 0.002%. At the dose concentration 0.01 percent (3571.42 µl/ L) mean mortality of 82.95% was obtained in case of nano-formulation which was very high as compared to the mean mortality of 38.77% caused by its commercial analogue. Amongst all the lower concentrations tested, the concentrations between 0.001 to 0.002 percent (35.71 to 71.42 µl/L) caused approximately the same required response mortality in *T. vaporariorum* i.e. 37.20 to 39.87 percent. This clearly indicated superior insecticidal activity of nano-formulation and therefore, lower doses for nano-formulation were tested to establish those dose concentrations which invoked equivalent mortality response against *T. vaporariorum* as the commercial formulation. Therefore, decreasing the recommended concentration (0.01%) of commercial formulation by any factor between 5 to 10 yielded the concentration of nano deltamethrin (0.001% to 0.002%) which induced almost equivalent quantitative mortality as recommended concentration of deltamethrin (Table 3).

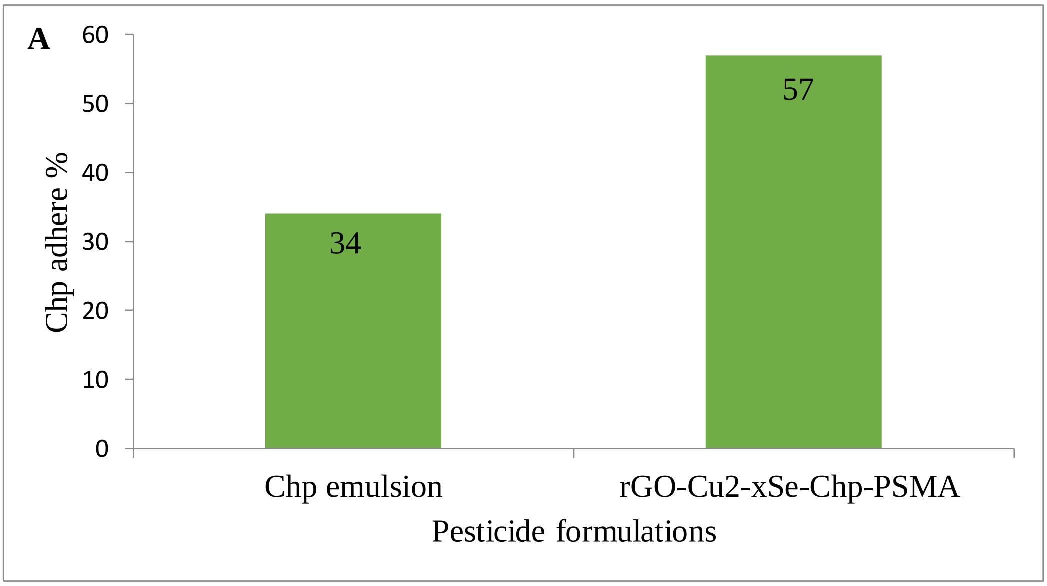
Table 3**.** Relative concentration fold of nano-deltamethrin with respect to commercial formulation at equivalent corrected percent mortality (adapted from Shifa *et al.,* 2019)

Pesticide	**Conc. (%)**	**Corrected percent mortality**	**Relative fold (in terms of concentration)**
Deltamethrin-(Commercial formulation)- D	0.01	38.77	1
Nanodeltamethrin-ND	0.001-0.002	37.20-39.87	5-10

The result is supported by the developed nano formulation of the Mancozeb offered dose reduction and was found to increase efficacy for a longer period as nano formulations were found to be more active than commercial formulations. Through field observation, Majumder *et al.* (2020) observed that a single application of 60 g a.i./ha was effective in comparison to its commercial formulation where 650 g a.i./ha is recommended. Therefore, there has been almost 10 times reduction of chemical use and cost. Similar results were reports on controlled release of nano formulations for acephate against mustard aphids (Kumar *et al.,* 2010) as well as carbofuran and imidacloprid against potato aphid (Kumar, 2011). So, the investigations were quite vital and could be considered as novel techniques for effective pest management.

3.3 Action mechanisms of nanopesticides such as controlled release, higher affinity to the targeted plants and pests

Agricultural products are destroyed by a range of pests during the production and storage. In spite of usefulness and acceptance of pesticides in controlling a various pests, they can cause damage to human health or property from their contact and residues in food materials as well as water bodies. Polymers, in the form of micro-nanocarriers such as beads, granules and gels are vital materials for the development of controlled release formulations (CRF) of pesticides which provide slow and controlled release of pesticides (Mishra *et al.*, 2020). However, reduced graphene oxide (GO) was used by Sharma *et al.* (2017) for controlled release and targeted pesticide delivery due to its ability to bind drug with the appearance of native larval gut condition. The graphene oxide is decorated with copper selenide which is able to show photocatalytic characteristics. In case of pesticide delivery, the photocatalytic property gives assistance in programmed pesticide residue degradation. This nano-carrier shows resistance to drift in addition to targeted release, which enhance >35 % larval mortality. To compare the ability of rGO-Cu_2-xSe-chp-PSMA (Poly styrene-*alt*-maleic acid) to overcome the drift loss by runoff, the material was compared with the control chlorpyrifos (chp) emulsion spray. The cauliflower leaf sprayed with rGO-Cu2-xSe-chp-PSMA and chlorpyrifos emulsion was allowed to just dry, following which exposed to aqueous washing with sprayer to simulate rain (with same volume of water and spraying pressure).



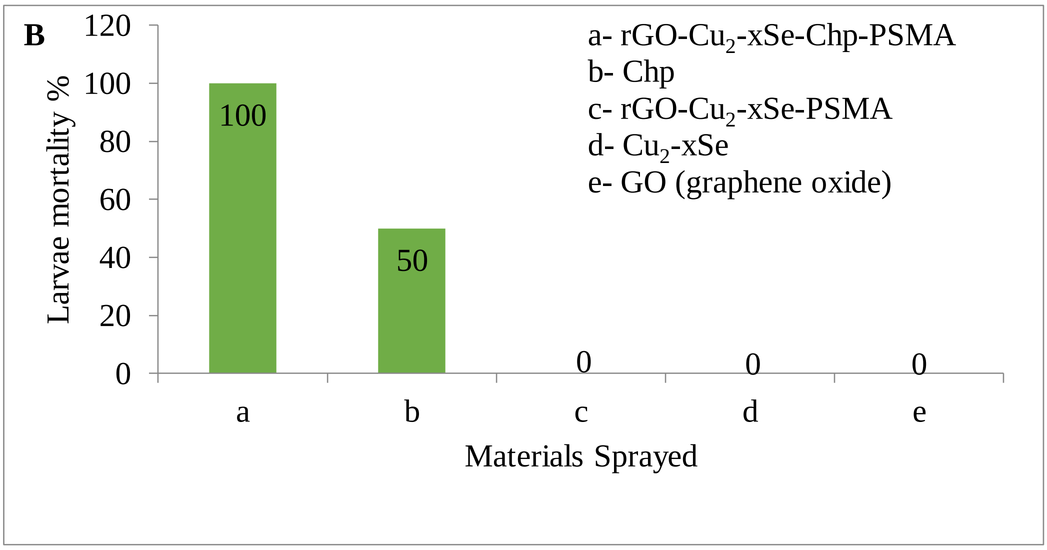


Figure 4. Efficiency of rGO-Cu_2-xSe-Chp-PSMA in resistance to runoff and pest mortality in comparison to chlorpyrifos (chp) emulsion. (A) Percent chlorpyrifos adhered on leaf, sprayed in the form of rGO-Cu_2-xSe-Chp-PSMA and chlorpyrifos emulsion. (B) Mortality percent of the pest after 72 hours of feeding the leaf sprayed with 10 µg of chlorpyrifos in the treatment forms followed by simulated rain washing (material toxicity is negated by maintaining material control), a) rGO-Cu_2-xSe-Chp-PSMA, b) Chp emulsion, c) rGO-Cu_2-xSe-PSMA, d) Cu_2-xSe, e) GO. Results in figures 4A and 4B are expressed as Mean±SEM. Statistical analysis was performed using student t-test (Redrawn from Sharma *et al*., 2017).

The composite rGO-Cu_2-xSe-chp-PSMA shows significantly enhanced adhesion of chlorpyrifos (57%), compared to the control chlorpyrifos emulsion spray (34%) (Figure 4A). This is happening due to the resistance of the GO based composite to aqueous runoff and ability of carbon to bind with organic surface. Another cause may be the unevenly layered lamellar surface and the protuberance caused on the GO with successive coating which may anchor on the pores in the leaf of a plant (Yang *et al*., 2008). In addition, sharp GO surface have the piercing effect in rGO-Cu_2-xSe-chp-PSMA composite may give extra backing to hold the pesticide particle against the water flow, related to the susceptible surfactant assisted emulsion (Nie *et al*., 2006). Finally, it is an obvious phenomenon that for any particles to roll out it should be curved hence this 2d material resist such drift. Finally, at the end of 72 h, the composite rGO-Cu2-xSe-chp-PSMA has been found to be 50% more effective than chlorpyrifos emulsion. The other materials such as control rGO-Cu_2-xSe-PSMA, rGO and Cu_2-xSe show no mortality in the observation period (Figure 4B). This ensures that the composite rGO-Cu_2-xSe-chp-PSMA can cause maximum pest control. This may be due to the ability of the composite to resist the runoff, enhanced drug acceptance and targeted pesticide delivery. Similar results were found by using controlled release (CR) nanoformulations of Mancozeb for the protection of tomato plant from early blight disease. This could be due to large entrapping of the chemical inside the developed formulations over commercial one and also reported nanoformulations were more effective than commercial formulations (Majumder *et al.,* 2020). On the other hand, in case of developed formulations, the micelles, formed by the aggregation of amphiphilic polymers, entrap the active ingredient and protect it from environmental and microbial degradation making active ingredient release optimum and for a longer duration than the commercial formulation. Comparable results have been described for carbofuran, b-cyfluthrin, imidacloprid, thiram and carbendazim (Loha *et al*., 2011; Kaushik *et al.,* 2013; Shakil *et al.,* 2010; Koli *et al.,* 2015 and Adak *et al.,* 2012). Nano based pesticide formulations have been reported to have better environmental stability, controlled release, targeted activity and physical stability. These materials can successfully defend the active ingredients from early degradation such as volatilization, photolysis, rapid evaporation, etc. (Kah *et al.,* 2014). Moreover, use of agro nanofungicides, to increase plant uptake and curtail the volatilization, leaching and runoff of fungicide act as strong antifungal agents in combating the *Ganoderma boninense* which is responsible for basal stem rot (BSR) disease of different plants. The results discovered that chitosan nanoparticles have the capacity to act as dual manners of action. One is itself as a biocide and another as a nanocarrier for the prevailing fungicide formulations. Additionally, the particle size of the chitosan-based agro nanofungicides plays a critical role in defeating and controlling the disease causing phytopathogenic organisms. The synergistic outcome of the chitosan-hexaconazole-dazomet nanoparticles as a double-fungicide system displayed the highest disease reduction of infected seedlings with 74.5 % than the untreated one (Maluin *et al.*, 2020).

3.4 Maintenance of environmental sustainability by the application of nanopesticides in agriculture

Eco friendly pesticide delivery systems have created wide attention in recent years for sustainable agricultural development. For instance, carboxymethyl chitosan modified carbon nanoparticles (CMC@CNP) as the carrier for emamectin benzoate (EB, a widely used insecticide) was reported by Song *et al.* (2019). This is a multifunctional nanoplatform and its sustainable antipest activity was also investigated. EB was loaded on CMC@CNP nanocarrier and the EB@CMC@CNP nanoformulation exhibited enhanced solubility and dispersion stability in aqueous solution. Different from such as free EB and EB@CMC@CNP exhibited significantly enhanced anti-UV property which confirmed its antipest activity.

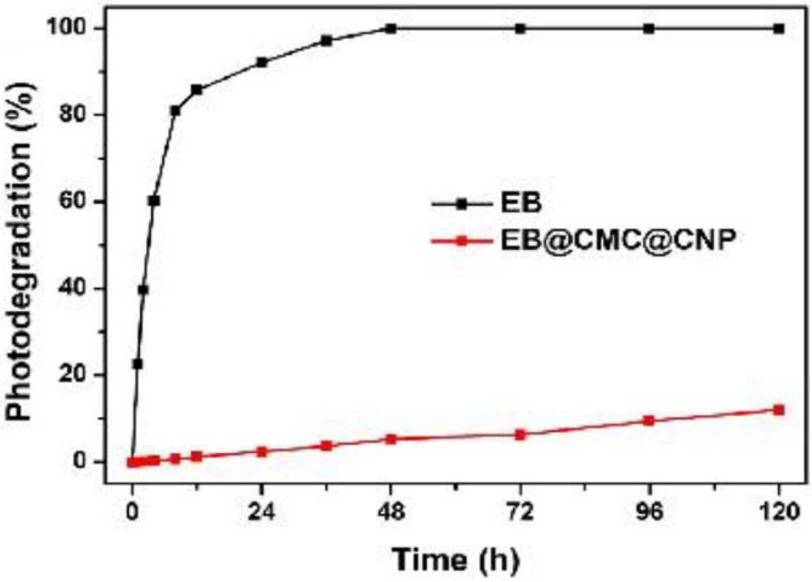


Figure 5. Degradation rate of free EB and EB@CMC@CNP, under the irradiation of 254 nm UV light, 36 W, 20 cm (Modified from Song *et al.,* 2019).

3.4.1 *Anti-UV Light Performance of emamectin benzoate*

EB is a high-efficiency pesticide but the poor anti-UV light property has greatly limited its application. The previous reports have pointed out the half-life of EB is just several hours (Guo *et al.,* 2015). Therefore, in practical application, the farmers have to spray traditional EB formulations persistently to ensure their antipest activity. Considering the high absorbance of CNP in UV region, it is assumed that it can protect EB from degradation via absorbing the high-energy UV light (Tu *et al.,* 2014). As shown in Figure 5, the free EB degraded rapidly under the irradiation of UV light (254 nm, 36 W, height 20 cm). During the first 4 hours, about 60.33% EB was lost in case of free EB. On the contrast, with the protection of CMC@CNP nanocarrier, the EB degradation ratio is only 12.03% at 120 hours post irradiation. The above results surely confirmed that CMC@NPs is a brilliant nanocarrier for enhancing the UV-resistance performance of EB. The significantly prolonged half-life of EB@CMC@CNP has great value in practice, including reducing the dosage and spraying times of pesticide as well as improved antipest activity. Therefore, EB@CMC@CNP exhibited superior pest control performance than free EB. By considering its low cost, easy preparation technique and enhanced bioactivity, CMC@CNP would be considered as a brilliant pest control agent for green agriculture in future (Song *et al.*, 2019). This result is supported by the development of a nanoencapsulated pesticide formulation becasuse it is highly stable and easily permeable with slow releasing properties as well as enhanced solubility. These characteristics are mainly achieved due to protecting capacity of encapsulated active ingredients from premature degradation which increases their pest control efficacy for a longer period. So, the dosage of pesticides could be reduced by applying nanoencapsulation technique for pesticide formulation which is free from human exposure and environment friendly for crop protection (Nuruzzaman *et al.*, 2016).

3.4.2 *Beneficial effect of controlled release formulation as nano pesticide*

The world is struggling hard towards sustainable agricultural practices for a better tomorrow. Herein, one of the primary focuses is effective and environment friendly pest management for improved crop productivity. Notwithstanding, newer and effective chemicals as pesticides, there are still substantial crop losses are happening. If this loss could be tackled, it would alleviate indiscriminate and excessive use of chemical pesticides. Now, it is proved by the scientific community that the total amounts of sprayed pesticides are not being utilized by the crops completely. A significant percentage remains unused due to various limiting factors such as leaching and bioconversion. These are creating adverse consequences on human health and ecosystems as well (Figure 6).

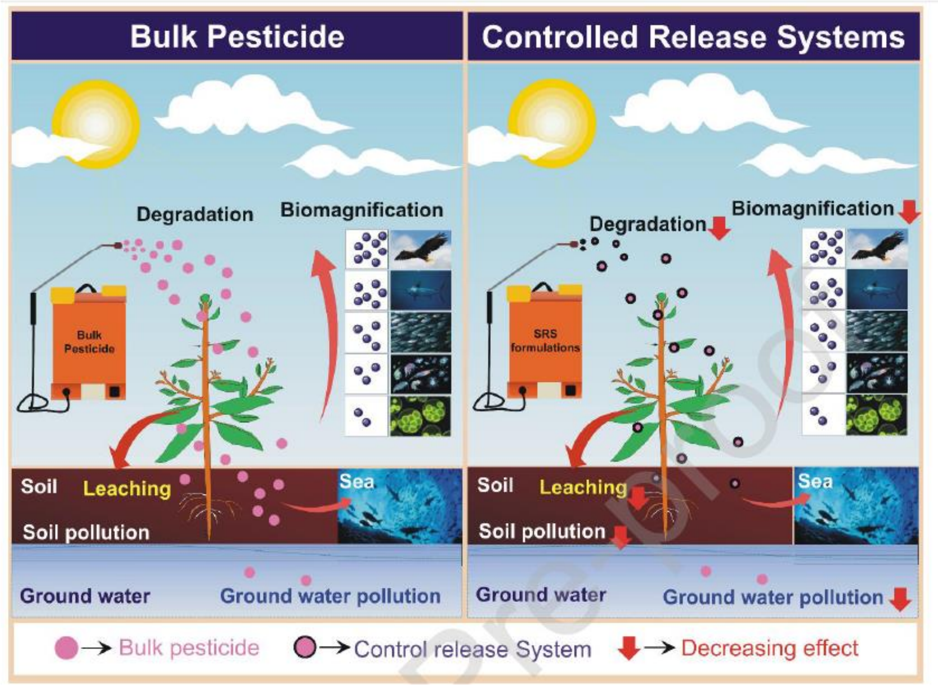


Figure 6. Schematic representation of advantages of CRSs over conventional pesticides use (Singh *et al.*, 2019).

So, controlled release systems (CRS) of pesticides formulation could be the newer and innovative strategies which are already showing promise and a viable approach. Therefore, the development of non-toxic and promising pesticide delivery systems are time demanding techniques for increasing global food production while reducing the negative environmental impacts to ecosystem (Grillo *et al.,* 2016).

3.4.3 *Catalytic degradation and bio-safety of pesticide residues*

Nano-based pesticide formulation can accelerate the catalytic degradation of toxic residues and reduce the pesticide residues in environment by introducing bio-degradable material carriers and photocatalysts (Caboni *et al.*, 2003).

Figure 7. Catalytic degradation and bio-safety of pesticide residues

Therefore, nano-based pesticide formulations have many advantages over the conventional equivalents such as high efficiency, environment friendliness, high-targeting delivery and smart controlled release. Due to the technological advancement, large scale applications of nanopesticides in crop production have just become possible

CHAPTER IV

CONCLUSIONS

Introduction of nanotechnology and nano-particle engineering have provided breakthroughs in the field of agriculture as well as the agro-chemical industry. It is quite obvious that nano-pesticides provide higher efficiency and target specificity in pest control compared to the traditional chemical pesticides. As losses of nanopesticides are very low, application of these novel technology significantly reduce the environmental pollution due to pest control. Therefore, the impacts of nanopesticide on non-targeted organisms, human health, biodiversity and environment would be very low compared with its conventional one. In fact, the higher efficacy of the developed formulations for a longer duration has been due to slow release of the formulation. A large number of nanopesticides have already been tested in the field conditions that showed higher performances compared to the synthetic chemical pesticides. For example, rGO-Cu_2-xSe composite was able to hold 40 % (w/w) pesticide and stay as the reservoir in the leaf without drift loss. This pesticide was readily accessible for the larva due to its physio-chemical changes. Thus, the composite rGO-Cu_2-xSe has demonstrated targeted and effective delivery of pesticide. Further, the carrier has the capacity to destroy the pesticide after significant pest control stage. Similarly, a nanocarrier has been developed based on CMC (carboxymethyl chitosan) modified CNP (carbon nanoparticles) for successful pesticide delivery and pest control. EB is consided as a typical hydrophobic pesticide which exhibits poor stability under UV-light and burst release properties, was loaded on CMC@CNP through simple physisorption process. The prepared EB@CMC@CNP presents excellent solubility and stability in aqueous solution, which has significant importance for the dispersion and application of pesticide. Moreover, benefiting from the high UV light absorption of CNP, the stability of EB improves a lot, with a remarkable prolonged half-life than free EB. Based on the above improved properties, EB@ CMC@CNP exhibits satisfactory antipest activity to *Mythimna separata*. Besides, the long-term pest control experiment solidly verifies the improved persistence of EB@CMC@CNP compared to the free EB. In consideration of the simple preparation, excellent antipest activity, and free of toxic organic solvent as well as additives, the CMC@CNP-based pesticide delivery system has a bright future in plant control and sustainable agriculture. Therefore, inclusion of nanopesticide for plant protection can be termed as the emergence of new era of pesticides in agriculture.

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