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Trending nanoformulated pesticides: A review

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ABSTRACT

Nano-technological advancements are embracing the field of agriculture pesticides, where its applications are in infancy. Conventional pesticide formulations suffer many problems making their applications less economical and more hazardous. The technological advancement pertaining to controlled release of pesticides is signified with advantages of prevention from degradation, volatilization and enhanced bio-application outcomes. Various degradable polymers have been explored for trapping the active ingredients to make formulation of nano sizes, proving multiple benefits of their usage. This review provides an insight into the various methods and materials explored at laboratory or commercial levels in the recent times to advocate the future research and use.

Key words: Encapsulation, Nano-emulsions, Nano-formulations, Nano-gels, Pesticides

The increasing population has led to an increase in demand for food, and to meet it, there is a need for better protection of agricultural crops from infestation. Chemical control strategies play a foremost role and the market is over-flooding with the range of pesticides that decrease the infestation and increase crop production. But commonly used formulations of agrochemicals were found to contaminate the environment, particularly in the case of intensive cropping. The conventional formulations involve the mixing of active ingredient with other inert materials for their nontoxic, convenient, and additional accurate handling for effective application in the field. Since, the immediate release of active ingredient which is the main drawback associated with these formulations are associated with quick loss of these chemicals by natural, photolytic, hydrolytic and microbial degradations. Additional loss by evaporation, volatilization and leaching results in decrease in active agent, below the minimum effective concentration required to maintain the biocidal efficacy. In addition, their excess use, non-target attack and existence of resistance against them is posturing hazardous effects on human as well as environment (Damalas and Eleftherohorinos 2011, Roy *et al.* 2014). Sustainable agriculture demands eco-friendly approaches which is the key focus of the agrochemical industry in present era (Savary *et al.* 2006, Yusoff *et al.* 2016).

Identifying novel active ingredients and improving the delivery system of existing pesticides are main routes to overcome the problem. Among the two, exploration of the delivery systems for slow and sustained release of agrochemicals is considered to be a better and easy solution with greater interest to environmental scientists. Various formulations have been developed that may modify performance of active compound with less impact on environment. Further refining is answered by nano-technological applications which seems to provide an alternative by developing nano-delivery systems in the form of so-called "nano-agrochemicals" (Ragaei and Sabry 2014, Nuruzzaman *et al.* 2016). These nano-formulated pesticides have many influential properties as better solubility, stability, controlled release and targeted delivery of the active ingredients.The technique had brought a revolution in current agricultural practices, with an improvement in both the quality and quantity of yields (Sekhon 2014, Kah 2015, Das *et al.* 2014).

Many of the polymer- or non-polymer-based approaches with exclusive properties of low toxicity, biodegradability, biocompatibility and simple preparation processes are being employed for improving the agrochemical formulations (Zhao *et al.* 2017). The method seems to be an intelligent design of the ideas that may promote the development of more sustainable agrochemicals. So, the present review is encompassing the nano explorations of agrochemical nanoformulations facilitated *via* eco-friendly polymers for slow and control pesticidal delivery mechanism along with other imported related inputs. These nanoformulations are classified as: Nano-encapsulation, Nano-emulsions, Nano-gels, Other important inputs.

Nano-encapsulation

Nano-formulations predominantly involved the technique of nano-encapsulation as a controlled delivery system for pesticides. Various materials have been explored for encapsulating and for carrying the pesticide active ingredient. Most common among the involved strategies

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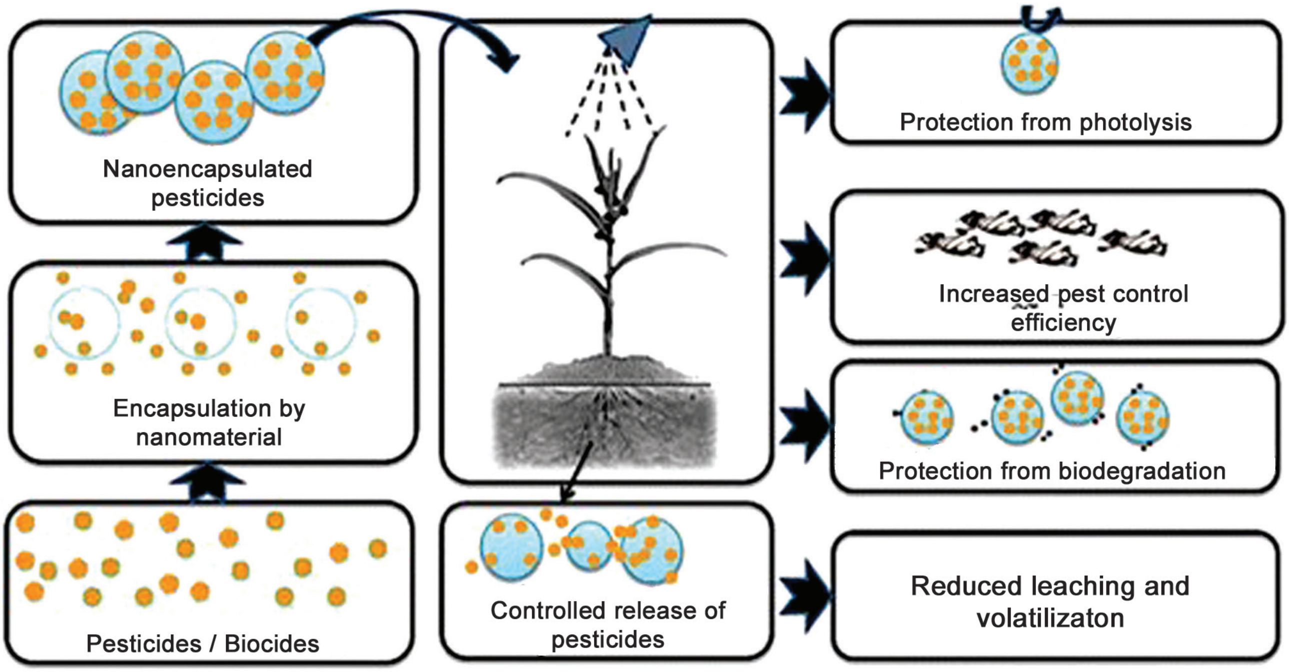

Fig 1 Mechanism of action followed by nano-encapsulated pesticides.

is the use of polymer-based nano-encapsulation, providing multi benefits, viz. protection from photolysis, increased efficiency, protection from biodegredataion with reduction in leaching and volatilization. Polysaccharides (e.g. starch, chitosan, alginates) and polyesters (e.g. poly-ε-caprolactone, polyethylene glycol) of biodegradable and biocompatible nature were well explored for synthesizing nano-pesticides. The common mechanism of action followed by the nano-encapsulated pesticides is represented by Fig 1 (Nuruzzaman *et al.* 2016).

Polysaccharides based nanoformulations

Chitosan was the most explored eco-friendly material that was modified by Lao and Coworkers to amphiphilic-N-(octadecanol-1-glycidyl ether)-O-sulfate chitosan (NOSCS) and used as carrier for herbal insecticide rotenone. The releasing tendency of the polymer in an appropriate way makes it almost 10 times more efficient in comparison to the chemical compound without nano-encapsulation (Lao *et al.* 2010).

In another study, an amphiphilic chitosan derivative (*N,N*-dimethyl hexadecyl carboxymethyl chitosan (DCMC) was used as a carrier agent for rotenone. It had an efficiency of 95% with 100:1 weight ratio and 99% rotenone release capacity in 48 h, making it an effective carrier agent for pesticide formulations (Kamari *et al.* 2016a). Oleoyl-carboxymethyl chitosan used for encapsulating rotenone reported to have efficiency and loading capacity of 97% for 100:1 w/w ratio of the carrier and active ingredient. The release capacity of oleoyl-carboxymethyl chitosan was 96% within 50 h with its feasibility as a novel water-solubilising agent (Kamari *et al.* 2016b).

6-*O*-Carboxymethylated chitosan was explored by Feng and Peng (2012) to encapsulate herbal insecticide azadirachtin. The controlled release nanoparticles had about 50% of loading efficiency. Comparison of the results of simple azadirachtin and the encapsulated formulation indicated that all content of control samples were lost in 5 days of sun exposure, whereas a minimal residual concentration was detected throughout the 12 days of the experiment in latter one. The developed formulation was, thus, considered to be more effective at controlling the degradation rate and the release mechanism of the botanical insecticide.

Carboxymethyl chitosan (CMCS) in aqueous solution was mixed with azidobenzaldehyde (Az) to produce an amphiphilic bio-copolymer to encapsulate methomyl. The system self-assembles into nanocapsules with loading efficiency up to 90%. The insecticidal activity of loaded nanocapsules against the armyworm larvae was found to be superior in comparison to the commercial formulations (Sun *et al.* 2014).

The efficiency of the modified polymeric material containing chitosan and natural rubber was considered for loading 1-hydroxynaphthalene and 2-hydroxynaphthalene in aqueous solution. The release amount of the pesticides in refreshing and non-refreshing neutral aqueous media was studied spectrophotometrically. The results indicated a constant, controlled and sustained release of pesticide for a period of 35 days (Rahim *et al.* 2016).

The inclusion complex of carboxymethyl-β-cyclodextrin-Fe_3O_4 magnetic nanoparticles-Diuron (CM-β-CD-MNPs-Diuron) were synthesized and evaluated for their potential toxicity on soil microbes by various techniques, viz. microcalorimetry, urease enzyme and real-time quantitative PCR (qPCR). The results indicated the significant effect of CM-β-CD-MNPs-Diuron on urease activity and micro-calorimetric analysis that was further in agreement with qPCR (Liu *et al.* 2014).

Kumar *et al.* (2014) synthesized, optimized and characterized imidacloprid loaded non-toxic anionic agent (sodium alginate). The governing factor of the delivery system involved the release of active compound in physiologic fluids as the sodium–calcium exchange.

Polyethylene glycol as pesticide carrier

Polyethylene glycol is another important material that had been well explored for producing encapsulated nanopesticides. Yang *et al.* (2009) reported the synthesis of garlic essential oil loaded polyethylene glycol (PEG) nanoparticles. The comparative insecticidal evaluation of the free garlic oil and the encapsulated formulation indicated the 11% and 80% efficiency, respectively, against adult red flour beetle *Tribolium castaneum*. Bhan *et al.* (2014) reported the melt-dispersion method for the preparation of PEG encapsulated Temephos nanopesticide as more active and safe formulation against larvae of *C. quinquefasciatus.*

Later, Venugopal and Sainadh (2016a) reported the novel eco-friendly nanoformulation of mancozeb pesticide for plant disease control using polyethylene glycol as a capping agent. Biological evaluation of the formulation was conducted against *Candida albicans* and *Staphylococcus aureus*. The bioefficacy of β-cyfluthrin-PEG formulations were used against *Callosobruchus maculatus* (Coleoptera: Bruchidae) for their comparative evaluation with commercial suspension concentrate (SC) (Loha *et al.* 2012).

The copolymers of polyethylene glycol and dimethyl esters to provide nanomicellar aggregates for the encapsulation of carbofuran [2,3–dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate] as controlled release formulation was reported by Shakil *et al.* (2010) and the amphiphilic copolymers of polyvinyl chloride (PVC) and polyethylene glycol (PEG) was explored for producing a controlled release (CR) formulation of a bioactive derivative, Azadirachtin-A obtained from *Azadirachta indica* A. Juss (Meliaceae) seeds (Kumar *et al.* 2010).

The other PEG based functionalized amphiphilic copolymers were utilized for controlled release (CR) formulations of Thiram. The kinetics of developed CR formulations in comparison to the commercially available 75 WS indicated that the release from the commercial formulation was faster than with the developed CR formulations but the polymers acted as barriers to moisture leading to reduced rate of seed deterioration and degradation of Thiram (Kaushik *et al.* 2013).

Controlled release formulation of imidacloprid was developed as nano-micellar aggregates of PEG and aliphatic diacids having high solubilisation power and low critical micelle concentration (CMC). The nano-formulation was found to have higher efficacy in comparison to the commercial standards (Adak *et al.* 2012).

Pankaj *et al.* (2012) presented an investigation on the bioefficacy studies of carbofuran nano-formulations prepared with PEG-600 & PEG-900 in comparison to commercial formulation of carbofuran 3G against the root-knot nematode, *Meloidogyne incognita* infecting tomato.

An ABA triblock linear dendritic copolymers composed of poly(citric acid) (PCA) as A block and PEG as B block was used for the preparation of nano-imidacloprid. Higher loading capacity of the polymer and slower release rate from nano-form at optimum *p*H of Glyphodespyloalis′s gut (pH=10) confirmed the selective and controllable action of nano-imidacloprid. The bioassay results on the model insect showed that by using the nanoform of imidacloprid, essential dosage of pesticide and environmental risk decreased significantly (Memarizadeh *et al.* 2014).

Tong *et al.* (2017) reported the use of mPEG-PLGA for the preparation of water-based formulation of metalachlor with no organic solvent or surfactant, reducing the most important sources of pesticide pollution. The bioassay analysis indicated the higher effects of the nano-particles in comparison to the non-nano form on *Oryza sativa* and *Digitaria sanguinalis* along with toxicity reduction of the latter to the preosteoblast cell line.

Majumder *et al.* (2017) reported a controlled release (CR) nanoformulations of mancozeb (manganese-zinc double salt of *N, N*-bisdithiocarbamic acid), using PEG based functionalized amphiphilic copolymers. *In-vivo* evaluation of the formulation was made for the management of *Alternaria solani* on tomato. The results indicated comparatively better efficacy of the developed formulations than the commercials products in terms of number of infected leaflets/plants along with increase in number of fruits plant^{-1} at 50 ppm. The regulated release of the formulation also leads to reduced number of applications.

Miscellaneous polymer based nano-formulations

Qian *et al.* (2013) reported the controlled release formulation of imidacloprid by incorporating it in poly (styrene–diacetone acrylamide). The results exhibited that the formulation at higher temperature and more diacetone acrylamide had lower value of T_{50}, indicating quicker release of the active ingredient under the conditions.

The another reported technique involved the polymerization of citric acid onto the surface of oxidized multiwall carbon nanotubes that leads to MWCNT-*graft*-poly (citric acid) hybrid materials. Trapping of pesticides such as zineb and mancozeb in aqueous solution by MWCNT-*g*-PCA hybrid materials led to encapsulated pesticide (EP). Experiments indicated that new hybrid material had a superior toxic influence on *Alternaria alternata* fungi in comparison to their bulk counterparts (Sarlak *et al.* 2014).

To minimize the harmful effect of atrazine, poly (epsilon-caprolactone) (PCL) nanocapsule has been developed for controlled release formulation with enhanced herbicidal activity in comparison to commercial formulation (de Oliveira *et al.* 2015a) followed by another report by de Oliveira *et al.* (2015b) about the modified release system of PCL nanocapsules containing atrazine as a post-emergence herbicidal activity against mustard (*Brassica juncea*) as target plant species model. The results demonstrated that the nano-formulation provides an effective post-emergence herbicidal activity along with the use of lower dosages of the nano-encapsulated atrazine without any loss of efficiency and added environmental benefits.

Campos *et al.* (2015) made another input by introducing nano-capsules synthesized from solid lipids and loaded with carbendazim and tebuconazole for fungicidal applications. The nano-formulated molecules were evaluated for their release profile, stability and cytotoxicity. The association efficiency of the particles (>99%) indicated the strong interaction of the carrier material and the active ingredient with decreased toxicity.

Nano-emulsions

Preparation of nanoemulsions (NEs) was another effort to improve solubility and spreading capacity of pesticides by dispersion into two liquid phases. The advantages of NEs were found in their greater spread ability, wettability, and superior mechanical stability in comparison to normal emulsions. These characteristic of NEs found helpful in less degradation and volatilization of active ingredient (AI) and improve their bioavailability for long time period (Mason *et al.* 2006, Anton *et al.* 2008, Guillette and Iguchi 2012).

Casanova *et al.* (2005) evaluated the nanoemulsion of a nicotine carboxylate using a series of fatty acids (C10-C18) and surfactant against adults of *Drosophila melanogaster* by assessing the lethal time 50 (LT_{50}). The encapsulation efficiency and the bioactivity was found to be decreased with increasing size of the fatty acids which was attributed to the higher amount of active compound inside the nanoemulsions.

Wang *et al.* (2007) developed an assemble of oil-in-water nanoemulsion (O/W) by a two-step process using the neutral surfactant poly(oxy-ethylene) lauryl ether and methyl decanoate to encapsulate highly insoluble β-cypermethrin. The potential applications of the system were compared with a commercial *β*-CP microemulsion in terms of the stability of formulations. The enhanced stability is considered to decrease the concentration of insecticides in commercial spray, without losing efficiency.

Anjali *et al.* reported the preparation of nanoemulsion of permethrin and neem oil by solvent evaporation method for their larvicidal potential against *C. quinquefasciatus*. The formulations were found to be good choice as selective larvicidal agents against the *C. quinquefasciatus*. The results also indicated that the efficacy of the formulation is dependent on the size of droplets as the LC_{50} values increases with decrease in droplet size (Anjali *et al.* 2010, Anjali *et al.* 2012).

Xian *et al.* (2012) prepared natamycin nanoemulsion with ketoconazole and terbinafine as a positive drug control and investigated their potential on *Candida albicans, Penicillium* and *Saccharomyces cerevisiae,* for their minimum inhibitory concentration (MIC) and minimum fungicidal concentration (MFC). The results indicated it to be an appropriate method to reduce the dosage so as to reduce costs and unanticipated side effects on animals.

The practical approach in the field involved the preparation of 5% nanoemulsion formulation of chlorpyriphos which was physio-chemically characterized for their larvicidal potential against the perpetually troublesome mosquitoes (*Aedes aegypti*) at Institute of Pesticide Formulation Technology, Gurgaon. It was reported that at lower concentration, nanoemulsions are more effective than commercial formulations against mosquitoes due to smaller droplet size of nanopesticide with increased surface area and better surface coverage property (Hazra *et al.* 2013).

The transcuticular nanoemulsion formulation of an antimicrobial agent, ampicillin was prepared to work against the Huanglongbing (HLB), a serious disease affecting the citrus industry. The water in oil (W/O) nanoemulsionformulation seems to provide a useful model for the effective delivery of chemical compounds into citrus phloem for controlling citrus HLB (Yang *et al.* 2015).

Díaz-Blancas *et al.* (2016) reported low energy method for formulating tebuconazole (TBZ) nanoemulsions (NEs). The system involved an organic phase (OP) consisting of an acetone/glycerol mixture containing TBZ and Tween 80 (TW80) as a non-ionic and Agnique BL1754 (AG54) as a mixture of non-ionic and anionic surfactants. The method was concluded to be a useful tool in sustainable agriculture.

Gumber *et al.* (2017) reported the preparation of carbendazim nanoemulsions for their larvicidal potential. The results indicated their strong efficacy with low toxicity in comparison to the standard organophosphorus molecules.

Nano-gels

Nano-gels are another input in the field with prestigious benefits and good future of the material in agriculture as seed dressing/coating and at household level to control insects and pests, because of its lower particle size, large surface area and greater adhesive properties.

A nanogel formulation of permethrin was developed for long lasting impregnation of the pesticide in the dresses of personals deployed to work in forest areas to protect them from mosquito bite. The developed formulation was evaluated according to WHO specifications with respect to wash resistance. All the laid down parameters were qualified by the formulations (Mourey *et al.* 2007).

Other important contributions in nano-gel formation involved the increase in the effectiveness of pheromones in terms of their increased shelf-life through their entrapment by low-molecular mass gelators (LMMGs) such as all-*trans* tri(*p*-phenylene vinylene) bis-aldoxime. Methyl eugenol (ME) was entrapped into the entangled three-dimensional nano-sized supramolecular networks of the polymer. It provides high pheromone retention capacity, enhanced shelf-life and protection of ME from environmental decompositions. The additional benefit involved its use in even rainy season as *B. dorsalis* shows maximum activity during the rainy season resulting in the most significant yield loss of crops (Bhagat *et al.* 2013).

Brunel *et al.* (2013) used chitosan nanogel for enhancing the activity of nascent copper against *Fusarium graminearum.* The results indicated the synergistic effect of the formulation to inhibit the fungal pathogen. The use of nanogels of myristic acid-chitosan loaded with cumin essential oil was reported by Ziaee *et al.* (2014). Granary weevil (*Sitophilus granarius* L.) and confused flour beetle (*Tribolium confusum* Jacquelin du Val.) were used as model insects for bioefficacy study of the *Cuminum cyminum* L. oil and oil-loaded nanogels (OLNs). The insecticidal bioassay revealed that OLNs were more toxic than the non-formulated oil against tested beetle pests. The persistence of the oil and OLNs was also evaluated against two tested species. Results indicated that *C. cyminum* oil completely lost its insecticidal activity after 12 days, whereas the OLNs have lower release and loss rate when applied against *S. granarius* (60 %) and *T. confusum(*15%).

Other important inputs

Choudhury *et al.* (2012) presented a hydrophilic nano-formulation of acephate, an organophosphorus insecticide as a very useful method for industries for making farmer-friendly pesticide formulations.

Nano-hybrid organic-inorganic materials were explored by Hussein and co-workers to develop the formulation of 2,4-dichlorophenoxyacetate (2,4D). The inorganic Zn–Al layered double hydroxide (ZAL) was used to study the release property of 2,4D and the mechanism of release has been interpreted on the basis of the ion exchange process between the 2,4D anion intercalated into the inter lamellae host and carbonate or chloride and/or hydroxyl anions in the aqueous solution. The release of the guest molecule was found to be rapid initially followed by a sustained release depending on the type of anions and their concentrations in the release medium (Hussein *et al.* 2005). Hashim *et al.* (2014) proposed the synthesis of cloprop-layered double hydroxide and cloprop-zinc-layered hydroxide nanocomposites, by using co-precipitation and direct reaction method.

The porous silica particles were utilized for controlled release of validamycin. The results indicated that the carrier material makes the active ingredient more active for longer period (Liu *et al.* 2006). In another reported study, silica nanoparticles were utilized for loading insecticide Chlorfenapyr. The association of two increased their activity many folds by providing more loading capacity and controlled release patterns. The insecticidal activity in laboratory and field tests were also found to be doubled (Song *et al.* 2012).

Cao *et al.* (2016) reported the pyraclostrobin loaded mesoporous silica nanoparticles (MSNs) capped with water-soluble chitosan derivative (*N*-(2-hydroxyl)propyl-3-trimethyl ammonium CS chloride). The nanoparticles showed an initial burst and subsequent sustained release behaviour and utilization of half doses in comparison to the technical grade with almost the same fungicidal activity against *Phomopsis asparagi* (Sacc.), indicating the reduction of the applied pesticide and enhanced utilization efficiency.

Nano-silica and Nano-fibrillated cellulose nanocomposite were utilized for slow-release of tebuconazole. The 15 days of immersion showed that the pure biocide had 95 % release compared with 30–45 % release of the tebuconazole loaded in the nanocomposites (Mattos and Magalhaes 2016).

Qian *et al.* (2011) loaded validamycin over nano-sized calcium carbonate and evaluated its efficacy against *Rhizoctonia solani.* The material displayed better germicidal efficacy in comparison to technical validamycin evaluated after 7 days. The release time was also extended up to 2 weeks along with strong loading efficiency, stability, and good environmental compatibility.

Saini *et al.* (2014) evaluated *in vitro* insecticidal activity of pyridalyl nanosuspension in comparison to technical material and commercial formulation against larvae of *Helicoverpa armigera*. The studies indicated the better efficacy of the nano-suspension than technical material and commercial product. Another study by Saini *et al.* (2015) indicated decline of the residues of pyridalyl in tomatoes with in nano-formulated form. The results of terminal residue showed that pyridalyl residues were below the available MRL. Low pesticidal residues of the nano-formulated form suggested that this pesticide is safe to use under the recommended dosage.

Sabbour *et al.* (2016) prepared nano-imidacloprid (IMI) by hydrolyzing it with titanium tetra isopropoxide in a mixture of about 1:1 anhydrous ethanol and water and evaluated them against the desert locust, *Schistocerca gregaria* under National Research Centre (NRC) laboratory conditions and semi field conditions in green house in NRC.

Yearla and Padmassree (2016) reported the use of subabul stem lignin as a matrix material to fabricate a stable diuron nanoformulation (DNF). Optimized DNF has 5.17 ± 0.49 % diuron loading efficiency and 74.3 ± 4% encapsulation efficiency. The seedlings of canola (*Brassica rapa*) grown in the soil supplemented with ODNF showed early signs of leaf chlorosis and mortality when compared with seedlings grown in the presence of commercial diuron formulation and bulk diuron.

Polypropylene glycol as encapsulating agent was explored for the preparation of novel nano-mancozeb formulation by Venugopal and Sainadh (2016b). The bio activity nature of nano formulated mancozeb is many times more when compared to the commercial mancozeb.

Conclusion

The application of nano science in agriculture may provide solutions to many problems such as slow and controlled release leading to the decreased load of pesticides to the environment, enhanced bioavailability and protection against degradation with increased bioefficacy of the nanomaterials to achieve insect control at the desired level and period (Kumar *et al.* 2010). Therefore, the initial studies produced favourable results for the use of nano-formulated pesticides. Contrarily, the nano-sized materials owing to their altered physical and chemical properties in comparison to their bulk counterparts can become toxic reaching the nano-size. The preliminary studies reflect the nano-technological modifications of bioactive materials as positive candidates for future research. Multilateral aspects are still needed to understand the imminent impacts of nano-pesticides as an eco-friendly alternative.

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