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### A review on development of nano formulations of essential oils for stored grain pest management

#### Rani KS, Rajasri M and Manjunath MM

#### Abstract

The chemical pesticides used against storage insects may cause negative impact on human health and environment. Hence, alternative practices for the management of storage insect pests are the needed particularly safer alternatives like use of botanicals and their essential oils. Plant-derived pesticides are reported as effective in controlling various insect pests through natural mechanisms, with biodegradable organic materials, diverse bioactivity, and low toxicity to non-target organisms. Nano-delivery formulations of biopesticides offer a wide variety of benefits, including increased effectiveness and efficiency (well-dispersion, wettability, and target delivery) with the improved properties of the essential oils. The application of botanical insecticides in nanoformulations offers potential increase of agricultural productivity. This review article discusses the use of nanotechnology in combination with different essential oils for management of storage pests.

Keywords: Insect pests, botanicals, nano delivery formulation, essential oils

#### 1. Introduction

Insect damage to stored grains is a major problem worldwide. About 10-40% of produced grains are lost every year due to insect damage in developing countries alone, resulting largely from the lack of modern storage technologies (Shaaya *et al.*, 1997) <sup>[37]</sup>. Pest infestation of stored products has many disadvantages such as losses of product weight, nutritive contents, commercial and aesthetic value as well as it may have a health hazard to consumers.

The management of insect pests of stored products should be carried out to meet the demands of increasing population. (Abhilash and Singh, 2009) <sup>[1]</sup>. Several fumigants have been tried, from the last three decades particularly phosphine and methyl bromide had been used extensively for the disinfestation of stored products. The Montreal Protocol has directed phasing out the use and production of methyl bromide because it is harmful. It has a high potential for depleting the ozone layer because of its high chemical reactivity. That is why most of the grain storage facilities are depending upon single method of phosphine fumigation because of its less cost, permissibility on most commodities, effectiveness against all life stages, minimum residual toxicity and utility in a broad range of storage facilities. The indiscriminate and continuous use of phosphine resistance in many of the stored grain pests especially in bulk storage facilities and rice storage godowns. The growing awareness of hazards of excessive use of pesticides globally had led researchers for safer and more environment friendly alternatives for pest control under storage (Rajasri *et al.*, 2014) <sup>[33]</sup>.

Presently, botanicals occupy a very small niche in the world of synthetic pesticides, but the increasing environmental concerns had led to a surge in use of environmentally sustainable and friendly green alternatives. The presence of essential oils and their components, having fumigant action and insecticidal properties from plant sources can be explored in stored grain protection which are having an advantage in terms of safer to mammals and fast degradation Some essential oils have acute toxicity, repellent action, feeding inhibition or harmful effects on the physiology of insects (Prates *et al.*, 1998)<sup>[32]</sup>.

Secondary metabolites in the form of plant essential oils play an important role in plant-insect interactions because these compounds have insecticidal activity against insects. Essential oils generally contain a complex mixture of monoterpenes, phenols and sesquiterpenes. Some plants capable of producing essential oils are distributed in several families, such as Cupressaceae, Lauraceae, Zingiberaceae, Asteraceae, Myrtaceae, Lamiaceae, Piperaceae, Apiaceae, Rutaceae and Poaceae.

These essential oils have different mechanisms of action as pesticides like acting on the insect's nervous system; suppression and disturbance of normal growth, development, metamorphosis, and reproduction of insects; and inhibition of mitochondrial membrane respiratory enzymes or regulation of oxygen consumption and carbon dioxide released in insects (Liao *et al.*, 2016)<sup>[23]</sup>.

The application of essential oils to storage pest control requires an appropriate formulation formed by biodegradable compounds that protect essential oils from degradation and evaporation, while simultaneously allowing sustained release (da Costa *et al.*, 2014)<sup>[8]</sup>.

One of the research topics that require attention to overcome these obstacles is the use of nanotechnology. A nano-based formulation aims to improve the properties of essential oils such as higher surface area, increased systemic activity, smaller particle size, higher mobility, slow release and decreased toxicity to non-target organisms (Sasson *et al.*, 2012)<sup>[36]</sup>.

The toxicity of essential oils extracted from various botanicals was assessed against several major stored-product insects. The present review consists of extensive information on use of nanoformulations of essential oils to increase the efficacy against stored grain insect pests.

#### 2. Different essential oils and their properties

Essential oils have received much attention due to their multifunctions as antimicrobial, antifungal, antitumor and insecticidal agents (de Souza *et al.* 2005)<sup>[9]</sup>. Essential oils and especially their main compounds monoterpenoids, offer promising alternatives to classical pesticides (Aslan *et al.* 2004)<sup>[4]</sup> (Table 1). Essential oils are volatile and can act like fumigants offering the prospect for use in stored-product protection (Lee *et al.* 2002)<sup>[22]</sup>, contact insecticides, antifeedent or repellent effects (Kim *et al.* 2003, Park *et al.* 2003) <sup>[20, 30]</sup> and may also affect some biological parameters such as growth rate, life span and reproduction (Tunc *et al.* 2000)

Neem (*Azadirachta indica*) (Sapindales: Meliaceae) contains the most important compound is a triterpenoid, Azadirachtin and other constituents such as nimbin, nimbidin and salanin which are widely used in agriculture to combat insects and plant pathogens. These compounds possess insecticidal, ovicidal, antifeedant and growth inhibiting effects against many spp. of insect pests (Rashmi *et al.*, 2019)<sup>[34]</sup>.

Clove, *Syzygium aromaticum* (Myrtaceae) tropical annual crop producing essential oils containing eugenol (2-methoxy-4-allylphenol) (88.61%), eugenol acetate (8.89%) and Transcaryophyllene (1.89%) (Han *et al.*, 2006)<sup>[14]</sup>. Eugenol has the role of allergen, plant metabolite, human blood serum metabolite, and ensitizer. Eugenol has a molecular weight of 302,238 g/mol. Trans-caryophyllene is found in many essential oils, especially clove oil. These compounds have roles as non-steroidal anti-inflammatory drugs, fragrances, metabolites, and in-sect attractants. Trans-caryophyllene has a molecular weight of 204.35 g/mol (Ikawati *et al.*, 2022)<sup>[17]</sup>.

Eucalyptus, especially *E. globulus* (Myrtaceae) is the most representative species in the international pharmacopeia (Bajaj, 1995) <sup>[5]</sup>. Eucalyptus oil is effective against storage pests *viz.*, *Sitophilus oryzae*, *Tribolium castaneum*, *Rhyzopertha dominica*, *Sitophilus zeamais* etc. (Mossi *et al.*, 2011) <sup>[27]</sup>. Pesticide property of Eucalyptus oil is due to the presence of volatile compound "eucalyptol or 1,8-cineole".

(Hernandiaceae) is used to heal wounds, the drinkable bark decoction of stems is used for the treatment of malaria with documented insecticidal efficacy. Perilla aldehyde, the major compound of the *H. voyronii* essential oil is used as a flavouring component to baked foods, sweets, meat products, dressing for salads, sauces, salted vegetables and beverages. Furthermore, perilla aldehyde is a generally recognized as safe substance (Benelli *et al.*, 2020)<sup>[6]</sup>.

*Baccharis reticularia* (Asteraceae) is an endemic shrub in Brazil and found in several biomes and it is popularly known as rosemary of the beach. Its phytochemical composition revealed the presence of  $\alpha$ -pinene,  $\beta$ -pinene,  $\beta$ -myrcene, limonene, (E)-caryophyllene and bicyclogermacrene which are having repellent activity against insect pests (Lima *et al.*, 2021)<sup>[24]</sup>.

Citrus (*Citrus* sp.) (Rutaceae) essential oils are the byproducts of citrus industries. Thus, the concurrent large availability of citrus essential oils and their usual low cost (*i.e.* in particular for sweet orange, *Citrus sinensis* L.) make these compounds a potential alternative to synthetic chemical insecticides. The efficacy of citrus essential oil is apparently associated to the content of monoterpenes and particularly of limonene (Ibrahim *et al.*, 2003) <sup>[16]</sup>. Limonene is biodegradable in aerobic conditions and similar to phosphine undergoes to phytochemical reactions, producing hydroxyl radicals, ozone and nitrate radicals (Altshuller, 1983) <sup>[3]</sup>.

Garlic (*Allium sativum*) (Amaryllidaceae) is popular all over the world and its strong insecticidal activity has also been demonstrated by several studies. Several garlic products such as garlic essential oil and garlic powder are available in the international market for use mainly as pest control. Diallyl sulfide (21.3%), diallyl disulfide (59.7%) and diallyl trisulfide (10.9%) were identified as major components of garlic oil which have insecticidal property.

Coriander, *Coriandrum sativum* (Apiaceae) is a native of the Mediterranean region and is grown in North Africa, central Europe, and Asia as a culinary herb and medicament. The active compound of coriander essential oil against insect pests is linalool, camphor, and geranyl acetate (Lopez *et al.*, 2008)<sup>[25]</sup>. It has insecticidal, nematicidal and anti-bacterial property.

#### 3. Nanotechnology in Agriculture

Pesticides are important inputs for enhancing crop productivity; >90% of pesticides run off into the environment and reside in agricultural products. Formulations also contain harmful solvent and have poor dispersion; dust drift stands out as the main drawback of conventional pesticide formulations. Therefore, nano-based pesticide formulation development has aimed at the precise release of necessary and sufficient amounts of their active ingredients in response to environmental triggers.

Nanotechnology has been applied in numerous fields such as textiles, geosensing technology, paper, food, fertilizers, pesticides, plant protection, nutrition paints, food biofuel, biomass, and agrochemical industries to create novel products with a wide range of applications. Nanoparticles have been applied in the agriculture sector to protect plants, increase soil fertility, control weeds, and improve soil nutrients. They are also used to develop fertilizers at nano range or to develop species-specific pest repellents. For example, the nanoparticles are coupled with zinc metals using biodegradable compounds to form zinc nanoparticles (Zn NPs), and the products obtained are eco-friendly and used to improve soil fertility. Similarly, fungicides, insecticides, herbicides, chemicals, or genes can be combined with

nanoparticles to serve as magic bullets that target plant parts for pest control (Perea-de-Lugue and Rubiales, 2009)<sup>[31]</sup>.

Table 1: Botanicals containing essential oils indicating their bioactive components and applications

Plant species	Common name	Family	Bioactive compound	Function
Azadirachta indica	Neem	Meliaceae	Azadirachtin	Insecticide
Citrus sp.	Citrus	Rutaceae	Limonene	Insecticide and Acaricide
Syzygium aromaticum	Clove	Myrtaceae	Eugenol and Caryophyllene	Insecticide and Herbicide
Eucalyptus sp.	Eucalyptus	Myrtaceae	1,8-Cineole	Insecticide and Acaricide
Hazomalania voyronii	Malagasy plant	Hernandiaceae	Perilla aldehyde	Insecticide
Baccharis reticularia	Alecrim-da-areia or Rosemary of the beach	Asteraceae	$\alpha$ - pinene, $\beta$ - pinene, limonene	Insecticide
Allium sativum	Garlic	Amaryllidaceae	Diallyl sulfides	Insecticide, Fungicide, Nematicide
Coriandrum sativum	Coriander	Apiaceae	Linalool, camphor, geranyl acetate	Insecticide, Nematicide, Antibacterial property

To be precise, nano pesticides would be safer for use and would have improved pesticidal potential, such as via nanoencapsulation of the products (Fig.1.) The nanoencapsulation comprises nanosized molecules of the active pesticide compound that are sealed by a thin-walled sac. Such nanoencapsulation of insecticides, fungicides, or nematicides offers effective control of pests, preventing the accumulation of residues in the soil and its run off to water bodies. It also has the advantages of protection of the active pesticide ingredient from degradation, improving the effectiveness, and greatly decreasing the pesticide input to at least 10-15 times less than those applied with classical formulations (OECD and Allianz, 2008)<sup>[29]</sup>.

The important points that need to be strategized in the nano formulations are:

- 1. Use of water-based dispersion system.
- 2. Leaf-targeted deposition and dose transfer mechanism of nano delivery.
- 3. Increased bioavailability mechanism of nano-based formulations.
- 4. Natural degradation and biosafety of residues (zhao *et al.*, 2017).

The efficient use of nanotechnology for the formulation of nano-based products is shown in Fig. 2. However, various carriers and structures are used to develop such products.

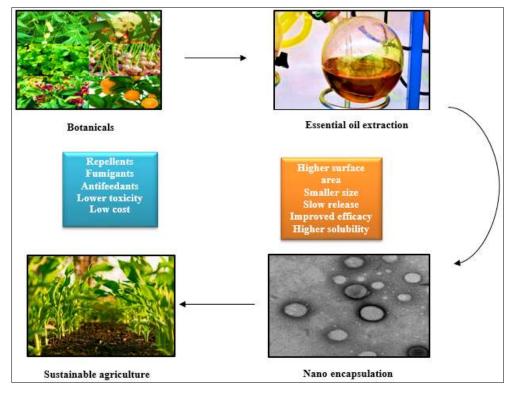


Fig 1: Schematic representation showing combination of nanotechnology with essential oils for sustainable agriculture

Stored-grain pests are one of the biggest challenges to control in an agricultural system. Several nanomaterials loaded with natural products have been evaluated against stored-grain pests (Yang *et al.*, 2009, Zahir *et al.*, 2012) <sup>[41, 42]</sup>. Products based on alumina, silica, SiO<sub>2</sub>, Zn, and Ag nanoparticles have been significantly active against such pests (Vani and Brindhaa, 2013)<sup>[40]</sup> and these nanoemulsions have been used to evaluate and control stored-grain insects using specific bioassay procedures.

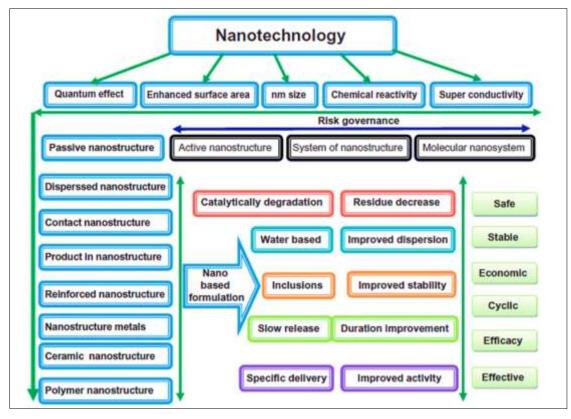


Fig 2: The efficient use of nanotechnology for formulation of nano-based products (Lade et al., 2019).

## 4. Development of nanostructured systems with essential oils

The advantages of essential oils include the presence of other components that might have synergistic effects with the main active agents in the oil (Jiang *et al.*, 2009)<sup>[18]</sup>. Development of nanoformulations contributes majorly to the effectiveness of essential oils. Several nanoformulations of essential oils were developed by employing different methods and different carriers.

Different combinations of emulsions were formulated keeping eucalyptus oil (EO) concentration at 6% with fixed ratio of EO: tween 80 (1:2) by Adak et al., 2020 [2]. Centrifugation and thermodynamic characterization (heating and cooling, freezing, and thawing) were carried out to check their stability. Emulsions formed from two rotation speeds *i.e.*, 5000 and 10,000 rpm were milky in appearance and phase separation was observed. The prepared emulsions were characterized for its particle size, PDI, zeta-potential analysis. Droplet sizes were ranged between 2.27-2771.00 nm depending on oil concentration and EO: tween 80 ratio. Ideal PDI value was recorded in nanoemulsions with 6% EO compared with 8% EO. The PDI of the EO: tween 80 at 1:2 and 1:2.5 were 0.37 and 0.76, respectively. The higher  $\zeta$ potential value leads to a more stable emulsion than the lower  $\zeta$ -potential. Among all the combinations, EO: tween 80 at 1:2 and 1:2.5 ratio possessed ζ-potential of 6.20 mV and 7.69 mV, respectively.

Choupanian *et al.* (2017) <sup>[7]</sup> formulated neem oil using nonionic naturally based polysorbate (PolyS) and alkylpolyglucoside (APG) surfactants as inert ingredients. The smallest particle sizes were detected in formulations comprised of a polysorbate surfactant, ranging from  $208\pm1.2$ (N-PolyS1) to  $253\pm1.6$  (N-PolyS2) nm in diameter. The zeta potential of the prepared formulations ranged from 31.27 to 39.12 mV, indicating the stability of the prepared nanoemulsion formulations, 1 hr after preparation.

Giunti *et al.* (2019) <sup>[13]</sup> characterised the sweet orange essential oil which was entirely composed by monoterpene hydrocarbons (98.59%). The main constituents were *R*limonene (93.35%),  $\beta$ -myrcene (3.38%),  $\alpha$ -pinene (1.14%), linalool (0.54%) and sabinene (0.50%). The prepared nanoemulsion of this oil showed an average size of the droplets within the nanometre range, either after 24 h from its preparation, as well as after 1 year of storage. Furthermore, the low values of the polydispersity index (0.12-0.19) indicated the size homogeneity of the formulation. Finally, nano-emulsion exhibited a negative surface charge ( $\zeta$ ) slightly higher than -30 mV.

The polyethylene glycol (PEG) nanoparticles were used as carrier for the essential oil of garlic and evaluated the insecticidal activity of the formulations against *T. castaneum*. The nanoparticles were prepared by the fusion-dispersion method and showed an encapsulation efficiency of 80%. The sizes of the spherical particles were smaller than 240 nm, as measured using TEM and dynamic light scattering techniques. The results indicated that PEG nanoparticles loaded with the essential oil of garlic offer a useful means of controlling pests during product storage (Yang *et al.*, 2009)<sup>[41]</sup>

Sabbour (2020) <sup>[35]</sup> extracted the four oils from coriander, Janesville, caraway, and black seed and used as a core material and urea and formaldehyde as shell materials. Sulfuric acid solution (10% w/w) was prepared in laboratory to control the pH (4.4) of emulsion and tween 80 (polysorbate 80) was used as an emulsifier. The suspension obtained of nanocapsules was cooled down to ambient temperature, rinsed with deionized water, filtered, and finally dehydrated by freeze-drying using a LIO-5P, which is a freeze dryer for laboratory use. Nano-emulsion was prepared by high pressure homogenization of 2.5% surfactant and 100% glycerol, to create stable droplets which that increased the retention of the oil and slow release of the nanomaterials.

Nano-emulsions were prepared by a low-energy titration method (Lima *et al.*, 2021)<sup>[24]</sup>. The oily phase constituted by the essential oil (or limonene,  $\alpha$ -pinene, and  $\beta$ -pinene) and non-ionic surfactant (or mixture of sorbitan monooleate, polysorbate 80 and/or polysorbate 20) was mixed. The nano-emulsion final concentration was 25 mg/mL and the surfactant-to-oil ratio was 1:1. Droplet size, polydispersity index, and zeta potential are parameters that indicate the stability of the emulsions. All emulsions had average droplet sizes below 500 nm, polydispersity indices (PDI) less than 0.6 and negative zeta potential values after preparation.

Kavallieratos *et al.* (2021) <sup>[19]</sup> formulated *Hazomalania voyronii* essential oil through a high-energy method, by using a high-pressure homogenizer. A 6% (w/w) of essential oil was added dropwise to 4% (w/w) Polysorbate 80 aqueous solution under high-speed stirring for 5 min at 9500 rpm. Dynamic light scattering analysis showed a monomodal size distribution with a mean diameter of  $53.54\pm0.20$  nm and a polydispersity index of  $0.340\pm0.013$  after preparation.

## 5. Bio-efficacy of nano formulated essential oils against storage pests

The above cited nanoformulations were evaluated against important storage pests for their efficacy.

Ikawati et al. (2022) [17] characterized nanoparticles loaded with clove (Syzygium aromaticum) essential oil-based polyethylene glycol (PEG) and evaluated their insecticidal activity against T. castaneum. The concentrations of clove oil ranged from 0.9 to 1.2% and of clove oil nanoparticles ranged from 12.6 to 15.2 percent (w/w). Clove oil nanoparticles produced contact toxicity for 16 weeks. After 16 weeks of storage, at 14.6% concentration, nanoformulation produced more than 70 percent mortality and at 15.2% concentration it caused 90 percent mortality. Encapsulation efficiency was one of the important factors for nanoparticle formulation and these clove oil nanoparticles produced high contact toxicity during 16 weeks of storage. The residual effects of clove oil nanoparticles to C. ferrugineus at 2.4% and 3% concentrations was studied. Clove oil nanoparticles resulted in contact toxicity at these two concentrations over 16 weeks. The nanoformulation caused more than 60 percent and 90 percent mortality even after 16 weeks.

Contact toxicity and grain treatment of eugenol against stored grain pests showed effectiveness on grain when treated as protectants. Eugenol was also highly repellent to storage pests. Development of eggs and immature stages inside grain kernels was completely inhibited by eugenol treatment (Obeng-Ofori and Reichmuth, 1997)<sup>[28]</sup>.

Kavallieratos *et al.* (2021) <sup>[19]</sup> developed a 6% (w/w) *Hazomalania voyronii* essential oil-based nanoemulsion (HvNE) and evaluated against *T. confusum, T. castaneum* and *Tenebrio molitor*, as an eco-friendly wheat protectant. of HvNE at 1000 ppm, the mortality of *T. confusum and T. castaneum* larvae and *T. molitor* adults 7 days post-exposure reached 92.1, 97.4 and 100.0 percent respectively.

Nano-formulations of four essential oils, namely, coriander, black seed, caraway, and Janesville were evaluated against *T. confusum* and *T. castaneum* in the laboratory and stored conditions. The nano-oils were tested at the concentration of 0.5% against the  $3^{rd}$  larval instars. Cumulative percentages of

mortality were determined after 7 days after treatment. The results obtained showed that the percentage of larval mortality of *T. confusum* and *T. castaneum* increased with an increase in the treatment concentrations. Larvae of *T. confusum* were more susceptible to the treatments than *T. castaneum*. Coriander oil followed by Janesville oil gave the highest mortality percentage after 7 days 80.3 and 85.4 percent respectively for *T. castaneum* and 84.8 and 87.9 percent for *T. confusum* as compared to control. Incorporation of essential oils into a controlled release nano-formulation prevented rapid vaporization and degradation, increased constancy and preserves the lower effective dosage/application (Sabbour, 2020)<sup>[35]</sup>.

Adak *et al.* (2019) <sup>[2]</sup> homogenized different combinations of eucalyptus oil (EO), surfactant (Tween 80) and water to obtain nanoemulsion at two combinations, 1:2 and 1:2.5 (EO: Tween 80) of 6% EO concentration. They reported that lethal concentration (LC<sub>50</sub>) of 1:2 and 1:2.5 formulated nanoemulsion of eucalyptus oil against *S. oryzae* were 0.56 and 0.45  $\mu$ l cm<sup>-2</sup> respectively and against *T. castaneum*, it was 1.11 and 0.89  $\mu$ l cm<sup>-2</sup> respectively. Whereas, LC<sub>50</sub> of crude eucalyptus oil was 0.795 and 4.178  $\mu$ l cm<sup>-2</sup> against *S. oryzae* and *T. castaneum* respectively.

Dhivya *et al.* (2019a) <sup>[10]</sup> formulated nanoemulsion using sweet flag oil (6%) different ratio of oil and surfactant 1:0.5, 1:1, 1:1.5 and 1:2. The minimum droplet size 17.9 nm was recorded in 1:2 (v/v) of oil and surfactant. The developed formulations were evaluated for insecticidal action against *S. oryzae.* The insecticidal action increased with an increase in surfactant concentration and dose. The median lethal concentration (LC<sub>50</sub>) value was 0.51% for 1:2 ratio formulations while it was 2.35% for 1:0.5 ratio formulation. The LC<sub>50</sub> value decreased with decrease in droplet size and increase in surfactant concentration.

Dhivya *et al.* (2019b) treated the cowpea seeds with *A. calamus* nanoemulsion at 1% concentration and recorded 90 percent mortality of *C. maculatus* 24 hours after treatment. While the microscale emulsion at same concentration has shown only 78.33 percent mortality.  $LC_{50}$  value for *A. calamus* nanoemulsion was 0.41% which was significantly lower than micro-scale emulsion, which had 0.74%.

Manjunath *et al.* (2020) <sup>[26]</sup> tested the nanoscale ZnO and chitosan encapsulated with Azadirachtin and NSKE against *C. serratus* revealed lowest percent pod damage in nanoscale chitosan encapsulated NSKE @ 1% in 5 ml kg<sup>-1</sup> pods followed by nanoscale ZnO encapsulated NSKE @ 0.1% in 5 ml kg<sup>-1</sup> pods untreated control treatment recorded 49.33 percent mean pod damage.

Abdel-Halim and Manal (2018) synthesized nanoparticles coated with clove oil (20%) to form solid lipid nanoparticles (SLNs/EO). The toxicity of essential oil and their SLNs/EO formulations were assessed against adults of red flour beetle, *T. castaneum*. The mortality was recorded after 5, 7, 10 and 14 days of exposure. The data showed that, SLNs/clove was more toxic than clove oil alone (4.86-folds) after 7 days. Since the LC<sub>50</sub> values were 486.63 and 494.35 ppm after 7 days of treatment respectively.

Yang *et al.* (2009) <sup>[41]</sup> characterized polyethylene glycol (PEG) coated nanoparticles loaded with garlic essential oil and evaluated their insecticidal activity against adult *T. castaneum*. The control efficacy against adult *T. castaneum* remained over 80 percent after five months, presumably due to the slow and persistent release of the active components

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from the nanoparticles. In contrast, the control efficacy of free garlic essential oil at the similar concentration (640 mg kg<sup>-1</sup>) was only 11 percent. This indicated that it is feasible to use the PEG coating nanoparticles loaded with garlic essential oil to control the stored product pests.

Nano-encapsulation increased the droplet size, surface area and solubility of the *Baccharis reticularia* essential oil as compared to crude essential oils was reported by Lima *et al.*  $(2021)^{[24]}$  against *T. castaneum*.

Nano-emulsion formulations of neem oil containing polysorbate and alkyl polyglucoside surfactants were successfully created *via* the low-energy method by Choupanian *et al.* (2017)<sup>[7]</sup>. All the formulations provided a nano particle-size, with the smallest size being 208 nm. Overall, the study showed that the particle size between the EC formulation and nano-emulsions and within the nano-emulsion formulations contributed to the effectiveness, speed of action, and stability of azadirachtin. Thus, they concluded that nanoformulation could be an alternative to conventional insecticides for the control of *T. castaneum* adults.

Sweet orange essential oil was characterized by the prevalent presence of a single molecule, *R*-limonene which proved to be a good repellent and insecticidal component against *T. castaneum* and *T. confusum* by Giunti *et al.*, 2019 <sup>[13]</sup>. Sweet orange essential oil nano-emulsion showed interesting insecticidal activity against both insect species when applied as cold aerosol which acted as both fumigant and contact insecticide.

#### 6. Conclusion

The potential applications and benefits of nanotechnology are enormous to exploit in pest management. The use of essential oils plants can provide an effective means of controlling storage pests and the presence of other components in the essential oil can synergise the action of the main active principle. For eco-friendly management of several important storage pests, essential oils based on nano-formulations could potentially provide an enhanced level of protection for stored durable commodities against multi species infections. Among the plant secondary metabolites constituting the essential oils, terpenes and specifically monoterpenes are considered as the principal molecules responsible for the bioactivity against insect pests, as well as against microbes. The potential of these essential oils will help to resolve current problems of agricultural pests and soon, commercial products will emerge that combine the benefits of botanical insecticides with nanotechnology that are less harmful to the environment and human health.

#### 7. Future perspectives

- Future research studies about the mechanisms of action of the botanicals and their active ingredients against different insects are to be studied in detail.
- Before implementing the use of botanicals and their active ingredients, large scale experiments are needed to evaluate their mammalian toxicity and to substantiate their efficacy under conditions of commercial storage to validate their economic values as grain protectants.
- The main difficulties that to be considered are issue of scale of nanocarrier production, as well as the extraction of active ingredients from botanicals in the quantities required to control agricultural pests before nanotechnology can be fully commercialization.

 Nano-delivery strategies includes like development of a water-based dispersion system, leaf-targeted deposition and dose transfer mechanism of nano-delivery, increased bioavailability mechanism of nano-based formulations and natural degradation and biosafety of residues must be studied.

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