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NANO- ENHANCED ESSENTIAL OILS AS INSECTICIDE

Nefla Y[1]***** **and G B Kalariya**[2]

[1]Department of Entomology; [2]Agricultural Technology Information Centre,
Navsari Agricultural University, Navsari 396450, Gujarat, India
*Email: neflayousuf91@gmail.com (corresponding author): ORCID ID 0009-0004-6432-1054

ABSTRACT

With the growth of the world population, there is a corresponding rise in the need for agricultural output. Consequently, there has been an over reliance on pesticides to augment the productivity of crops. It resulted in significant environmental damage, harm to non-targeted insects and contributed to the emergence of insect resistance. Consequently, the use of environmentally acceptable biopesticides made from essential oils in integrated pest control programmes as a supplement or substitute for chemically produced insecticides is the need of the noun. Essential oils (EOs) are volatile molecules that occur naturally in plants and possess a unique scent. They are utilised as toxicants, repellents and phagodeterrants. The inherent characteristics of these substances disrupt multiple metabolic processes of insect pests, ultimately resulting in their death. Although EOs possess favourable characteristics, they also have various limitations. In order to tackle the problems related to the utilisation of EOs, it is necessary to employ nanotechnology to integrate them into nanoformulations. Integrating essential oils with controlled-release nanoformulations may offer a more efficient remedy compared to using a single, unbound ingredient.

Key words: Controlled release, essential oils, integrated pest management, nanoformulations, nanotechnology, phagodeterrant, polymeric nanoparticle, repellent, stability

India's population growth has been a challenge in meeting the country's food and nutrition requirements, necessitating increased effort to address this issue (Pandey, 2023). This has led to a rise in the need for agricultural production, as the global population is expected to grow by 35% by 2050 (Dijk et al., 2021). Pesticide use has globally enhanced agricultural productivity by 15-20 times, according to Popp et al. (2013). Due to their emphasis on output rather than product quality, farmers frequently opt for chemical pesticides as their primary solution when they encounter insect infestations. Excessive utilisation of chemical pesticides has a harmful impact on human well-being, leading to an elevated susceptibility to cancer, cardiovascular illness, neurological diseases and endocrine disruption (Aktar et al., 2009). Workers who have been exposed to herbicides containing HCH have reported experiencing neurological problems (Dassanayake et al., 2021). In addition, it induces environmental hazards such as atmospheric contamination, water contamination, and soil contamination (Sarwar, 2015), as well as the emergence of insect resistance. The widespread and unselective application of chemical pesticides has resulted in a decline in soil fertility and microbial populations, consequently contributing to a fall in agricultural production (Tripathi et al., 2020). Therefore, there is a growing requirement to use non-chemical pesticides as a substitute for synthetic pesticides in order to safeguard the environment from insecticidal contamination, mitigate the development of resistance in plants and enhance crop productivity (Ibrahim, 2020). Essential oils are an effective alternatives for addressing these issues.

Essential oils (EOs)

As a potential substitute for existing insecticides, plants possess a profusion of bioactive compounds. Essential oils are volatile compounds that are endogenously synthesised by plants to serve specific functions, including attraction or protection. These compounds are composed of natural antimicrobial and antioxidant agents and typically have a distinct odour (Somesh et al., 2015). They are lipophilic and typically have a lower density than water (Bakkali et al., 2008; Dhifi et al., 2016). Anti-parasite, bactericidal, fungal, virucidal and insecticidal properties are found in some essential oils (Burfield et al., 2005).

Leaves, flowers, peels, seeds, wood, fruits, resin, rhizomes and roots are all viable sources from which EOs can be recovered (Tongnuanchan and Benjakul, 2014). EOs are classified into various families, including Apiaceae, Asteraceae, Compositae, Lauraceae, Myrtaceae, Piperaceae, Zingiberaceae, Poaceae, and Rutaceae (Ebadollahi and Sendi 2015). The members of these botanical families comprise a variety of bioactive compounds that exhibit insecticidal properties (Table 1). The quantitative and qualitative production of EOs can be influenced by various external factors, including photoperiods, light quality, climate and seasonal variations, moisture, salinity and soil type, in addition to the overall development stage of the plant (Sangwan et al., 2001). Components of the EO can be separated into volatile and non- volatile residues. Comprising 90% to 95% of the oil, the volatile fraction comprises monoterpenes, sulfenoids, their oxygenated derivatives, aliphatic aldoes, alcohols, and esters, whereas non-volatile residues account for the remaining 1-10%. Hydrocarbons, fatty acids, sterols, carotenoids, lipids and flavonoids are among these substances (Zebec et al., 2016).

EOs consist of lipophilic compounds that have the ability to induce toxicity, control insect proliferation, function as phagodeterrents, repellents, and synergists (El-Wakeil, 2013), impede oviposition, and even attract insects. Metabolic eugenol and geraniol, are efficacious attractants that have been employed to lure the Japanese beetle, *Popillia japonica* Newman. It has been reported that fruit flies, *Bactrocera dorsalis* (Hendel), can be attracted with methyl-eugenol (Vargas et al., 2000). In contrast to mint oil, garlic oil exhibited a higher efficacy in repelling *Aphis craccivora* Koch (Ahmed et al., 2007). *Tribolium castaneum* (Herbst.). The fifth instar of the red rust flour beetle is repulsive to essential oil extracted from *Tagetes terniflora* (Pandey et al., 2018) and *Artemisia vulgaris* (Wang et al., 2006). The EO extracted from turmeric leaves exhibits antifeedant properties against both adult and larval stages of the rice weevil, *Sitophilus oryzae* (L.), *Rhyzopertha dominica* (L.), specifically the lesser grain borer (Tripathi et al., 2002). Garlic EO has antifeedant properties against *T. castaneum* and *S. oryzae* (Chaubey, 2016). EOs inhibit reproduction and egg hatching in addition to killing adults and larvae. The oviposition inhibition of *T. castaneum* using the fumigation method with α-pinene and β-caryophylene, either individually or in binary combination was studied by Chaubey (2012). The oviposition-deterrent properties of cymene, pulegone, eugenol and citronellal were assessed against *Aedes aegypti* (L.) (Waliwitiya et al., 2009). The toxicity of essential oils was found to be promising through contact action or fumigation (Chaubey, 2007). As a fumigant, lemon grass oil is exceptionally lethal to *R. dominica* and *S. oryzae* (Tewari and Tiwari, 2008). The EO of *Pistacia lentiscus* has a negative impact on the fecundity and reproduction rate of the Mediterranean flour moth, *Ephestia kuehniella* (Bachrouch et al., 2010). EO derived from geranium grass inhibits the development of the pulse beetle, *Callosobruchus maculatus* at all stages (Ketoh et al., 2006). The growth and pupation of *R. dominica* are inhibited by mandarin orange oil (Abbas et al., 2012).

Mode of action

Distinct modes of action are exhibited by EOs in their insecticidal properties. EOs can be absorbed by insects via the epidermis, inhalation, or ingestion. They induce mortality through the activation of diverse signalling mechanisms and insecticidal pathways due to their well-permeable nature and lipid-based chemical structure (War et al., 2012). They are also effective synergists and can enhance the bioavailability of products that are administered concurrently (Jensen et al., 2006). The entry point, molecular weight and mechanism of action of the toxin are the principal determinants of toxicity (Devrnja et al., 2022).

Table 1. Bioactive compounds of plant essential oil against pests

S. No	Plants name	Bioactive compound	Insect pests	References
1	Neem	Azadirachtin	*Helicoverpa armigera*	Dawkar et al., 2019
2	Citrus	Limonene	*Tribolium castaneum*	Babarinde et al., 2020
3	Eucalyptus	1,8-Cineole	*Tribolium castaneum* *Rhyzopertha dominica*	Mossi et al., 2011
4	Mint	Menthol	*Callosobruchus maculatus*	Saeidi and Mirfakhraie (2017)
5	Black pepper	Piperine	*Rhynchophorus ferrugineus*	Hussain et al., 2017
6	Coriander	Linalool	*Lasioderma serricorne* *Tribolium castaneum*	Sriti et al., 2022
7	Rosemary	a-pinene	*Sitophilus oryzae*	Khani et al., 2017
8	Teabush tree	1,8-Cineole	*Brevicoryne brassicae* *Plutella xylostella*	Tia et al., 2021

Inhibitors of Acetylcholineesterase: Acetylcholineesterase is the enzyme that catalyses the hydrolysis of acetylcholine, the primary neurotransmitter involved in transmitting nerve impulses between neurons and involuntary muscles. The neurotoxic pesticides (Park et al., 2016, Bhavya et al., 2022) primarily target this enzyme. Studies have shown that certain elements of EO function as competitive inhibitors, whereas others function as uncompetitive inhibitors (López et al., 2015). They consist of monoterpenoid compounds that function as enzyme analogues, competing with one another to attach to the active site of the enzyme. Competitive inhibitors change the activity of the enzyme and the production of products because they often bind to the complex between the enzyme and the substrate rather than the enzyme alone. Their neurotoxic effects may resemble to those of organophosphates or carbamates, indicating their insecticidal properties (Jankowska et al., 2017).

Alternant of GABA Receptors/ octopaminergic and mitochondrial functions: GABA, an inhibitory neurotransmitter, is present in the nervous system and muscles of insects, where it binds to particular receptors called GABARs. The GABA receptors are responsible for the transport of chloride ions via chloride-mediated channels in neurons, which can disrupt the activity of GABA synapses (Anderson and Coats, 2012). EO enhance the absorption of chloride ions caused by GABA (Tong and Coats, 2010). They can also modify octopamine (OA), a neurotransmitter, neurohormone, and neuromodulator present in the neurological system, neuroendocrine cells and hemolymph (Perić-Mataruga et al., 2006). The hormone affects multiple types of insect activity and is crucial in the insect distress response, aggressive behaviour and social behaviour (Zhou et al., 2008). OA interacts with G protein-coupled membrane receptors (OARs) and stimulates the enzyme adenylyl cyclase, which catalyses the conversion of ATP to cAMP. This leads to an elevation in cAMP (a signalling molecule) and the stimulation of protein kinases A (PKA) and phospholipase C (PKC). It elevates the levels of calcium inside the cells, leading to notable alterations in cell functioning (Farooqui, 2012). EOs can modify the functioning of mitochondria in many ways, such as blocking the activity of ATPase, altering the ratio of oxygen to carbon dioxide and inhibiting the passage of electrons through the hydrogen carrier (Liao et al., 2010). The mechanism of action was initially discovered in adult *S. oryzae* when the respiratory enzyme, ATPase was inhibited when exposed to different essential oils (Abdelgaleil et al., 2010).

Why nanotechnology in essential oils?

Although EOs have favourable characteristics and are generally recognised for their insecticidal effects, they also certain difficulties in using them. These compounds are extremely unstable and can easily break down. They also have little solubility in water. Their chemical makeup is highly variable and depends on various factors such as plant variety, time of year and climate (Fabroni et al., 2012), and air, radiation, humidity, and extreme temperatures that can cause rapid evaporation and degradation of certain active components. Standardisation is therefore necessary to control this variability. Nanomaterials can be used to create nano formulations of EOs, which can help overcome some challenges. By incorporating EOs into nanomaterials, the active components are shielded from degradation and evaporation, resulting in improved stability, durability and dispersibility (Campolo et al., 2017). Nanoencapsulation is a technique used to shield the core material from harmful environmental factors such light, moisture and oxygen. It also helps to prevent unwanted consequences in its properties like odour and volatility (Lai et al., 2006).

Types of nanoformulations

Nanoformulation contains substances with a size of 1-100 nanometers and is more efficacious compared to utilising the bulk material. In addition, they decrease the amount of pesticides used and enhance the retention of the active ingredient (Liu, 2006). Nanoemulsions, nanostructured lipid carriers, and polymeric nanoparticles are often employed formulations (Esmaili et al., 2021).

Nanoemulsions are colloidal dispersions that merge hydrophobic and hydrophilic phases, specifically water and oil at the nanoscopic scale (Singh et al., 2017). These emulsions can be classified as either oil-in-water (O/W) or water-in-oil (W/O) types, as shown in Fig. 2. The EOs are often composed of synthetic non-ionic surfactants, such as Tween 80 or Span® 80. O/W nanoemulsions are frequently employed due to the lipophilic property and solublility of EOs in water (Palazzolo et al., 2018). High-energy techniques encompass ultrasonic, high-pressure homogenizer and microfluidizer-assisted fabrications, whereas low-energy techniques involve phase inversion temperature, phase inversion composition and solvent diffusion or spontaneous emulsification (Esmaili et al., 2016). Lipid-based nanocarriers are based on lipids for delivering a variety of water-soluble organic compounds due to their hydrophobic properties. Furthermore, they

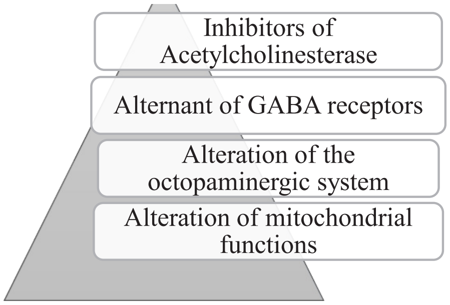

Fig. 1. Mode of actions of EOs in insects

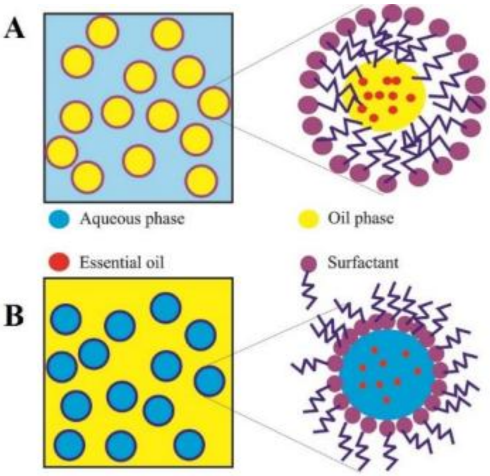

Fig. 2. A: oil in water nanoemulsion,
B: water in oil nanoemulsion (Source: Esm)

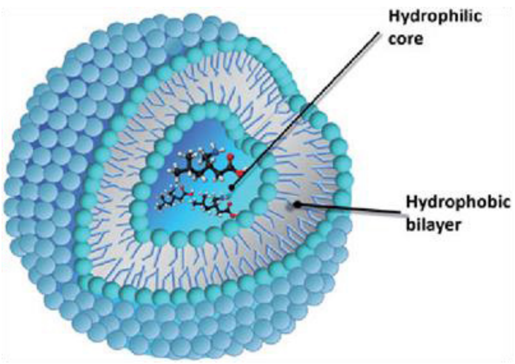

Fig. 3. Liposome
Source: (Ioele et al., 2021)

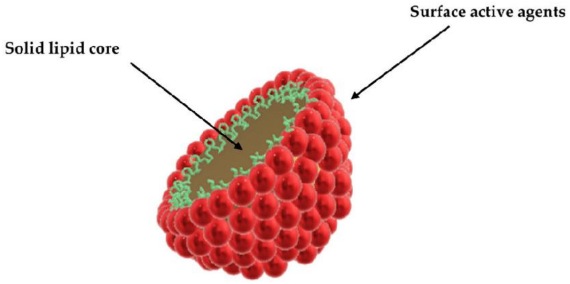

Fig. 4. Solid lipid nanoparticle
Source: (Zoabi et al., 2021)

are more biocompatible and capable of encapsulating highly lipid-rich active substances than polymer nanoparticles (Carbone et al., 2014). The phospholipid and cholesterol-based liposomes were hydrated in aqueous medium to form a bilayer spherical structure (Fig. 3). Incorporating cholesterol into the liposomal structure enhances the bilayers' stability and reduces cargo leakage (Mishra et al., 2018). Furthermore, the encapsulation of EOs in liposomes helps to protect the liposomes from oxidation and evaporation (Trucillo et al., 2020). The most commonly used liposome production methods include thin-film hydrating, freeze drying, reversing evaporation and ethanol injection (Zahin et al., 2020). The preparation of solid lipid nanoformulation (SLN), a biodegradable and biocompatible substance, involves dispersing physiological lipids (Fig. 4) and stabilising surfactants in an anhydrous phase with a resolution of 50 to 200 nanometers (Osanloo et al., 2018). At certain temperature, this substance exists in a solid state and is formulated to release its contents in a regulated manner (Lim et al., 2012). Nanostructured Lipid Carriers (NLC) are Lubricant nanoparticles comprised of both solid and liquid lipids (Fig. 5). They possess a reduced melting point in comparison to SLN. At ambient temperature, they are capable of retaining their solid-state state. Microemulsion, solvent displacement, and high-pressure homogenizer are methods of preparation of NLC Polymeric nanoparticles are Colloidal polymer particles having size range from 1 to 200 nm (Sur et al., 2019). They may be bio-degradable or non-degradable and easy preparation process. The low toxicity are the advantage of polymer particle (Ferrari et al., 2018). Nanocapsules are heterogeneous structures comprised of a hydrophobic active constituent encased in a polymeric membrane at their centre. On the other hand, nanospheres are homogeneous vesicular structures characterised by the uniform dispersion of the active constituent within the polymer matrix (Fig. 6). Among the varieties of polymeric nanoparticles, these two are the most frequently employed. The synthesis of polymeric nanoparticles can be achieved through the utilisation of natural or semi-synthetic polymers, including chitosan, hyaluronic acid and albumin; cellulose derivatives, including carboxymethyl cellulose and hydroxypropyl methylcellulose; and poly (lactide-coglycolide), polyglycolic acid, and polyacrylic acid (Teimouri et al., 2018). In addition, nanoparticles are generated through a multitude of techniques, including electrospray, solvent evaporation, ionotropic gelation and nanoprecipitation (George et al., 2019).

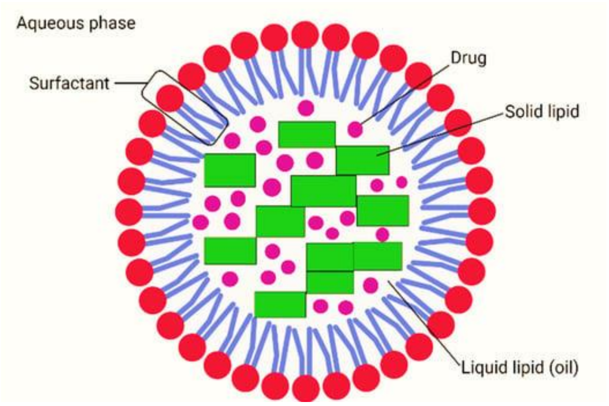

Fig. 5. Nanostructured lipid carriers
Source: (Syed et al., 2022)

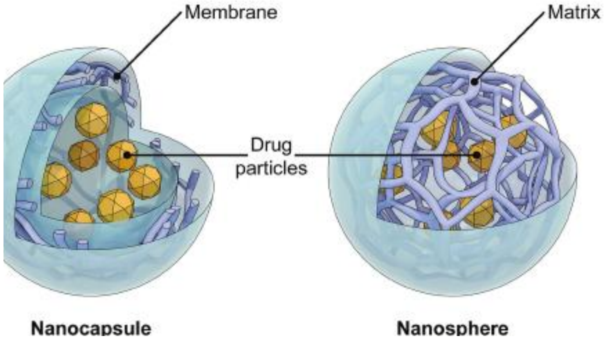

Fig. 6. Nanocapsule and Nanosphere
Source: (Suffredini et al., 2013)

CONCLUSIONS

Insects that harm crops present a major risk to agriculture, resulting in considerable reductions in agricultural yield and incurring economic harm on a global scale. Conventional pest control techniques, such as chemical pesticides, have caused concerns because of their negative impacts on the environment and human health. Consequently, there is a growing demand for the development of alternative and sustainable ways for controlling pests. An effective method involves utilising essential oils and natural plant extracts that are recognised for their insecticidal characteristics. Recently, scientists have investigated the possibility of using essential oil nano-formulations as a more efficient and precise approach to controlling insect pests. Rosemary oil had the highest cumulative mortality rates against *E. cautella* (Sabbour and Abd El-Aziz, 2019). Chitosan NP encapsulated-*Piper nigrum* oil exhibited greater fumigant toxicity compared to pure oil when tested against *S. oryzae* and *T. castaneum* (Rajkumar et al., 2020). The antifeedant index of the nanoemulsion of patchouli essential oil is higher compared to its coarse emulsion when tested against the tobacco leaf eating caterpillar, *Spodoptera litura* (Manjesh et al., 2022). The nanoformulations of lemon peel essential oil have been found to have a more detrimental effect on the army worm, *Agrotis ipsilon*, compared to its pure form (Ahmed et al., 2023). This paper provides a concise overview of the favourable characteristics of essential oil in combating insect pests and further enhances these features through the integration of nanotechnology.

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AUTHOR CONTRIBUTION STATEMENT

All authors contributed equally.

CONFLICT OF INTEREST

No conflict of interest

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