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Review Article
Essential Oils Development Through Nanoparticles for Managing Stored Product Insect Pests

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Abstract
Essential oils are biodegradable nature, systemicity after application, ability to modify the conduct of target pests and good security profile. This review was aimed to focus on the plant nanopesticides for the improvement to control stored product pests. The Essential oils (Eos) are portrayed by fast corruption, selectivity, low mammalian harmfulness and negligible effects on the environment. Recent investigations indicated that some chemical constituents of these oils interfere with the octopaminergic nervous system in insects. The worldwide post-harvest grain losses were caused by insect pests (Coleoptera and Lepidoptera), which infest sustenance grains and seeds in the fields and in addition in the stores. Control of these insect pests depends primarily on the utilization of chemical insecticides; botanical insecticides can be prescribed as ecochemical choices. Essential oils can be grouped according to their mode of actions or the way oil destroys or controls the target pest as well the action sites. As this target site is not shared with mammals, most essential oil chemicals are relatively non-toxic to bees, fish and mammals. Nanotechnology is rising as a highly gorgeous tool for formulation and delivery of insecticide active components as well as enhancing and offering new active ingredients for controlling many of stored product insect pests over the world. This strategy will be very useful either in the field or in the storages, if it possesses high amorphous silica content with uniform size distribution. Nanoparticles offer a greater surface part and circulate easily in insects; therefore, they are considered special harness substances, as well as they can be removed during 24 h from the insect body. Insecticides based on essential oils have verified efficacy against stored product insects. Direct sprays, fumigants and granular formulations are the known methods for applying nanomaterials. These features showed that the plant essential oils could be used in a variety of ways to control stored product insects.

Key words: Fumigation, nanopesticides, essential oils, botanical insecticides, repellent and antifeedant, nanoformulations, stored product insects

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INTRODUCTION

The worldwide post-harvest grain losses caused by insect pests harm and different bioagents[1-3] run from 10-40%. Two main groups of insect pests, for example, Coleoptera (beetles and weevils) and Lepidoptera (moths and butterflies) include the most economically important post-harvest insects. They infest sustenance grains and seeds in the fields and in addition in the stores. The major stored pests are *Sitophilus oryzae*, *Rhizopertha dominica*, *Tribolium castaneum*, *Sitotraga cerealella* and *Bruchus chinensis*. *Callosobruchus chinensis* (L.) is a serious pest of chickpea, mungbean, peas, cowpea, lentil and ashar. They cause physical harm, grain spilling or weakening, loss of weight and quality, force misfortune, germination diminishment, lose an incentive for showcasing and utilization or planting[3].

Most of them have the habit of destroying more than what they eat[4]. It has been estimated that about 2.5 million t of pesticides are used on crops each year and the worldwide damage caused by the greater part of them have the propensity for decimating more than what they eat[4]. It has been evaluated that 2.5 million t of pesticides are utilized each year and the overall damage caused by pesticides comes to $100 billion yearly. The reasons for this are the high toxicity and non-biodegradable properties of pesticides. Also, the residues affect public health[5]. Control of these insect pests depends primarily on the utilization of chemical insecticides, for example, pyrethroids, organophosphorus compounds and fumigants, for example, phosphine and methyl bromide[6,7]. The EOs seems, by all accounts, to be promising aromatic plants and their vegetable oils are among the most broadening of the methodologies inalienable in IPM is vital for better environmental protection. Plant essential oils have generally been utilized to kill or repulse insects[8], being considered as other option to stored grain conventional pesticides in view of their low toxicity to warm blooded well evolved creatures and their high volatility[9,10].

In excess of 1,660 insect species have been accounted for to be related with stored-food[11]. The development and advancement of all stored product pests is needy upon temperature, relative humidity and the accessibility of sustenance assets. The advancement times will fluctuate with temperature; abstain from food and other natural and ecological variables. This association with conduct impacts the capacity to recognize nearness of insects, utilizing traps[12].

They have great ecotoxicological properties (low lethality to people, promote corruption and lower natural effect) making them reasonable to overseeing insects in natural cultivating[13]. These essential oils are optional metabolites and incorporate alkaloids, amides, flavones, lignans, neolignans or phenols which are essential in insect plant relationship[14]. They are found in glandular hairs or secretory depressions of plant-cell divider and are available as beads of liquid in the leaves, stems, bark, blooms, roots as well as natural products in various plants. The fragrant attributes of essential oils give different capacities to the plants including (i) Attracting in or repulsing insects, (ii) Shielding themselves from warmth or cool and (iii) Using compound constituents in the oil as resistance materials. Huge numbers of the essential oils have different uses as nourishment added substances, flavorings and segments of beauty care products, cleansers, aromas, plastics and as tars[13,14].

Plants are the most effective makers of phytochemicals in nature including optional metabolites that are utilized by the plant as protection framework against stored product insect pests[15]. The goal of this work was to focus on the plant nanopesticides for the improvement of novel definitions to control stored product pests. To shed light on the EOs importance for stored product insect control, their mode of action and their impact on insect management development, because of their biodegradable nature, systemicity after application, capacity to alter the behavior of target pests and favourable safety profile, it is hoped that nanoformulations of essential oil pesticides play a significant role in achieving evergreen revolution.

IMPORTANCE OF ESSENTIAL OILS

Aromatic plant species included about 17500 among higher plants and almost 3000 essential oils are identified, of these oils 300 have been used for cosmetic and perfume industries[16,17]. Essential oils and their derivatives are considered to be safe alternative means of controlling many harmful insects. Their rapid degradation in the environment reduced the polluting substance and decreases the risk of developing resistance and they are also safe to parasitoids and predators[18]. Plant essential oils are characterized as any unpredictable oils that have solid sweet-smelling parts and that give particular smell, flavor or fragrance to a plant and have a generally lower density than that of water[17]. There are numerous resources of essential oils (e.g., garlic oil or capsicum oleoresin) (Table 1).

The fragrant qualities of basic oils give different capacities to the plants including (i) Larvicidal and antifeedant activity[19], (ii) Capacity to delay development, adult emergence and fertility[20], (iii) Oviposition deterrence[21], (iv) Repellence effects[22], (v) Protecting themselves from warmth or cool and (vi) Using compound constituents in the oil as protection materials. Most

Table 1: Egyptian medicinal and aromatic plants, which can be used as botanical insecticides

English name	Scientific name	Family name	Used part(s)
Lantana	*Lantana camara* L.	Verbenaceae	Leaves+flowers
Eucalyptus	*Eucalyptus globulus* Lab.	Myrtaceae	Leaves
Lemon grass	*Cymbopogon citratus* Stapf	Gramineae	Leaves
Datura	*Datura stramonium* L.	Solanaceae	Leaves+fruits
Nerium	*Nerium oleander* L.	Apocynaceae	Leaves
Althea	*Althaea officinalis* L.	Malvaceae	Roots+leaves
Neem	*Azadirachta indica* A. Juss.	Meliaceae	Leaves+fruits
Visnaga	*Ammi visnaga* L.	Apiaceae	Fruits
Basil	*Ocinum bacilicum* L.	Lamiaceae	Leaves
Pipermint	*Mentha pipermita* L.	Labiatae	Leaves+flower tops
Spearmint	*Mentha spicata* L.	Lamiaceae	Leaves+flower tops
Capsicum	*Capsicum frutescens* L.	Solanaceae	Frutis
Garlic	*Allium sativum* L.	Lilliaceae	Cloves
Castor beans	*Ricinus communis* L.	Euphorbiaceae	Frutis
Thymue	*Thymus vulgaris* L.	Lamiaceae	Leaves
Marjoram	Majorana hortensis L.	Lamiaceae	Leaves
Pelargonium	*Pelargonium graveolens* L'Hér.	Geraniaceae	Herbs
Pomegranate	*Punica granatum* L.	Punicaceae	Pomegranate peel
Melissa	*Melissa officinalis* L.	Lamiaceae	Herbs

Source: El-Wakeil[102]

EOs involved monoterpenes intensifies that contain 10 carbon molecules frequently masterminded in a ring or in non-cyclic shape and also sesquiterpenes which are hydrocarbons including 15 carbon particles[23]. A monoterpenoid, linalool was established to performance on nervous system which affects ion transport and helps to release the acetylcholine esterase into insects[24]. The most dominating gatherings are cyclic mixes with saturated or unsaturated hexacyclic or an aromatic framework[25]. Several essential oils have bactericidal, fungicidal and insecticidal properties[17].

EFFICACY OF BOTANICAL ESSENTIAL OILS

Stored food products are inclined to post harvest misfortune in quality and amount because of invasion by various gatherings of insects. Control of these insects depended on the utilization of manufactured pesticide sprays, for example, pyrethroids, organophosohorous pesticides and fumigants, phosphine and methyl bromide[6,7,26-28]. These chemicals are basic and financially savvy yet their monstrous utilize caused several problems predominantly resistant strains of insects and natural contamination with negative reactions on human safety and disturbing biological control framework[7,29,30].

So, as to get free the impacts of customary engineered pesticides, biopesticides in view of essential oils (EOS) seem, by all accounts, to be a corresponding or elective safe technique in crop production and integrated pest management[23,31,32]. The EO_S indicated harmful, anti-agents and anti-feedant impacts on stored product insect pests[8,33-37]. In spite of these promising properties, issues related with the EO unpredictability, poor water dissolvability and inclination for oxidation must be settled before they are utilized as an elective pest control framework. Antifeedant effect of 1,8-cineole has additionally been exhibited against *T. castaneum*[25]. In another investigation[38], a terpenoid lactone showed antifeeding action against *Sitophilus granarium*, *Trogoderma granarium* and *T. confusum*. Nourishing prevention exercises of leaf fundamental oil of *Curcuma longa* against *Rhyzopertha domestica*, *S. oryzae* and *T. castaneum* were accredited to the nearness of monoterpenes and dihydrocarvone[39]. Essential oils extracted/got from *Curcuma longa* and *Zingiber officinale* have additionally been discovered compelling as efficient anti-feedant and insect growth regulators[40,41]. Essential oils of majoram and rosemary oil were evaluted against onion thrips; these oils had an anti-feedant effects[42,43]. The oviposition deterrent index was 100% when mung bean seeds were treated with *Acorus calamus* oil[37]. These oils are rich in, linalool, eugenol, carvacrol and thymol that have impacts against insects and fumigant movement in above cases could be ascribed to them[25].

Fumigant toxicity of essential oils: Fumigants are pesticides acting in the vapor or vaporous stage on the objective pests[44]. The most widely recognized strategy used to control stored product pests is fumigation since it is compelling against most species, enables the insecticide spray to effectively achieve the insect pest inside the grain and leaves little buildups[45-48]. In fumigant danger test, the best effect was found with the EO from eucalyptus with a KT50 estimation[49] of 8.34 min.

The substances are transported to various tissues through the system of tracheas and tracheoles, hence achieving their site of activity[50,51]. The poisonous impact of a substance relies upon various toxic kinetic steps, yet in addition on its physicochemical properties. The EO segmented with high vapor pressure can volatilize effortlessly and are by and large more dangerous than those with low vapor pressures[52]. The fumigant lethality of 28 vegetable oils separated from different flavor and herb plants and some of their real constituents were surveyed for many coleopteran adults. The EOs of oregano and exquisite were exceptionally powerful and caused 100% mortality of *Plodia interpunctella* and *Ephestia kuehniella*[53-55].

The fumigant poisonous quality of essential oils was evaluated against stored product insects. The *T. castaneum* was observed to be the most resistant, contrasted and *S. oryzae*, *R. dominica* and *O. surinamensis*, to most essential oils tried[2,9]. Their findings reported that fumigant quality and repellence of this oil was vitally impacted by concentration as well as time after treatment. The oil caused 98, 99 and 100% mortality of tested insects. Fumigant toxic effect investigated by various essential oils and their monoterpenoids were likewise assessed against the bean weevil *Acunthoscelides obtectus* and *S. cerealella*[56]. The *S. oryzae*, *C. chinensis* and *Corcyra cephalonica* are the most dangerous insect pests of grains[57-60]. Producers are moving far from utilizing methyl bromide as post-harvest fumigant due to its ozone-draining nature and phosphine, because of rehashed use as it upsets organic framework prompting the resistance[61,62].

To control these insect pests without polluting the environment, biological products have been screened for their insecticidal efficacy. The lethality of fundamental oils to stored product insects is impacted by the synthetic creation of the oil, which thusly relies upon the source, season and natural conditions, strategy for extraction, time of extraction and plant part utilized[63,64]. Among the fundamental oil components, the monoterpenoids have drawn more consideration for fumigant efficacy against stored product insects[65-67]. The monocyclic monoterpene 1, 8-Cineole is the main component of various Eucalyptus which having fumigant activity against *T. castaneum*[66,68]. Dangerous impacts of couple of essential oils were surveyed to illustrate conceivable fumigant and contact efficacy against *R. dominica, S. oryzae* and *T. castaneum*[63].

The leaves of *Pinus longifolia* ordinarily known as Pine, yield oil which is generally utilized for the assurance from mosquito chomps[69]. It is likewise utilized as a natural drug in some provincial regions in India[69]. Essential oil from *Coriandrum sativum* contains several compounds including linalool, camphor, gterpinene, limonene, geraniol and carvone[70]. The essential oil of *C. sativum* showed volatile toxicity to stored product insect pests[70,71]. In prior studies, fundamental oil from *C. sativum* showed great fumigant, repellent and poisonous properties against larvae and grown-up of *T. castaneum*[60,72]. Additionally, the insecticidal action of three basic oils like pine, eucalyptus and coriander were examined to stored product pests[73].

Five fundamental oils in particular Cinnamon oil, Clove oil, Rosemary oil, Bergamot oil and Japanese Mint oil were against *C. chinensis* grown-ups in view of fumigation technique[74]. The insecticidal action of fundamental oils against 4 stored insect pests[75-79]. The efficacy of essential oil based on *Ocimum americanum* against *C. maculatus* adults[80]. The insecticidal properties of some vegetable oils against *C. maculatus* have been illustrated[81-85]. Tests were directed to decide lethals focuses (LC_{50} and 9_0) and mortality (fumigation to control bruchids in storage[86,87]. Fundamental oils have been perceived as an imperative source of biopesticides.

Contact toxicity of certain essential oils: Since it was suggested that EOs exerted their efficiency by different modes of action, (a) Act on insect respiration like a fumigant[57,66], (b) Act through contact or ingestion, (c) Prevent fertility[20], (d) Have an antifeedant efficacy[19], (e) Have a repellent effect or change insect behavior[22] and (f) Have a combination of all the previously mentioned actions[9]. The estimation of EOs efficacy against several lepidopterans is directed on acute toxicity by fumigant, contact or oral exposure[88,89]. The EOs have attracted the scientists in recent years as potential pest control agents[90]. The EOs are described by fast corruption, selectivity, low mammalian harmfulness and negligible effects on environment[91]. For instance, EOs from bergamot and geranium gave contact toxicity on *T. castaneum* and *R. dominica*. Essential oils were perceived as a vital wellspring of biopesticides especially in the recent years as potential pest control agents[89,92,93]. According to conformation of EOs, which included terpenes (mono- and sesquiterpenes and derivatives) mixtures. The EOs from bergamot and geranium showed contact toxicity on *T. castaneum* and *R. dominica*[91].

The partition coefficient of components of EOs may affect their penetration through the lipophilic portion of the cuticle, the interaction with hydrophobic compartments, the degradation of the essential oil component, movement of the compound to the target site[94] and the ability of the insect to excrete the compound[95]. It is known that EOs components with high log p-values are generally more toxic by contact than those with low ones[96]. By moisture and by detoxification enzymes, hence they present less persistence and reduced risks to non-target organisms[97]. More several applications and precise timings are therefore needed[98]. The EOs can cause lethal and sublethal effects on insect biology[32,90]. Some essential oils namely, garlic, rosemary, mint, thyme, geranium, jojoba and moringa in comparison with Neem formulations were screened for against *C. maculatus*. Insect growth and reproduction are affected by applying EOs[37,99], the deleterious effects of EOs on growth, development and nutrition of insect lepidopteran are recorded[88,90,100].

MODE OF ACTION OF ESSENTIAL OILS

Mode of action means studying the specific biochemical interface through which an essential oil produces its effect. Generally, the mode of action comprises the specific enzyme, protein or biological step affected[101]. Knowing the mode of action is integral for researchers to improve the quality and continuous ability of a product. To understand how oils work, it is necessary to recognize how the pest's targeted systems normally function. It is important to know the modes of action of essential oils, because it is used to avoid resistance development[102].

Mode of action types: There are many actions could be proceeded by plant essential oils such as; contact and fumigant insecticidal activities against stored product pests (*Acanthoscelides obtectus*)[103]. Lethal toxicity as well as Knockdown activity through contact were confirmed in the American cockroach[104], the German cockroach and the housefly[94]. Results of those studies concluded an observable neurotoxic site-of-action. Certain essential oil monoterpenes are effective inhibitors of acetylcholinesterase *in vitro*[105], but that achievement may not be related with toxicity to insects *in vivo*. The physiological effectiveness of essential oils on insects caused symptoms that suggested a neurotoxic mode of action[106]. Linalool, a monoterpenoid, acted on the nervous system, disturbing ion transport and releasing of acetylcholine esterase into insect pests. Octopamine has a biological role in insects, acting as a neurotransmitter, neurohormone and circulating neurohormone-neuromodulator[23] (Fig. 1). Octopamine uses its effects through interaction with 2 classes of receptors which on the basis of pharmacological criterion have been identified octopamine-1 and octopamine-2 interrupting the octopamine functioning in breakdown of nervous system, octopaminergic system displays a biorational target for insect control[102].

Acting of limonene and linalool in insects are not fully clear. Limonene (source, *Carum carvi* (L.)) may cause an increase in the impulsive activity of sensory nerves. This sensitive activity sends false signals to motor nerves and results in twitching, be deficient in coordination and shocks. The central nervous system may also be affected, resulting in other encouragement of motor nerves. Enormous over stimulation of motor nerves helps to rapid knockdown paralysis. Adult fleas and other insects could recover from knockdown, however, unless limonene is harmonized by piperonyl butoxide (PBO). Linalool is also synchronized by PBO[107-109].

Mode of action summary: Essential oils can be categorised into groups according to their mode of actions or the way oil destroys or controls the target pest. This is also referred to the primary site of action. For example, one oil may affect insect nerves, while another may affect moulting. There are many mode of actions for various essential oils shown in Table 2.

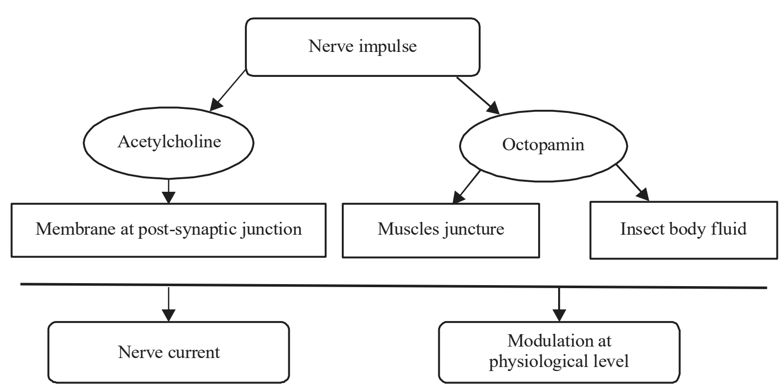

Fig. 1: Target sites in insects as possible neuro-transmitter mediated toxic of essential oils (Tripathi *et al.*[23])

Table 2: Mechanism of action of pesticides of plant origin

Systems	Mechanism of action	Compound/plant	Plant source	References
Digestive system	Antifeedant	Lavender oil	*Lavandula angustifolia*	Isman[8] and Abdelgaleil and El-Aswad[107]
Dermal	Contact	Lavender oil	*Lavandula angustifolia*	Shaaya *et al.*[9] and Abdelgaleil *et al.*[77]
Respiratory system	Fumigant toxicity	Lavender oil, Eucalyptus oil, Patchouli oil, Phenolic acids, Eucalyptol, Menthol	*Lavandula angustifolia*, *Eucalyptus obliqua*, *Pogostemon heyneanus*, *Ocimum basilicum*, *Hyptis* spp., *Mentha piperita*	Shaaya *et al.*[9], Keita *et al.*[81] and Ketoh *et al.*[82]; Sanon *et al.*[83] and Ngamo *et al.*[84]; Abdelgaleil *et al.*[77] and Rani[73]
Nervous system	Knockdown	Monoterpenes, limonene	*Carum carvi*	Abdelgaleil and El-Aswad[107], Abdelgaleil *et al.*[108] and Rattan[109]
Digestive system	Nutritional effects	Lavender oil	*Lavandula angustifolia*	Isman[8]
	Repellent	Lavender oil, basilica oil	*Lavandula angustifolia* *Ocimum gratissimum*	Ngoh *et al.*[104] and Fields *et al.*[110]
Reproductive system	Reproduction inhibitory	Eucalyptus oil, Patchouli oil, Phenolic acids	*Eucalyptus oblique*, *Pogostemon heyneanus*, *Ocimum basilicum*	Raja *et al.*[1] and Papachristos and Stamopoulos[111]
Cholinergic system	Inhibition of acetylcholinesterase (AChE)	Essential oils	*Azadirachtina indica*, *Mentha* spp., *Lavendula* spp.	Ngoh *et al.*[104] and Kavallieratos *et al.*[112]
GABA system	GABA-gated chloride channel	Thymol, silphinenes	*Thymus vulgaris*	Ratra and Casida[113] and Priestley *et al.*[114]
Mitochondrial system	Sodium and potassium ion exchange disruption	Pyrethrin	*Crysanthemum cinerariaefolium*	Casida[115]
Octopaminergic system	Octopaminergic receptors	Essential oils	*Cedrus* spp., *Pinus* spp., *Citronella* spp., *Eucalyptus*	Kostyukovsky *et al.*[105] and Enan[50]
	Block octopamine receptors by working through tyramine receptors cascade	Thymol	*Thymus vulgaris*	Enan[16,117]
Miscellaneous	Hormonal balance disruption	Azadirachtin	*Azadiractina indica*	Copping and Menn[118]

Source: El-Wakeil[102]

EFFICIENCY OF NANOPARTICLES TO MANAGE STORED PRODUCT INSECTS

In last years, consumer awareness of the health hazard from residual toxicity and insect resistance to the pesticides has led the researchers to look for alternative approachs[119]. One of these alternatives is using of inert dusts such as; clay, rock phosphate, sand, ashes, diatomaceous earth as well as synthetic silica that have been applied as insecticides for thousands of years and are also used in modern storages. In recent years, research on inert dusts as a stored-grain control materials began[120] in the 1920's. Normally, insects used variety of lipids on their cuticle for the defense of water barrier on their bodies thus avoiding the death from dryness. A mechanism used by the nanoparticles that becomes absorbed into the cuticle lipids by physisorption thus causing insect death exclusively by physical ways[121].

Nanoemulsions are emulsions whose tiny size is uniform and extremely small with the size ranges from 20-200 nm. The use of nanopesticides would be a contemporary measure for the control of insect pests and reducing the toxic effect of synthetic insecticides on the environment[122-124]. Poly vinyl alcohol (PVA) is a water soluble polymer based on petroleum resources with unique properties such as good transparency, lustre, antielectrostatic properties, chemical resistance and toughness[125]. Its water solubility, reactivity and quick biodegradability make it a possibility useful material in agricultural and water treatment spots. This strategy will be useful to control the stored product insects in the storages[123,126].

Types of nanoformulations: There are many forms of nanoparticles used against stored grain pests; silver nanoparticles like; $AgNO_3$, silica like; diatomaceous earth, synthetic silica (SiO_2), sands, Silica Aerogel Aluminium oxide (Al_2O_3), Zinc oxide (ZnO), Copper oxide (Cu_2O), Titanium dioxide (TiO_2). The metal nanoparticles can be used for preparing such formulations which will be used as insecticides[127,128]. Nanostructured materials are frequently fabricated using chemical techniques. It is very important to recognize the target nanoparticles through the scanning tunneling microscope (STM). A great potential for application in environmental protection has been made known by nanotechnology researchers[129,130]. Nanosilica, a type of unique nanomaterial is prepared from silica. In recent projects, it has been found to be useful as a catalyst and most importantly has been obtained to be useful as nanopesticide. Barik *et al.*[121] have assessed the use of nanosilica as nanoinsecticide. Nanoparticles may be applied in the new formulations of insecticides preparation against different insect species[131-133].

Synthesis of silica nanoparticles: Silica nanoparticles are made by hydrolysis and concentration of Tetraethyl Ortho Silicate (TEOS) in ethanol and then adding ammonia as catalyst which used for the synthesis of silica nanoparticles according to protocol of Ibrahim *et al.*[134]. In brief, suitable quantities of 99% ethanol, ammonia and deionised water were taken and mix carefully for 5 min. Then proper amount of TEOS was added droplet for 24 h at room temperature. Initially, solution including proper amounts of absolute ethanol, ammonia and deionized water were stimulated for 5 min to ensure complete mixing. Then an appropriate amount of TEOS in 99% ethanol was added to the above solution and the reaction proceeded according to reactants concentrations at ambient temperature for 24 h. Subsequently, the colloidal solution was isolated by high-speed centrifuge and the silica particles had been washed by 99% ethanol for 3 times to remove undesirable particles followed by drying in oven at 100°C for 2 h to prevent continuous reaction[135].

Characterization of nanoparticles: Nanoparticles are classified according to their size, morphology and surface charge, using atomic force microscopy, scanning electron microscopy as well as transmission electron microscopy. Traits such as; the size circulation, average particle diameter, charge affect the physical solidity and the *in vivo* distribution of the nanoparticles[136,137]. Electron microscopy techniques had been used to determine the properties like surface morphology, size and overall shape. Structures like physical solidity and redispersibility of the polymer dispersion as well as their *in vivo* performance are affected by the surface charge of the nanoparticles as mentioned by many scientists like Ubrich *et al.*[138] and Rahman *et al.*[139].

Using nanoparticles against major stored product insect pests: Nanotechnology is rising as a highly gorgeous tool for formulation and delivery of insecticide active components as well as enhancing and offering new active ingredients for controlling many of stored product insect pests over the world.

Essential oils-nanoparticles: Nanoemulsions could be useful for the formulations of pesticides[140]. Nanoparticle materials which newly is expected to reduce the application volume and slow down the quick release kinetics[141,142]. Using nanoparticles for coating the imidacloprid (IMI) increased its toxicity[143]. Their results showed that both nanoparticles (silica and silver) were greatly effective on larvae and adults up to 100% mortality. Amorphous silica nano particles had been got to be highly operative against the stored insects causing 100% mortality against *T. castaneum*[144]. The activity of insecticidal polyethylene glycol-covered nanoparticles loaded incorporated based garlic essential oil against *T. castaneum* adult was investigated[145]. It has been found that mortality of *T. castaneum* was 80%, almost certainly due to the slow and constant release of the dynamic components from the nanoparticles[128,146].

Silver nanoparticles: Silver nanoparticles (Ag NPs) have been manufactured using various natural products like *Azadirachta indica* (Tripathi *et al.*)[147]; *Glycine max* (Vivekanandhan *et al.*)[148] and *Camellia sinensis* (Begum *et al.*)[149]. The ethanolic leaf extract of *Annona squamosa* was assessed against *S. oryzae*[150]. The entomotoxic effects of the Silver nanoparticles (Ag NPs) against *S. oryzae* were assessed[128]. The aqueous extracts of *E. prostrate* leaves which synthesized Ag NPs have the prospective to be used for *S. oryzae* controlling[123]. The insecticidal activity of nanostructured alumina against *S. oryzae* and *R. dominica*, in stores[151], who stated that a significant mortality was recorded after 3 days of continuous exposure to nanostructured alumina-treated wheat.

Aluminum and zinc oxides: Two nanomaterials namely aluminum and zinc oxides have been tested against adults of *S. oryzae* in the laboratory[152]. Their findings revealed that aluminum nanoparticles (Al_2O_3) were well effective agents in comparison with zinc nanoparticles (ZnO) which had reasonably effect on *S. oryzae*. Mortality (%) increased by increasing the exposure time and concentration levels. The nanoparticles of aluminium oxide had been highly effective against *S. oryzae* and considerably reduced the insect loss and had enormously oviposition deterrent effect[153-155], they mentioned that zinc oxide (ZnO) nanoparticle high efficiency in declining *S. oryzae* infestation. Mortality of *S. oryzae* reached to 86% by using Aluminium nanoparticles as well as to 65% of *S. oryzae* by applying Zinc nanoparticals[156]. Al_2O_3 caused the greatest deterrent effect on *S. oryzae* and *S. zeamais* compared to nanoparticle of Titanium oxide (TiO_2)[157]. The nanocides can be removed by traditional milling procedures. Applying aluminum and zinc oxides nanoparticles are considered as seed protecting agents[152].

Diatomaceous earths: Diatomaceous earth (DE) is the residue of microscopic plants (diatoms) that existed in the oceans. The insecticidal activity of DE is due to the razor sharp edges of the diatom remains. The DEs with slighter particle sizes are more toxic than the larger ones. Besides particle size, other characteristics affected DEs insecticidal effectiveness, such as active surface and oil adsorption ability, SiO_2 content, moisture content, etc[158-162]. As insects are crawling throughout the treated grain and dustbins, the DE comes in contact with the insects and the sharp edges penetrate the insect's exoskeleton. The body fluids were sucked by the powdery DE causing death from dehydration[163]. Several diatomaceous earths formulations have been successfully assessed against several stored-product insects[58,164,165]. It is played a vital role, if it possesses high amorphous silica content with uniform size distribution[135]. It caused 100% mortality by spraying amorphous silica nanoparticles on *Corcyra cephalonica*. Nano-DE powerfully killed the eggs of *T. confusum* more than *T. castaneum* after 120 storage days[165]. Also, adult emergence (%) were strongly declined by DE and Nano-DE treatments[164], who confirmed that efficiency of Nano-DE on infestation (%) of *T. confusum* were more efficient than on *T. castaneum.*

Silicon dioxide nanoparticles: The propensity for applying nanoparticles for insect control has improved. Surface-functionalized silica nanoparticles were obtained to be very toxic against adults of *S. oryzae*[166]. Amorphous SNP was found to be highly useful causing more than 90% mortality of *S. oryzae*[153]. Two silicon dioxide nanoparticles of Aerosil and Nanosav caused more mortality to *R. dominica* and *T. confusum* adults. The silica nanoparticles have a high toxicity on *R. dominica* and *T. confusum* adults. The *T. confusum* was more tolerant than *R. dominica*[167].

Nanosilica (nanobiopesticide): Amorphous nanosilica is one of the promising new substances that may achieve a good and safe management level for the stored product insects. The ones nanosilicas may be absorbed into the cuticular lipid stuffs through physisorption and hence inflicting loss of life of those insects totally. Software of nanoparticles on the leaf and stem surface does no longer alter both photosynthesis and respiration in several agencies of horticultural and crop plants[168]. Surface charged modified hydrophobic nanosilica (~3-5 nm) could be used for controlling range of insect pests successfully for caring the humankind[169-173]. Nanoparticles offered a greater surface part and circulate easily and in lepidopteran insects, therefore they are considered special harness substances as well as they will be removed during 24 h from the insect body[172]. Particles considerably smaller than micron order would be less injurious in the insect hemolymph[174]. Using hydrophobic silica nanoparticles widely decreased the seed damage potential of *C. maculatus* which was noticed to be significant compared to control[175]. It is projected that insecticidal efficacy of the silica becomes enhanced if the particles are finely separated[174].

Mode of action of nanoparticles: The mechanism relies on those insects used a variety of cuticular lipids for keeping their water barrier and thus avoid death from waterlessness. Several studies reported the potential of some nanomaterials as insecticides in insect management programs such as nanosilica[167,176] or silver nanoparticle[177] and aluminum nanoparticles[151]. Nano-silica gets absorbed into the cuticular lipids of insects by physisorption causing death of insects purely by physical resources. The following steps would be followed, if nanoencapsulation is released: diffusion, biodegradation, dissolution and osmotic pressure with an accurate pH[178,179]. Aluminosilicate filled nanotube could stick to surfaces of plant leaves while nanoingredients of nanotube have the ability to stick to the surface hair of insects and goes into the insect body which affects directly on many physiological jobs[180]. The potentized drugs pointedly increased some plant characteristics such as; chlorophyll, protein, water content in the leaves and plant growth as compared to the control[181]. Research on *Bombyx mori* showed that nanoparticle might stimulate more production of fibroin protein which helps in producing carbon nanotube in future[182,183]. Using nanoparticles in insect control programs must be geared toward introduction of faster and ecofriendly insecticides in the coming years[184]. Manufacturers are focusing on formulation of nanoscale insecticides for delivery into the target host tissue through nanoencapsulation.

EOs IN INTEGRATED PEST MANAGEMENT

Using essential oils in a successful IPM programs, different methods have to be integrated together physical control, biological control and nanoparticles containing essential oils for controlling the most destructive stored product pests. Today it is very clear that EOs can be in harmony and more effective in IPM programs to achieving more safety and environmental health. Damage to grain was lower in *Oryza sativa* treated with the essential oils of *Cymbopogon citratus* and *Cymbopogon nardus* than in the control rice grains[185]. Applying the crude plant extracts of *Citrus sinensis* and *C. aurantium* caused 89 and 76% mortality to *S. oryzae* and *R. dominica*, respectively after 3 days post-treatment[186]. The essential oil of *Cymbopogon martini* was an effective repellent against *C. chinensis* and *T. castaneum*. The lethal and sublethal activity of ethylene glycol nanoparticles based on essential oils are assessed against *T. castaneum* and *R. dominica*. Additionally, no chemical derivates were noticed during this period[154].

Table 3: Effect of sack treatment with unedible oils and neem seed formulations on the total number of eggs laid on mung bean seeds

		Average number of eggs laid after different investigating months								
Treatments	Concs. (%)	1	2	3	4	5	6	7	8	9
NeemAzal F	0.1	2.50	64.00	81.00	355.75	Parasite	-	-	-	-
NeemAzal T	0.1	0.00	15.25	70.75	245.00	522.50	Parasite	-	-	-
NeemAzal T/S	0.2	0.00	0.00	0.00	10.00	66.50	220.50	Parasite	-	-
Ethyl oleate	0.1	0.00	0.00	2.25	31.50	111.50	371.50	Parasite	-	-
A. calamus oil	0.1	0.00	0.00	0.00	0.00	0.00	6.00	51.25	272.5	Parasite
Control		17.25	83.50	3900.00	Parasite					

Source: Dimetry *et al.*[34], Concs: Concentrations

Table 4: Insecticidal activity of two oils on *C. maculatus* adults

Concentrations of oil used (%)	Corrected accumulated mortality after 96 h (%) Ethyl oleate	*A. calamus*
1.0	50.0	80.0
0.5	45.0	65.0
0.25	30.0	50.0
0.125	20.0	25.0

Source: Hafez *et al.*[37]

CASE STUDY

Using essential oils for controlling *C. maculatus* adults: This is one of NRC research projects dealing with the current review, diverse formulations of neem and oil extracted from *Acorus calamus* were assessed for controlling *C. maculatus* infestations in store of *Vigna radiata.* Oviposition, infestation (%) and adult emergence were recorded after puting seeds in treated cloth sacks for nine months. For each treatment, cloth sacs were soaked once for 5 min in the formulated solutions and allowed to dry before mung bean seeds were placed. Treatment effects on mung bean seed flavor, consumer acceptability and germination were investigated at the end of the storage period. The results showed that emergence of adults were completely inhibited immediately after applications for all treatments, except NeemAzal F which a few number of living adults were found. The *A. calamus* oil prevented beetle oviposition on the sacks and the development of infestations for at least 5 months (Table 3). Oviposition was avoided by ethyl oleate for 2 months. Neem prevented oviposition and infestation development for 3 months. Untreated sacks (control) had been infested completely in the first 3 months of storage. No harmful effects had been detected on germination, flavor and consumer acceptability[34].

In another study conducted by Hafez *et al.*[37], who tested efficacy of *Acorus calamus* and ethyl oleate oils against *C. maculatus* adults and immature stages. The results showed lethal effects of both ethyl oleate and *A. calamus* oils; conversely, *A. calamus* oil proved to be more toxic to the adults comparing to the ethyl oleate oil (Table 4-6). Ethyl oleate had an inconsiderable effect on the incubation period as well as the resulting eggs. The *A. calamus* oil decreased the hatchability with a serious increase in sterility percentage. The two tested oils had slight extension in either larval or pupal stage of the resulting progeny of *C. maculatus*. Both oils showed oviposition deterrent activity towards *C. maculatus* adults[37].

ADVANTAGES AND DISADVANTAGES OF PLANT ESSENTIAL OILS

The advantages are reflected in their rapid degradation, quick action, low toxicity to warm-blooded organisms, they are less stable and therefore have smaller negative impact on beneficial and non-target organisms[18]. They typically kill insects quickly or prevent their feeding immediately after application. Botanical insecticides could have both the act of advantages and disadvantages when being used in environment[187]. The features of the plant oils were calculated in some points; rapid degradation, fast act, low toxicity to warm blood organisms and because their stability are lower in nature[188]. For this reason, they are smaller negative impact on the beneficial and non target organisms. Also, essential oils after short time of application can kill their target insect or prevent their feeding and most of them aren't or a little toxic when inserted into the body through the mouth, they are safe to warm- blooded organisms[18]. Due to these facts the essential oils are considered to be safer as compared to the many insecticides.

The essential oils also have some disadvantages as they are rapidly degraded in environment and needed their frequent use[122,150]. Essential oils are expensive than synthetic insecticides, many of essential oils after long studies and many experimental tests of applications are still not available for many requirements during their registration steps[188]. Although deemed to be considerably less toxic in comparison to synthetic insecticides, certain EOs could be used compatibility with biocontrol agents to be safer for humans and fish[187,189-192].

Table 5: Effect of two oils against the adult stage of *C. maculatus*

Oils	LC_{50}	Slope	Toxicity index at LC_{50}	No. of folds compared with ethyl oleate
Ethyl oleate	0.858606	0.966681	35.452116	1.0
A. calamus	0.304394	1.585326	100.0	2.820706

Source: Hafez *et al.*[37]

Table 6: Effect of seed treatment with vegetable oils on the fecundity and percentage reduction in the total output of eggs of *C. maculatus* adult females

	Total number of deposited eggs/2 females				Reduction in the total output of eggs (%)			
	Concentrations (%)				Concentrations (%)			
Oils	0.125	0.25	0.5	1.0	0.125	0.25	0.5	1.0
Ethyl oleate	67.67±8.8** (54-84)	94.67±7.4* (80-104)	108.5±8.4 (94-123)	118.0±1.7 (112-121)	44.84	22.83	11.55	3.81
A. calamus	13.67±3.1## (10-20)	4.67±3.1## (0-12)	0.0##	0.0##	88.68	96.19	100.00	100.00
Control	122.67±9.9 (107-141)							
F-value	48.168**	68.287**	80.486**	143.371**				
LSD at 0.05	27.174	25.818	25.930	20.090				
LSD at 0.01	41.173	39.119	39.288					

Source: Hafez *et al.*[37], *p<0.05, **p<0.01, ##p<0.001

FUTURE APPLICATION OF ESSENTIAL OIL PRODUCTS

The development of EOs as plant protection products is especially suited to organic farming. They are natural in origin and biodegradable and have diverse physiological targets within insects and may also interrupted the evolution of insect resistance. According to progressing activities in essential oils works, there were many publications concern about nanoparticles against grains stored products, Silver nanoparticles (AgNPs) were manufactured by using aqueous leaves extracts of *Euphorbia prostrata*[127,128]. Assessments of the insecticidal activity had been conducted for identifying the efficacy of aqueous leaves extracts of *E. prostrata*, silver nitrate ($AgNO_3$) solution (1 mM) and synthesized Ag NPs against the adult of *S. oryzae*. Nanoemulsions prepared from the tested plant oils showed a considerable insecticidal activity against many insect pests[124,130,193]. With a rational design related to their extraction, formulation, application and toxicological evaluation, these oils would play a role in insect management.

CONCLUSION AND RECOMMENDATION

Insecticides based on essential oils might be applied as fumigants, granular formulations or direct sprays with a range of effects from lethal toxicity to repellence and/or oviposition deterrence. In terms of specific constraints, the efficacy of these materials falls short when compared to synthetic pesticides. Application of nanostructured materials for pollution prevention through environmentally benign synthesis and manufacturing are also being developed. In fact numerous products enabled by nanotechnology are formerly in the market and nanoparticles in eco-friendly insecticides, because of their biodegradable nature, systemicity after application, capacity to alter the behaviour of target pests and favourable safety profile and most likely to be adopted for use in the near future. So, it is recommended that the silica nanoparticles could be used effectively in a stored grain IPM and will be efficient against many insects.

SIGNIFICANCE STATEMENT

This review article revealed that plant oils either in normal status or nanoparticles could be beneficial for the researchers, farmers and traders to protect and manage stored product insects which caused severe losses and may be dangerous for human by transferring fungal diseases.

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