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Review

Green nanoparticles application in the management of stored grain pests, *Tribolium* sp.

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ABSTRACT

Globally, the stored grain insects severely damage grains of food and storage products. One of the primary stored insect pests is *Tribolium castaneum*, *which* is being controlled by using synthetic insecticides. The synthetic insecticides despite being effective, have many disadvantages, such as costly, non-biodegradable and negative impact on the environment. Thus, the farmers and storage house managers- look for potent and financially viable solution to reduce the economic and environmental negative impacts. One the most promising alternatives is the usage of green nanoparticles which have been recently extensively studied for their insecticidal properties against both stored grain pests and agricultural crop pests. Apart from the silver nanoparticles a variety of other nanoparticles are being used for the control of stored grain pest, including silicon dioxide, diatomaceous earth, aluminium, silver, zinc oxide, essential oil nanoparticles, and nano silica particles. In conclusion, our review suggests that silver nanoparticles have the potential of strong contender in the search for a replacement of existing insecticidal use to control the harm caused by stored grain pest.

Figures : 02 References : 41 Table : 01
KEY WORDS : Green synthesised nanoparticles, silver nanoparticles, Stored grain insect pest, *Tribolium spp*.

Introduction

Grain storage is a component of the post-harvest process that transports food products from the farm to the user. One of the most significant and fundamental problems with grain storage is the loss of grain quality and quantity lost due insect infestation, which destroys the grains and affects their dry mass and nutritional content[15]. Around the world, a variety of insect pests severely destroy grains that have been kept, with damage rates ranging from 5 to 30% in tropical nations and 5 to 10% in temperate areas[31]. Storage and field pests, numbering over 20,000 species, are liable for the annual loss of over $100 billion worth of food, which is one-third of the world's total food output. Based on present estimates, insect pests reduce the yield of wheat by 5%, pulses by 15%, rice and maize by 25% in India. The quality, quantity, and market value of the goods are all impacted due to insect infestation/invasion[36]. Due to microbiological degradation and insect pest infestation, post harvest losses occur between 10 to 25% globally[32]. *Tribolium castaneum*, a red flour beetle, is a pest of stored products worldwide that is especially harmful to foodstuffs and grains[35], both in terms of quality and quantity[24]. This insect significantly decreases the weight and nutritional value of grains, lowering their market value and germination rate[14]. The aim of this article is to look at how green nanotechnology is being used to control *Tribolium sp*. in current time and the prospective future times.

Host products and damage

Tribolium castaneum, is a highly wide spread pest of wheat flour, dried fruit, pulses, and prepared cereals including almonds, beans, pasta, and oats that expands broadly and worldwide as it affects crops that are kept in different kinds of environment conditions and causes major harm to them[15]. *Tribolium sp.* considerably develops more quickly and has better survival and reproduction rates[9]. *Tribolium* and its larva infection of a commodity typically leave the item with a prolonged bad aroma, which might be dangerous or risky for our health if consumed[24]. All of the foregoing manifestations of damage typically result in a loss in total profit as a consequence of price loss and the additional expense required for treatment in the form of insecticides

TABLE-1 : Various plant derivatives involved in green nanoparticle synthesis to control stored insect pests

Plant Name	Types of nanoparticles	Size (nm)	Plant material used for extraction	Stored Insect Pests	References
Euphorbia prostrata	Silver nanoparticles (Ag NPs)	52.4 nm	Leaves extract	*Sitophilus oryzae* (3rd instar larva)	(41)
Sida acuta	Silver nanoparticles (Ag NPs)	25 nm	Leaves extract	*Culex quinquefasciatus, Anopheles stephensi, and Aedes aegypti*(3rd instar)	(37)
Avivennia marina	Silver nanoparticles (Ag NPs) lead nanoparticles	15-25nm	Leaves extract	*Sitophilus oryzae*(Adult)	(30)
Hibiscus tiliaceus	Silver nanoparticles (Ag NPs)	20-65 nm	Leaves extract	*Tobacco cutworm, Spodoptera litura, Helicoverpa armigera.* (3rd instar larva) *Tribolium castaneum, Rhyzopertha dominica F. and Sitophilus oryzae*(Adult)	(25)
Pongamia pinnata	Zinc oxide nanoparticles	21.3 nm	Leaves extract	*Callosobruchus maculatus* (Adult)	(18)
Trichodesma indicum	Silver nanoparticles (Ag NPs)	20–50 nm	Leaves extract	*Mythimna separata* (2nd instar larva)	(7)
Pimpinella anisum	Oil nanoemulsions	-	Seed oil	*Tribolium castaneum* (Adult)	(13)
Ricinus communis and Citrus paradise	Silver nanoparticles (Ag NPs)	-	Leaves extract	*Tribolium castaneum* (Adult)	(32)
Solanum lycopersicum	Silver nanoparticles (Ag NPs)	22nm	Peel extract	*Callosobruchus maculatus* (Adult)	(8)

Plant Name	Types of nanoparticles	Size (nm)	Plant material used for extraction	Stored Insect Pests	References
Spinach, Tulsi and Paddy	Zinc, Copper and silica nanoparticles	-	Leaves extract of spinach, Tulsi and husk extract of paddy	*Callasobruchus analis, Sitophilus oryzae*(Adult)	(39)
Rauvolfia serpentine	Nickel-oxide nanoparticles	-	Leaves extract	*Callosobruchus maculatus* (Adult)	(22)
Saccharum officinarum	Silica nanoparticles (SNPs)	96.6 nm	Sugarcane bagasse ash	*Tribolium confusum* & *Rhyzopertha dominica* (Adult)	(27)
Camelina sativa	Silver nanoparticles (Ag NPs)	-	Leaves extract	*O. surinamensis and S. granaries* (Adult)	(26)
Vernicia fordii	Zinc oxide (ZnO NPs) and copper oxide nanoparticles (CuO NPs)	22 nm & 24 nm	Seed extract	*Tribolium confusum* (3rd instar Larva)	(9)
N. oleander	Silver nanoparticles	20 to 30nm	Leaves extract	*Tribolium castaneum* (2nd instar Larva)	(15)

and costly insect proof packaging. So there is an imperative to develop less expensive and safer pest control technologies that can be applied to all of the insect's host populations[1].

Management of stored insect pest

The two most widely used fumigants in the world, phosphine and methyl bromide, in addition to pyrethroids and organophosphates, are currently used to control insect pest invasion in grains as well as dry food items like cereals, beans, pasta, chocolate, nuts, seeds *etc.* The continued usage of chemicals causes several issues with the health of humans and the environment[21]. The fundamental issues with this strategy also include the persistent insect immunity to pesticides, the carcinogenic risk of organic pesticides, and their hazardous residues on foodstuff after application. Due to this, it is urgently necessary to identify effective, environment friendly, secure, cheaper options for managing insect pests[15].

Green nanotechnology as alternative of chemicals

A modern and environmentally favourable method for creating eco-friendly insecticides is to synthesize NPs using plants[31]. The main reason why plant extracts are preferred over microbe culturing and isolation techniques is that they are toxin-free, provide natural capping agents, and are less expensive[15]. Nanomaterials have novel qualities like permeability, rigidity, thermal resistance, crystallinity and dissolution that are essential for the development of nano-pesticides. In insects, nanoparticles move more easily and possess a bigger area of surface contact. For the pest control of stored grains, a variety of nanoparticles are utilised, including silicon dioxide, titanium dioxide, diatomaceous earth, nano silica, aluminium, precious metals, silver, and polymers based on zinc oxide and metal oxides. Conventional chemical and physical techniques for producing nanoparticles result in toxic by-products which are destructive for the environment[20]. Because of its stability, excellent yield, economic effectiveness, low toxicity, and eco-friendliness, the green method to nanoparticle synthesis is recommended in this regard[3]. Several plants and their byproducts, including flavonoids, enzymes, proteins, and terpenoids, which serve as dual reducing and capping agents, are used in the green nanoparticle production technique[40]. Many plants, including *Sargassum muticum,* leguminous shrubs, various leaf broths, *Aloe barbadensis* plant extract, *Camellia sinensis, Azadirachta indica* (neem), *Avicennia marina*, and lemon grass leaf extract, have recently been used in the process of synthesising silver nanoparticles as reducing agents. The production of non-toxic, clean, safe, and suitable silver nanoparticles was carried out using *Nerium oleander* leaf juice as a successful reducing agent[5–15]. It would be acceptable to expand the biological pathway for large-scale manufacture of the biolarvicidal products since the herbal path of AgNPs' synthesis has been shown to be an environment friendly affordable, and alternate of chemical techniques of NPs production[6]. While many more researches are anticipated in the near future, very few have been done in the area of nanomaterial and stored pest management[17].

Mode of action of nanoparticles

Numerous theories have been put out regarding the explanation of the mechanism of activity of nanoparticles towards insect pests[34]. Because of its wide surface area compared with volume proportion, nanoparticles can injure insects by passing through their cell membranes. The existence of a variety of volatile and phytochemicals substances in such plant preparations, which include carbonyl hydrocarbons, carbonyl hydrocarbons oxygenated, phenyls, carboxylic and sesquiterpenes, may be the cause of AgNPs' potential overall toxicity[11]. The toxicity of nanoparticles was assumed to be due to their absorption through the exoskeleton(epithelium). Damage of midgut epithelial cells may result in alterations in membrane permeability, resulting in a distribution of the proton motive force, cell malfunction and death[12]. Several studies have demonstrated that nanomaterials such as aluminium, silver nanoparticles, and silica nanoparticles could be utilised as insecticides in pest management strategies. Nano-silica is absorbed by physisorption into the fatty substances (lipids) of insect cuticle. If the nanoencapsulation is freed, dispersion, osmotic pressure, biological degradation and dissolution will occur with the same potential of hydrogen (pH)[28,29].

Synthesis of green silver nanoparticles

Top-down and bottom-up strategies can be employed to manufacture the different types of nanoparticles[10]. The schematic representation of these strategies (Fig. 1).

- Some examples of green nanoparticle synthesis methods: -

Fruit juice Extraction: Fruit juice of Pineapple (*Ananas comosus* L. var. queen) was extracted, sieved, and stored to create the extraction sample, which was used to create silver nanoparticles. $AgNO_3$, was proceeded to prepare 10,000 ppm aqueous solution. Flasks carrying $AgNO_3$ were mixed with pineapple juice for bio reduction. Pineapple juice and aqueous $AgNO_3$ had a volume ratio of 1:10. Within minutes of adding the pineapple juice to aqueous $AgNO_3$, the colour of the

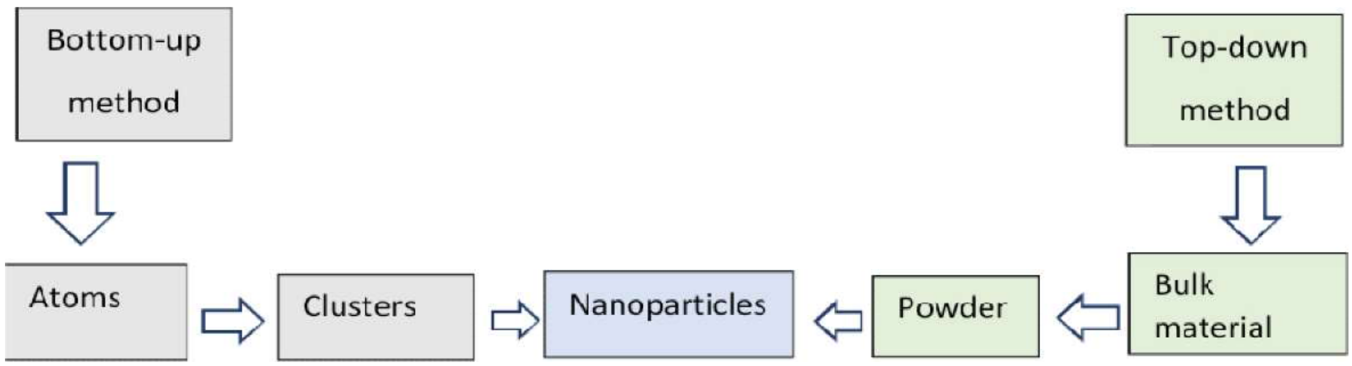

Fig.1 : Schematic representation of nanoparticles synthesis procedure *via* Bottom-up and Top-down Method

mixture changed and indicates the synthesis of silver nanoparticles with the recognisable colour. Periodic UV spectrophotometer sampling was used to track the bio reduction of Ag+ ions[2]. The schematic representation of these strategies (Fig. 2).

1. **Flower extraction**: Fresh marigold flower samples were taken, finely chopped, and boiled for 5–10 minutes in 100ml distilled water. It was then run through Whatman filter paper for filtration. A beaker containing 45ml $AuCl_4$ and 5ml of floral extract was used to create gold nanoparticles. For 3 to 4 hours, this solution was left in the dark. After an hour, a dark brown mixture was produced. Centrifugation at 15,000 rpm for 20 minutes was used several times to purify the gold nanoparticle solution. The particles were dissolved in deionized water after the supernatant was removed. By periodic sampling aliquots of the suspension, the bio decreases of Au^{3+} in aqueous solution were observed[4].
2. **Leaf extract**: Fresh green leaves of Jack fruit, *Artocarpus heterophylus* were gathered, washed and dried in shade at room temperature for a while. Finely chopped 50 g of jack fruit leaves were added to 200 ml of distilled water and heated at 100 °C, for approximately one hour. Whatman No. 1 filter paper was used to filter the acquired leaf extracts. Then 0.05 M $AgNO_3$ aqueous solution was made using double distil water and *A. heterophylus* leaf extract prepared before was mixed, and the mixture was constantly heated at 50 °C for 15 min. When the solution turned from dark brown to brown it indicated the creation of silver nanoparticles. The solution was then cooled down and centrifuged, after draining the supernatant, the nanoparticles were collected [19].
3. **Bark extract**: Trunk bark of *Callicarpa maingayi* was cleaned before being dried in an oven for 48 hours at 40 °C. After being crushed into powder, the powder was kept in opaque glass vials. Using a shaker, water and methanol (ratio) were combined with 20g of crushed bark stem for 72 hours at room temperature. Afterwards filtrated using Whatman No.1 filter paper. The purified extraction was then stored at 4 °C in opaque bottles. One g stem bark extract was added to 100 ml of distilled water, and the mixture was stirred continuously for 1 hour. Then, 100 ml of $AgNO_3$ was added, and the mixture was stirred for 48 hours at 25°C temperature. Brown colour of solution indicated the creation of silver nanoparticles[33].
4. **Seed extract**: The freshly picked olive seeds were dried under the sun. The dry seeds were crushed, and the seed powder was then screened through a mesh sieve to create the extract that was employed for reduction. A mixture consisting of 5 g of dry seed powder and 100 ml of distil water was boiled for 5 minutes and filtered to get the seed extract. For the manufacture of silver nanoparticles, a 1mm water-based mixture of $AgNO_3$ was produced. In order to bio reduce the Ag+ ions in the solution, 10 ml of olive seed oil extraction was added to 90 ml of an aqueous solution containing 1 mg silver nitrate. The mixture was then left at ambient temperature for 24 hours. Dark brown colour of solution showed the formation of silver nanoparticle synthesis [16].

Using green nanoparticles against stored insect pests

For the creation and distribution of insecticide compounds as well as for improving and providing novel active compounds for controlling numerous stored grain pests worldwide, nanotechnology has become more and more important. Green synthesis of nanoparticles has been investigated for the qualities including immediate toxicity, attractant, repellent or antifeedant, and fumigant, in addition to stopping the growth of many kinds of pests[31]. Also, some bioactive substances including phenolic and flavonoid chemicals are primarily found in some plant wastes. Recently, a

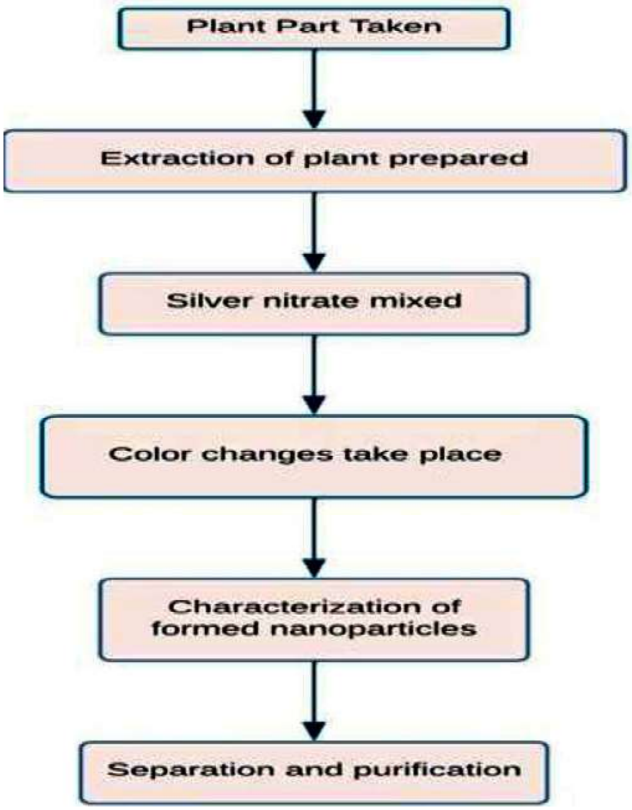

Fig. 2 : The general method of green silver nanoparticle synthesis

variety of plants, including *Sargassum muticum, Sesbania drummondii, Avicennia marina, Camellia sinensis*, Neem, and lemongrass leaves extract, have been employed in the process of creating silver nanoparticles[23]. In order to create acceptable, environment friendly and clean, nanoparticles, *Nerium oleander* leaves extract was used as an efficient reducing agent[15]. Nearly 70% of the insect pests were eradicated by the use of solid nanoparticles on the *Sitophilus oryzae* and rice weevil [31]. *Glycine max, Azadirachta indica* and *Camellia sinensis* are only a few of the natural ingredients that were used to make silver nanoparticles[15,38]. *S. oryzae* was tested against the silver nanoparticles of leaf extract of sugar apple (*Annona squamosa*) in ethanol that investigated the entomo-toxic effects of Ag nanoparticles against *S. oryzae*. Silver and silica nanoparticles also had a significant impact on adult and larval mortality when used as insecticides against the *Callosobruchus maculates* (cowpea weevil), according to some researches on this subject[17]. According to a study on *Callosobruchus maculatus*, silver nanoparticles have a highly effective insecticidal impact, killing 100 percent of the larvae and adults. The pest *Epitrimeruspyri* (mite) was effectively killed by NPs containing copper oxide and zinc oxide[31]. Bark of *Cinnamomum zeylanicum* was used in the past to create the silver and gold nanoparticles[35]. Insects can be effectively controlled by silver nanoparticles[41]. The biogenic silver nanoparticles utilising leaf extracts of *M. wightiana* were tested for their ability to kill stored product pests such as the rice weevil, lesser grain borer, and flour beetle. The findings demonstrated that biogenic silver was far more effective than artificial silver nanoparticles[25] which were used against *Sitophilus oryzae*, the rice weevil, and solid nanoparticles recorded about 70% of the mortality[31].

Different amounts of pure and green-synthesised AgNPs from extract of Kaner (*N. oleander*) leaf was given to larvae of *Tribolium castaneum* and *Callosobruchus maculates*. The herbal-synthesized AgNPs had a stronger larvicidal effect than only AgNPs and *N. oleander* extract of leaves[15]. Two plant oils *Citrus paradise* and *Ricinus communis* as well as green synthetic nanoparticles from these plants were employed to combat the stored grain insect pest, red flour beetle. All of the treatments have positive effects, although *R. communis* silver nanoparticles had a greater impact than *Citrus paradise* silver nanoparticles and these two plant oils. So, compared to *C. paradise* AgNPs, the green synthesised nanoparticles of *R. communis* are more effective at controlling *T. castaneum*[32]. The adult tenebrionid beetle, *T. confusum* was the target of using sweet orange (*C. sinensis*) peel juice to create and assess the herbal synthesized AgNPs' ability to cause mortality[31]. As a result, plant-based nano-pesticides may be useful in handling of stored commodities against insect pest. Some examples from the previous studies are mentioned in Table -1.

Conclusion

Green synthesized nanoparticles could provide excellent larval control of *Tribolium* sp. The production of green nanoparticles is a secure, affordable, and environmentally safer method for combating the most destructive economic insect pests, which significantly damages stored products that are consumed by humans and other animals. So in conclusion, this study could pave the way for an alternate, environmentally sustainable method for controlling pests of stored grains, with the help of green nanotechnology.

Conflict of Interest Statement- The authors declare that there are no conflicts of interest.

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