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Biowastes as Sustainable Source for Nanoparticle Synthesis and their Pesticide Properties: A Review

Intan Nur Zulayqha Nor Azmi,[1] Poh Wai Chia,[1,4,*] Rock Keey Liew,[2] Hanis Mohd Yusoff,[1] Tse Seng Chuah,[3] Fu Siong Julius Yong,[4] Collin G. Joseph,[5] Zhanhu Guo,[6] Ethan Buchar,[7] Erin Witherspoon,[7] William Winchester[7] and Zhe Wang[7]

Abstract

Over the last decade, nanoparticles derived from biowaste have been widely investigated as one of the greener approaches to preparing pesticides as its application offer the usage of environmentally friendly and earth-abundance resources, cost-effectiveness due to low energy consumption, biocompatibility, as well as flexibility in preparation of biomolecules as a medium or bio-reducing agents for pesticide production. Integrating biowastes in nanomaterials-based pesticide preparation marks a new age of innovation in nanomaterial technology to overcome the contemporary problems currently plaguing the agriculture sector with the possibility of mitigating environmental pollution. In this review, the synthesis of nanomaterials derived from biowastes as agrochemicals and their advantages are presented. It is expected that this review would serve as a guide for selected industry and scientific communities working with nanomaterials in the form of agrochemicals to enhance crop protection. It is anticipated that the next generation agrochemicals will mark the use of ecofriendly sustainable materials to which nanomaterials-based pesticides derived from the biowastes will play a major part ensuring food security thus achieving the Zero Hunger goal in the Sustainable Development Goals.

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1. Introduction

Pesticides a category of chemicals applied in agriculture sector to eliminate or control pests like weeds, fungi, insects and rodents while protecting and improving the crop yield. The term "pesticides" covers a wide range of chemicals, including insecticides, rodenticides, herbicides, fungicides and so on. Annually, approximately 2.5 million tonnes of pesticides are utilized globally for pest control.[1] Global usage of pesticides has soared from an average of 2.3 million tonnes in 1990 to 4.1 million tonnes in 2016.[2] Under general agricultural practices, pesticides are beneficial in crop production and pest management. Yet, the extensive usage of pesticides has created serious consequences due to their biomagnification and persistent nature. Consumers nowadays are more cautious of the persistence of pesticides and residue in food and food chains and thus the demand for innovative green pesticides is on the rise.[3,4]

Due to this demand, green pesticides have emerged as the main choice in agriculture due to the use of sustainable and biodegradable components. As green pesticides avoids the usage of hazardous chemicals whichcan result in the contamination of the water resources, soil and crops leading to environmental and human health issues.[3] Recently, researchers have discovered that secondary metabolites or allelopathic compounds produced from living organisms may provide an alternative source of pesticides. This extraordinary

[1] *Faculty of Science and Marine Environment, University Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.*
[2] *NV Western PLT, No 208B, Second Floor, Jalan Macalister, 10400 Georgetown, Penang, Malaysia.*
[3] *Faculty of Plantation and Agrotechnology, Universiti Teknologi MARA, 02600, Arau, Perlis, Malaysia.*
[4] *Instutute of Marine Biotechnology, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malasyia.*
[5] *Industrial Chemistry Programme, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia.*
[6] *Mechanical and Civil Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle Upon Tyne NE1 8ST, United Kingdom.*
[7] *Department of Chemistry, Oakland University, 146 Library Drive, Rochester, MI 48309-4479, United States.*
**Email:* pohwai_98@yahoo.com (P. W. Chia)

class of secondary compounds with novel chemical structures, possess new modes or mechanisms of action that can be potentially used in crop protection.[5] Despite their huge potential as agrochemicals, some constraints were also identified when employing these compounds in agriculture, such as the instability of the compounds, costly isolation process while yielding a modest amount of the allelopathic compounds.[6] Sometimes allelopathic compounds suffer from high dose or application rates, which render them unattractive or expensive to apply.[7] Though they are promising green alternatives to conventional pesticides, the market demand for allelopathic is still limited, making them less competitive and satisfactory compared to synthetic agrochemicals. As such, the search for cost-effective and efficient green pesticides is of current interest to researchers.[8]

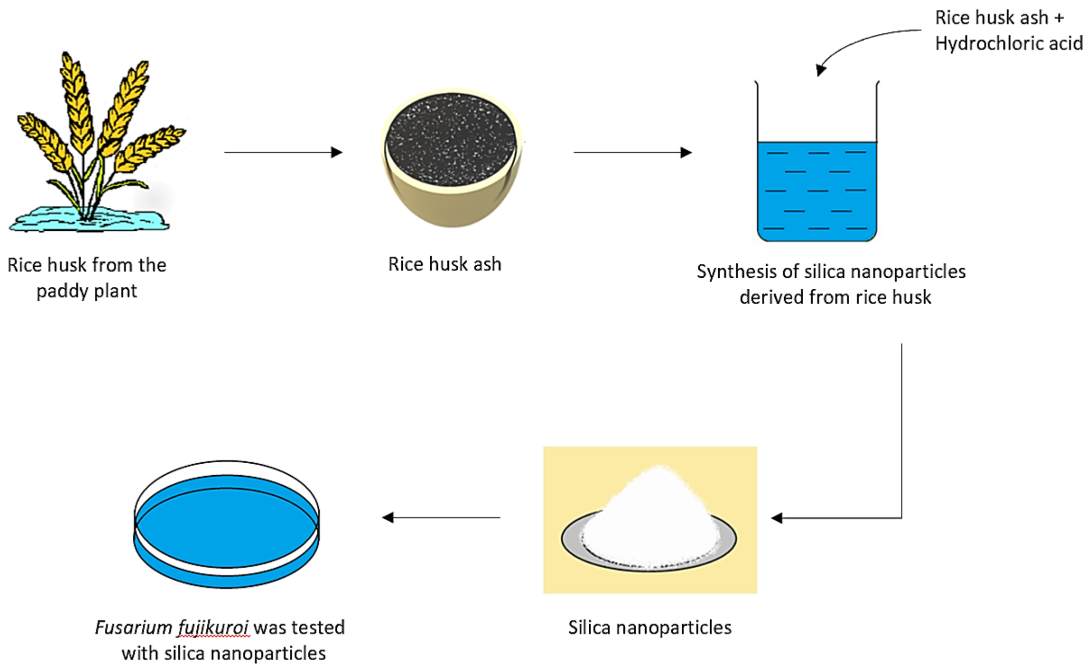
Particles that have a range size of around 1-100 nm are called nanoparticles.[9] The presence of matter at the nanoscale has marked a new milestone in materials science in the 21st century. The prefix "nano" comes from the Greek that suggests the meaning of "a billionth". Thus, a nanometer is known as a billion of a meter which is 250 million inches, and about 10 times the diameter of a hydrogen atom. Nanoparticles have been used in a wide range of applications, ranging from pharmaceuticals, food production, and agriculture, to cosmetics and environmental preservation. Nanoparticles have the prospective to improve the agriculture and food industry by supplementing nanotools for crop protection, while maintaining the high nutrient absorption rate for crops, eliminating pests and enhancing harvest yield. Overall, nanoparticles is one of the promising materials to food crop production, that is ecofriendly to agriculture, water, and soil.[10] Biowaste derived nanoparticles has emerged as a new-age material that can transform conventional agriculture practices. Nanoparticles derived biowastes possess several benefits, including minimizing the use of large quantities of pesticides, and increasing crop production via pest management. Production of nanoparticles-based pesticides from biowaste has the advantage of being cost-effective, sustainable, and environmentally benign. In the past, numerous literature documented the use of biowastes to produce nanoparticles-based pesticides, including rice husk,[11] lignocellulose waste,[12] *Pongamia pinnata*,[13] cashew nut,[14] lantana,[15] shrimp shell,[16] hibiscus,[17] pomegranate peels[18] and others. The huge volume of biowastes generatedfrom the food industry, poultries, and fisheries can serve as a precursor for producing nanoparticles-based pesticide while minimizing the environmental burden due to the rise of synthetic pesticides. In view of the usefulness of these biowastes for the production of nanoparticles-based pesticides, it is prudent to reviewed the current trend of research using biowaste as a sustainable and renewable source for the preparation of nanoparticle-based pesticides and their advantages in agriculture for crop protection.

2. Biowaste

2.1 Rice husk

Rice husk is a biowaste generated from the rice milling industry.[19] Every year, it was estimated that 100 million tonnes of rice husks are produced as a solid biowaste that can be used as a substitution for reactive silica.[19] In terms of chemical composition, about 90% of silica element was identified together with other metallic impurities in the rice husks.[19] Many farmers chose to use conventional insecticides but the build-up of these chemicals is a hazard to the environment as it also kills insects involve in pollination for other plants . While prolonged and repeated exposure to synthetic insecticides enable targeted insects to build up resistance. To address this issue, nanoparticles have become prominent in agriculture application especially in pests control. Furthermore, the United States Department of Agriculture had made a statement that the uses of silica nanoparticle are biosafe, enable its continuous usage in the fields. Silica nanoparticles (NPs) synthesized from rice husk (Scheme 1) were evaluated in the control of bakanae fungal pathogen (REF). The bakanae disease is caused by a seed-borne pathogen, *Fusarium fujikuroi*, that infects rice, diminishing its yield, globally.[20] When silica nanoparticles, synthesised from the rice husk ash, were applied to 5 pairs of adult *S. Oryzae (L.)* grains at 25, 50, 75, 100, 125, 150, 175, 200 ppm concentrations. 50 mg/L concentration, SiNPs are capable of reducing the fungal caused-bakanae disease after the onset of the first symptom. During the 4 days experimental duration, the highest fungal mortality was consistent throughout the entire four day duration with concentration of 175 and 200 ppm. While in concentration of 125 and 150 ppm, the highest mortality was on the fourth day. However, the reaction mechanism of SiNPs against *F. fujikuroi* remains unknown. The use of silica nanoparticles from rice husk as an insecticide provides an alternative strategy for pest management that had developed resistance to conventional insecticides.[21] Moreover, the SiNPs can serve as alternative pesticides in agriculture that aid in securing food productivity worldwide.[22] According to the World Health Organization and US Department of Agricultural, the use of SiNPs is considered safe to humans and it is now being approved as the nanobiopesticide.[23] The biowaste derived SiNPs has the potential to be a cheap and effective alternative to the current conventional method of synthesizing of SiNPs that are of significant as nanobiopesticide in agriculture field.

In another study, Abigail *et al*. (2016)[11] revealed the rice husk can be utilized for synthesizing silica nanosorbent for weed management, as well as for pesticide leaching control. According to their work, rice husk derived nanosorbent containing 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide was first synthesized and evaluated on the control of *Brassica sp* weed. To synthesize the rice husk nanosorbent, the rice husk microparticle was suspended into the distillled water



Scheme 1 Processing of making silica nanoparticles from rice husks. Rice husks were collected from rice processing factory, grinded into fine particles and burnt in furnace. The ash were collected and reacted with silver nitrate to form silver nanoparticles and subsequently tested against the *fusarium fujikuroi.*

where the pH is 3.0 by using 0.1 mol l^{-1} citric acid. Then agitated at 10 000 rpm for 30 minutes. After that, let it dry in an oven for 4 hours at 60 ^{o}C. To determine the amount of 2,4-D absorbed into the n-RH, 1 g gram of n-RH added into varying ratio of 2,4-D in the methanol. pH 5.0 and temperature of 30-degree celcius was chosen. The samples were centrifuged to get the supernatant. The amount of 2,4-D that was absorbed into the n-RH was calculated by substrate the concentration difference between initial and equilibrium solutions. The equilibrium of the methanolic solution will be centrifuged and dried in the oven. For the germination test, the inhibition was observed in the column segment in the depth of 0-4 and 4-8 cm, for both cases when application of 2,4-Dichlorophenoxyacetic acid and rice husk derived nanosorbent containing 2,4-D on *Brassica sp weed*. Interestingly, the column segments revealed that in the depth of 8–12 and 12–16 cm, increased growth was observed for the case of using silica nanosorbent containing 2,4-D compared to that of 2,4-D alone. This result indicates that the increased growth of *Brassica sp* weed could be attributed to the non-leaching feature of silica nanosorbent containing 2,4-D.[11] As such, the rice husk silica may act as a potential carrier for herbicide delivery that maintains the herbicidal efficacy, at the same time, reduce frequent application and leaching problem. The main advantage of using agro-industrial waste based nanosorbent is the potential of reducing environmental pollution and maintaining the bioefficacy of nanobiopesticide. Furthermore, the use of biowaste as a carrier is advantageous compared to that of polymer-based systems, as it is lower in cost, ecofriendly and bioefficacy which can last for a longer time.

2.2 Hazelnut waste

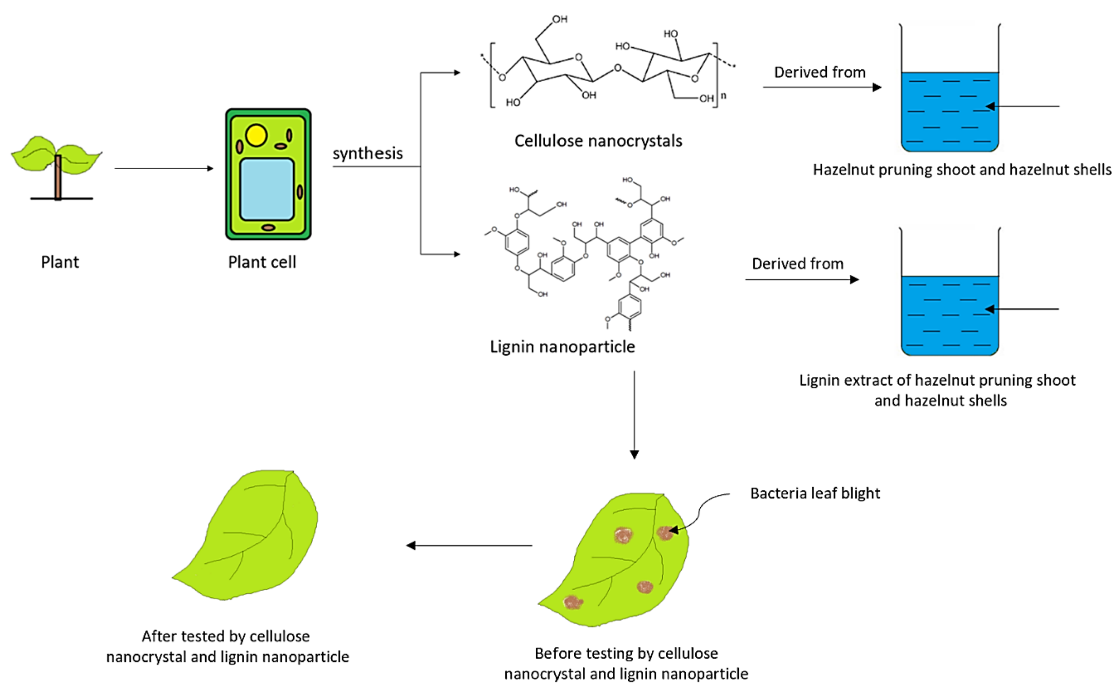
The hazelnut or *Corylus avellana L.* is one of the important agro-food from the food supply chain of dried fruit. In 2018, a report revealed by the Food and Agriculture Organization (FAO) showed that hazelnuts plantation in the world is about 660, 000 hectars and their production is recorded to be 835,000 tonnes of nuts per annual.[16] Unfortunately, the production of the hazelnut risk infection from bacteria blight (*Xanthamonas arboricola* pv. *Corylina* (Xac)). The bacterial blight causes symptoms to all parts of hazelnut trees, including duds, twigs, stem and fruits, which is why it is considered as the most dangerous bacteria in the hazelnut crops. To prevent this problem, copper-based pesticides were used by farmers to counteract and stop the growth of bacteria blight. However, the use of copper-based pesticides was banned, and new substitution was urgently sought after as regulated by the law of European Union (EU).

To prevent environmental risk, the lignocellulose biomass wastes from hazelnut processing industry was utilized as a novel source for synthesizing nanomaterials.[24] There are many advantages for employing waste lignocellulose in synthesizing nanomaterials, such as the inexpensive, environmentally friendly and high-performance features of this material in preparing the high-performance of nanomaterials. In the work demonstrated by Schiavi and co-workers (2022), the cellulose nanocrystal (CNC) was prepared from the hazelnut tree pruning shoot (HP) and hazelnut shells (HS) (Scheme 2). While the lignin nanoparticle LNP was synthesized from the lignin extract from the HP and HS. Over the years, cellulose nanocrystal (CNC) is known to possess several unique properties like low density, low thermal coefficient, and high elastic modulus. The applications of the CNC have been studied and applied in many sectors like medicine, pharmaceutical, agri-food sector and others due to CNC does not cause harmful effects to human health and it is eco-friendly. Likewise, the lignin-based materials can be used to prepare low cost, eco-friendly and high performance of nanocomposite. Numerous research has shown that the lignin nanoparticle possesses antioxidant activity and other bioactive ingredients, which is suitable to be used as nanocarriers. The laboratory result showed that both CNC and LNP could inhibit the bacterial growth of blight bacteria.[24] Moreover, the in vivo experiment revealed that both CNC and LNP strongly inhibit and diminish the disease, the effectiveness is comparable to that of copper oxychloride. In addition, both CNC and LNP were found to be phytobiological compatibility, further confirming the usage of these nanomaterials as sustainable nanopesticides. Currently, CNC and LNP are being studied further, including their biological mechanism to gain insight into the inhibition activity and soon will provide an alternative form of sustainable pesticides to farmers besides conventional agrochemicals.

In the same year, Schiavi *et al* (2022) revealed the CNC synthesize from the olive tree pruning waste that could be used to overcome the olive knot disease (*Pseudomonas savastanoi* pv. *savastanoi*). The olive tree, also known as *Olea Europea L.* is an evergreen woody plant planted on a large scale in certain countries. In Italy, the production of olive oil is estimated to be over 400 000 million tonnes per year. It is the second largest olive oil producing country after Spain. However, the production of olive oil could be slowed down if infected by pathogens or pests, such as the case of *Pseudomonas savastanoi* pv. *savastanoi* causing olive knot disease. Over the years, cupric salts were used to manage olive knot disease. Unfortunately, studies have shown that cupric salts accumulate in the soil, producing several phytotoxic effects and are harmful to humans. Building on their previous success of synthesizing CNC and LNP for overcoming blight bacteria, the author has applied the same strategy to synthesize the CNC from olive pruning waste. The resulting CNC was evaluated in the control of the causal agent of olive knot tree. In their work, the CNCs showed promising inhibition activity on bacterial growth and in bacterial biofilm formation. The ability of CNC in reducing bacterial epiphytic survival showed that the effectiveness of this nanocrystal is comparable to that of copper sulphate on leaf surfaces, with an application of 1% w/v of CNCs were used and no negative effects were observed on leaf development.[25] This approach will aid in the implementation of a sustainable plant protection strategy and simultaneously reduce the environmental impact of waste.

2.3 *Pongamia Pinnata*

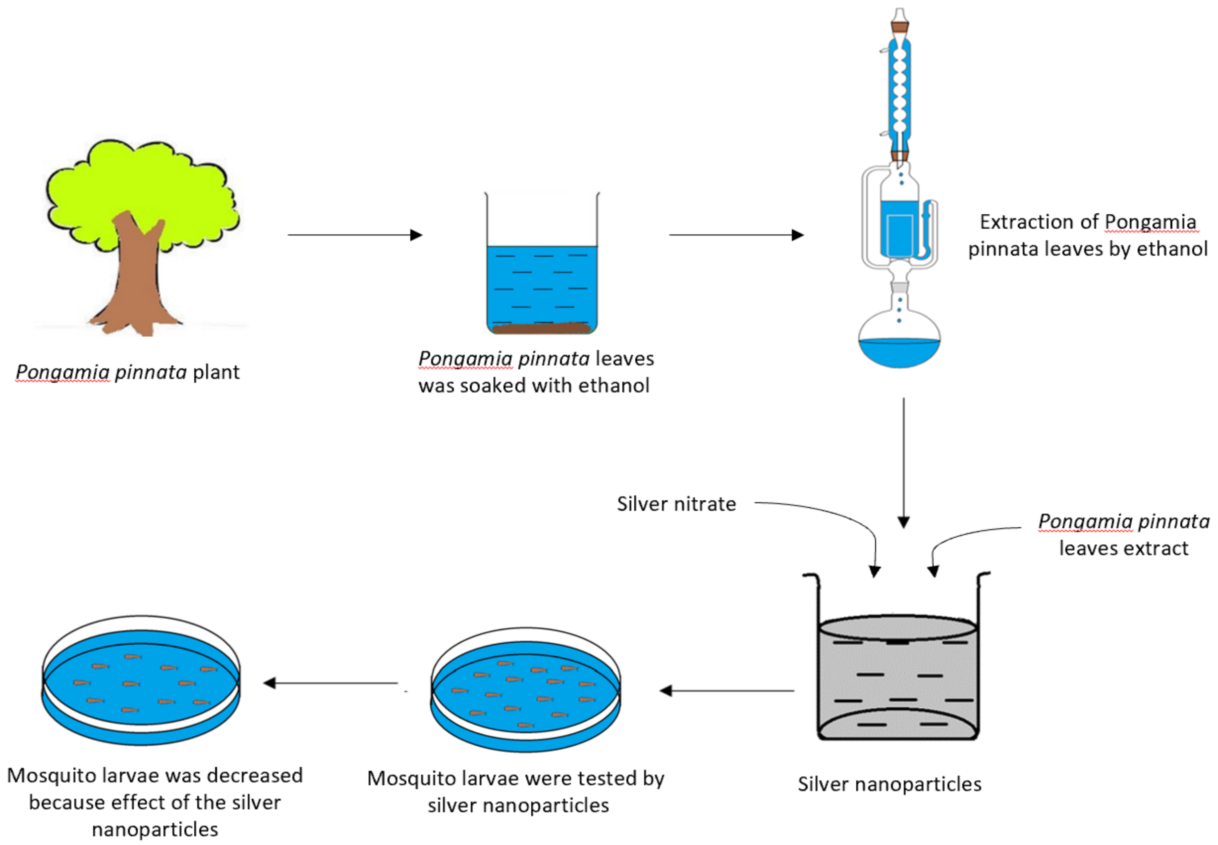
Pongamia pinnata is a tropical plant that is fast-growing, medium size tree with glabrous shrub and dropping branches. In India, this plant was planted along the roadside or highways to stop soil erosion.[26] The most significant properties of *Pongamia pinnata* is that the seed can be used as potential source of biodiesel due to the oil contained in its seeds[27] and for treating illnesses, such as fever, leprosy, bronchitis, diarrhea, skin diseases, ulcers and so on.[28] The leaf part of *Pongamia pinnata* remains largely as biowaste, especially in the fall season[29,13] disclosed that silver nanoparticle derived from the leaf of *Pongamia pinnata* possessed larvicidal



Scheme 2 Extraction of the plant into cellulose nanocrystals and lignin nanoparticle. The lignocellulose biomass wastes from hazelnut processing industry were collected and processed into nanomaterials. The laboratory result showed that both CNC and LNP could inhibit the bacterial growth of blight bacteria.

activity (Scheme 3). Due to the frequent use of synthetic pesticides, such as pyrethroids, neonicotinoids, carbamates and organophosphates that act selectively towards adult mosquitoes, it has led to the occur of pesticide resistant cases on targeted insects. In addition, excessive reliance on synthetic pesticides has caused environmental pollution.[30] Researchers found that mosquito larvae are susceptible to the silver nanoparticle derived from the leaf extract of *Pongamia pinnata* plant.[9] The leaf part is considered biowaste as after extraction of oil from the seed of *Pongamia pinnata*. According to literature,[13] the silver nanoparticles were tested against the *Aedes Albopictus* larvae, with a series of concentration silver nanoparticles derived from *Pongamia pinnata* (100, 150, 200 and 250 ppm). The result showed that the silver nanoparticles at 100 ppm possessed the highest larvicidal activity towards the larvae mosquitoes. These silver nanoparticles derived from the *Pongamia pinnata* could be further studied as pesticide as most commercial pesticides were found to target adult mosquitoes, and less attention was paid to targeting larvae mosquitoes. Besides, the silver nanoparticles derived from the *Pongamia pinnata* is a promising alternative for controlling mosquitoes in an environmentally sustainable manner compared to the use of synthetic pesticides.

In another study, Malaikozhundan and Vinodhini (2017)[31] has disclosed that the zinc oxide nanoparticles (ZnO NPs) derived from *Pongamia pinnata* were a potential source of insecticide against pulse beetle (*Callosobruchus maculatus*). The *Callosobruchus maculatus* (*C. maculatus*) is well-known as the storage pest or stored-grain pests in cowpea. Previously, the control of *C. maculatus* pests largely relied on synthetic insecticides and fumigants. Unfortunately, the excessive use of synthetic insecticides contaminated the grains with pesticide residues. Moreover, the heavy reliance on synthetic insecticides has made pests control even harder to achieve, as the pest has developed resistance to these synthetic chemicals. As such, there is a need to search for alternative insecticides that are highly effective and benign to humans. To overcome this problem, the ZnO NPs derived from the *Pongamia pinnata* leaves extract were prepared.[31] The ZnO NPs were tested on the *C. maculatus* at different concentrations, namely at 5, 10, 15, 20 and 25 µg mL^{-1}. The result showed that the number of eggs laid, and the percentage of hatchability of eggs reduced while the period of grub (larva) period and total development period increased within the 22-24 days with21 days as the control experiment. Moreover, the mortality of *C. maculatus* increased when increased concentrations of ZnO NPs were employed. Full mortality of *C. maculatus* was recorded at a concentration of 25 µg mL^{-1}. The finding of this work showed that ZnO NPs derived from *Pongamia pinnata* have high effectiveness as a control agent against *C. maculatus* or stored grain pest in future.



Scheme 3 Silver nanoparticle derived from the leaf extract of *Pongamia pinnata* plant. The leaf part of *Pongamia pinnata* remains largely as biowaste after extraction of its essential oil. The bioassay result showed that the silver nanoparticles at 100 ppm possessed the highest larvicidal activity against the *Aedes Albopictus* larvae.

2.4 Cashew nut

Cashew nut, also known as *Anacardium occidentale* (*A. occidentale*) is a main export commodity of India. Almost 80% of the exported cashew nut are produced in the Kollam district of Kerala state, which is also known as the cashew capital of the world. The cashew nut processing industry produces several by-products, including the peel of cashew nut which was regarded as a biowaste.

According to a study, the cashew nut shell liquid (CNSL) which was once considered as massive waste in cashew nut processing industry, can now be utilized in nanoemulsion for formulating aqueous-based nanopesticides to control *Anopheles culicifacies* (*A. culicifacies*).[32] CNSL is eco-friendly, easy to use, low-cost and biodegradable. Many studies have proven insecticidal of CNSL against mosquito larvae, and it is also safe when used on the non-target organisms.[33] In their work, the CNSL was collected from the Plaza Chemical Industry, India and derived into the nano-emulsion by mixing the CNSL, surfactant mixture and propylene glycol then stirring at 2000 rpm for two hours at room temperature. CNSL nano-emulsion was tested on the third instar larvae of *A. culicifacies* and was tested on the twenty larvae for each different concentrations 1.2 mg/L, 2.5 mg/L, 5 mg/L, 10 mg/L and 15 mg/L. This experiment was conducted in triplicates. Mortality of the larvae that were exposed to the treatment was calculated and recorded within 24 hours of exposure. The result showed that CNSL can be used as a pesticide because the efficiency of nano CNSL is more efficient than bulk CNSL at lower concentrations asthe smaller size of nano CNSL allows for higher absorption of the CNSL into the cuticle and kills the larvae. In addition, it was reported that CNSL also contains an active larvicidal compound, namely cardanol.[32] By using the cashew nut shell liquid which is an agro-industrial by-product as a material to synthesize the bio-pesticide, the disposal and synthetic pesticide issues can be reduced and cashew nut shell could be recycled in a good way in the future.[32]

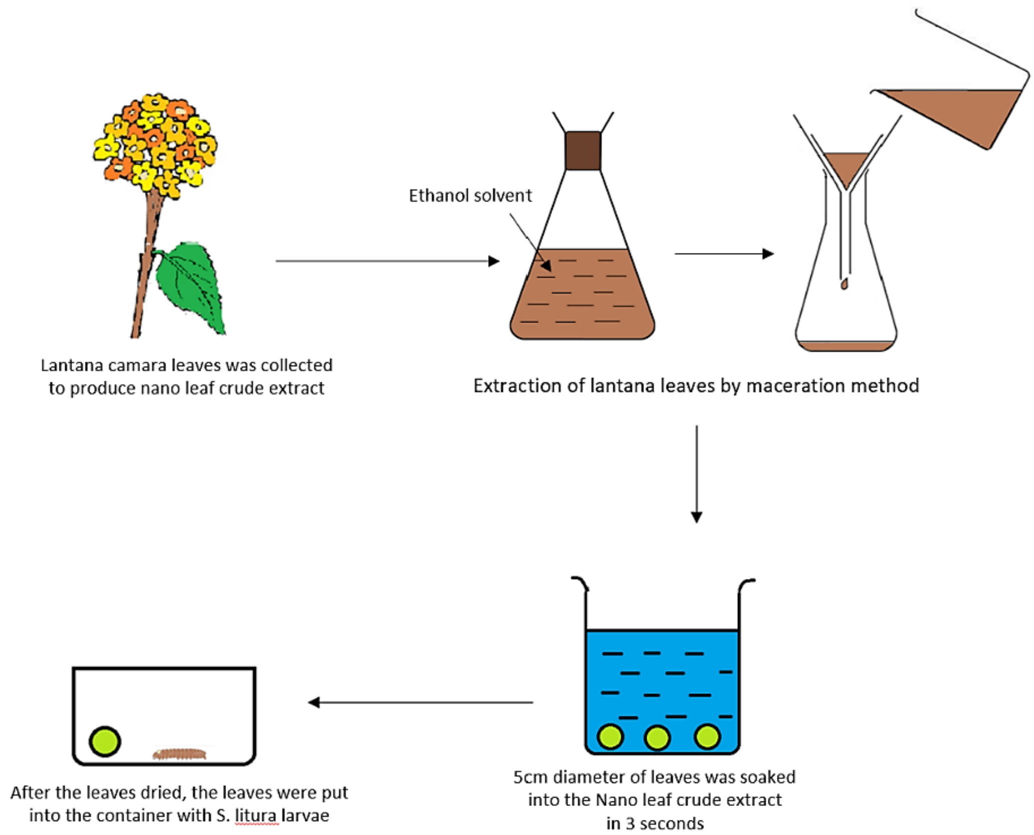
2.5 *Lantana camara*

Lantana camara is an ornamental plant that can be found widespread in the subtropical and tropical regions of America. For decades, this plant has been well-known to be a highly aggressive and toxic weed in terrestrial ecosystem.[34] In particular, the green foliage of *Lantana camara* can be toxic to animals if used as a feedstock.[35] Yet, this forest waste possessed insecticidal properties that are capable of inhibiting the growth of *Spodoptera litura* larvae, a notorious pest that lowered cotton production.[36,37] Kasmara *et al*. (2018) revealed the synthesis of biopesticide using the leaf extract of *L. camara* in *S. litura* control (Scheme 4). Many research has reported the use of nano biopesticides in pest control and the outcome was found to be positive, such as the high efficacy of the biopesticides and environmentally friendly.[38] In the case of *L. camara*, extract from the leaf crude was prepared from the ethanol fraction to produce nano extract formulation of *L. camara.* Subsequently, the efficacy of the nano biopesticide was evaluated based on the lethal dose on the mortality of third-instar *S. litura* larvae. The result showed that the mortality of third instar *S. litura* larvae increased when the concentration of nano crude extract of *L. camara* increased. In addition, the nano biopesticide was found to be more effective than the crude extract of *L. camara.* However, this nano biopesticide was found to be in moderate toxicity towards *S. litura*.[15]

In another study, Udapussamy *et al* (2022) synthesized the nano-emulsion using the essential oil from *L. camara* leaf and applied it as anti-mosquitocidal agent. The small size nanoparticles were found to have increased in physical and chemical properties, such as the improved stability and surface contact that can make it more efficient when applied as a biopesticide agent. The anti-mosquitocidal of the biopesticide was tested in laboratory setting, using the larvae and pupae of *Aedes aegypti*. Based on the result, the nano-emulsion showed inhibition of growth in the immature stage (larvae and pupae) and adult mosquitoes of *A. aegypti,* with LC_{50} recorded as the following output: 18.183 ppm (I), 23.337 ppm (II), 29.731 ppm (III), 38.943 ppm (IV) instars and 45.295 ppm (pupae), respectively. Moreover, the LD_{50} and LD_{90} values for adult mosquitoes were found to be 11.947 mg/cm^2 and 47.716 mg/cm^2, respectively. The result of this finding indicated that the nano biopesticide derived from the crude extract of the *L. camara* leaf was effective in the control of the mosquito vectors.[39] In addition, it was also evident that the use of forest waste, could play an important role in mosquito vector management.

2.6 Shrimp shell

The shellfish industry is one of the major sectors of fisheries and it contributes to huge economic value. In the shrimp processing industry, the flesh part is usually separated from the shell and head parts. The leftover shell and head of shrimp give rise to huge amounts of biowaste, which in turn posed a serious environmental concern and are sometimes accompanied by a severe obnoxious smell. These shrimp shells mainly contain protein, minerals and chitin. Fortunately, the deproteinization and demineralization of this biowaste lead to a precursor which further subjected to deacetylation affords the chitosan, which can be used in many beneficial ways, such as improving the production of orchids, increasing rice yields, wound healing, drug delivery and other purposes. According to a previous study,[12] the chitosan-fabricated silver nanoparticles have displayed excellent toxicity toward larvae and adult mosquitoes *(Aedes aegypti)* (Scheme 5) and the nanoparticles exhibited higher mortality even when in low dose. In the bioassay study, the LC_{50} of chitosan-fabricated silver nanoparticles generated the following output: 10.2 ppm for fourth instar larvae and 9.6 ppm for adult *Anopheles stephensi*; 11.3 ppm for fourth instar larvae and 12.0 ppm for adult of *Aedes aegypti*; 12.4 ppm for fourth instar larvae and 13.0 ppm for adult of *Culex quinquefasciatus*.[16] Overall, this result



Scheme 4 The *L. camara* leaf crude extract was prepared from the ethanol fraction to produce nano extract formulation of L. camara. The leaves were soaked into the crude extract and processed into nano-biopesticide before directed into the container containing the *S. litura larvae*. The bioassay result showed that the mortality of third instar *S. litura* larvae increased when the concentration of nano crude extract of *L. camara* increased.

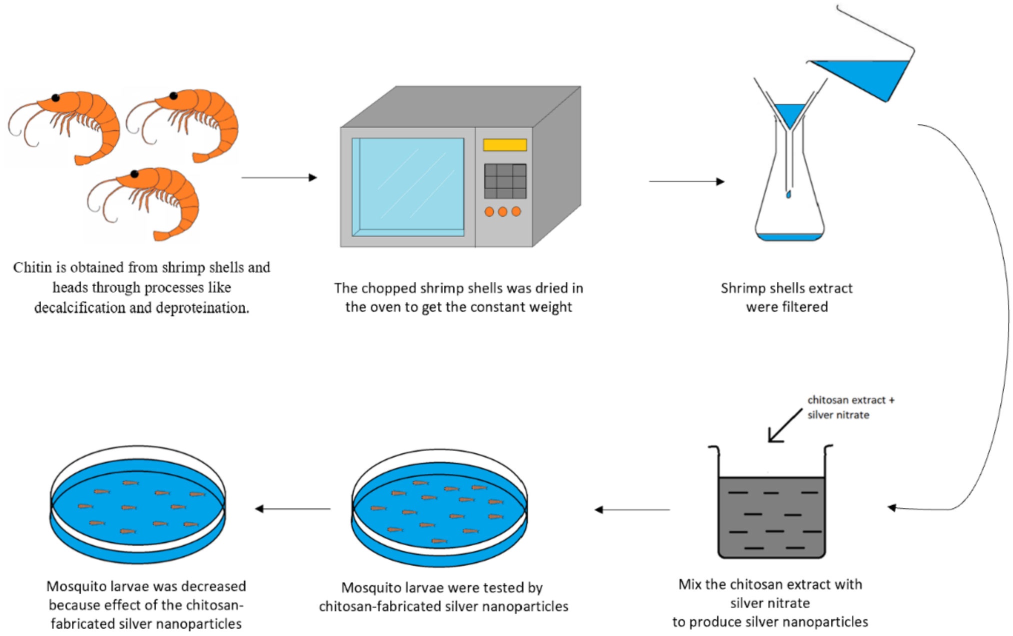
revealed that the chitosan-fabricated silver nanoparticles can be an excellent source of insecticide in controlling the growth of mosquito vectors.

Choudhary *et al* (2017) reported the use of chitosan-fabricated copper nanoparticles to combat the post flowering stalk rot (PFSR) disease of maize. The PFSR has caused a serious decline in the production of maize worldwide.[40] In the year 2014, the PFSR was reported to cause 22 to 64% yield losses in maize production in India.[41] Among the *Fusarium* species family, *Fusarium verticillioides* was identified as one of the major fungal species causing the PFSR diseases of maize.[42] In the field study, the best result was obtained when 0.06% of chitosan-fabricated copper nanoparticles were applied to treated seeds and the percent efficacy of disease control (PEDC) was recorded as 33.9%, after 4 hours of treatment. Overall, the chitosan-fabricated copper nanoparticles showed promising antifungal agent against PFSR of maize in pot condition and can be utilized as an alternative antipathogenic agent in sustainable agriculture and crop protection.

2.7 Hibiscus

Hibiscus, also known as *Rosa sinensis* is widely employed as a reducing agent and capping agent in the synthesizing of nanoparticles.[43] In the past, Hibiscus has been widely investigated and literature revealed that this plant contains poly-phenolic compounds, which may act as a potential antibacterial and antifungal agent.[44] Ogunyemi *et al* (2023) have converted the flora waste[40] from hibiscus flower into the production of cobalt oxide nanoparticles (Co_3O_4 NPs) and the nanoparticles were tested against *Xanthomonas oryzae pv. oryzae* (*Xoo*). In the past, the *Xoo* strain has been a major threat to the agriculture field due to the existence of bacterial leaf blight (BLB) disease that causes serious problems in the paddy plant (Scheme 6). In the field study, at a concentration of 200 g/ml of hibiscus-fabricated copper nanoparticles, the bacteria leaf blight BLB pathogenic bacterium *Xoo* was drastically reduced. This was evidenced when the disease leaf area percentage (DLA%) was reduced from 57.25% to 11.09%. Based on this research, the hibiscus-fabricated copper nanoparticles could act as a potential antipathogenic agent. Moreover, the research revealed that the use of cobalt oxide nanoparticles has no negative effects on paddy plant.[45]

In another study, Rani *et al*. (2016)[46] conducted a study in which they utilized *Hibiscus tiliaceus* as a reducing agent to synthesize silver nanoparticles. *Hibiscus tiliaceus*, a member of the *Malvaceae* family and a mangrove companion, is often considered as sea hibiscus or beach hibiscus. In this research,

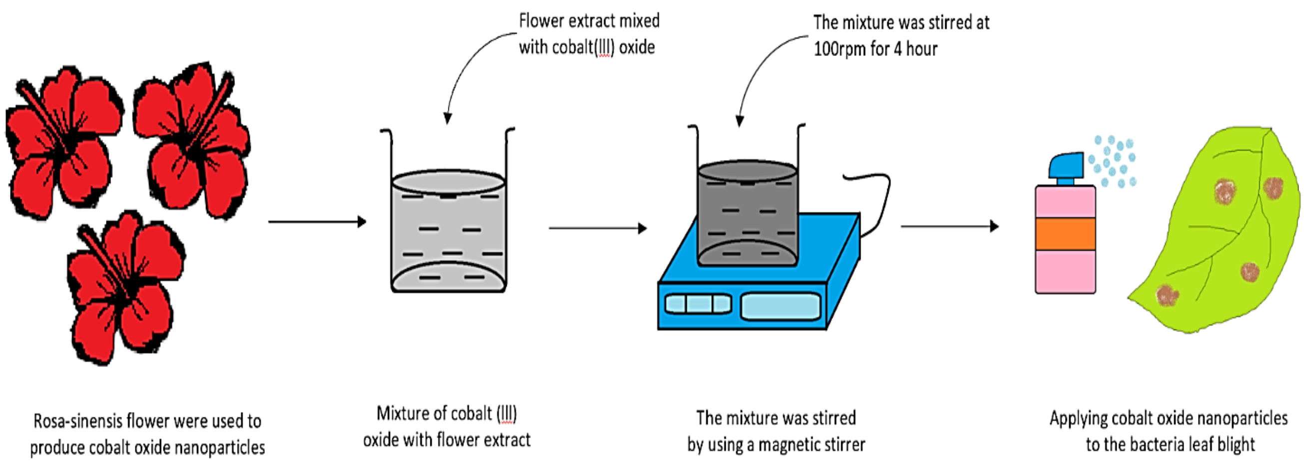


Scheme 5 Silver nanoparticles derived from chitosan based on the shrimp shell. The chopped shrimp wastes were dried in oven and shrimp shell extract was processed into silver nanoparticles. The chitosan-fabricated silver nanoparticles showed excellent insecticidal activity against the mosquito larvae.

Hibiscus tiliaceous leaf was extracted by double distilled water and then synthesized by mixing with silver nitrate to produce silver nanoparticles. The laboratory result showed that the hibiscus-fabricated nanoparticles displayed excellent antifeedant activity against *Helicoverpa armigera (H. armigera),* with the highest antifeedant activity recorded as 94.1%. The *H. armigera* usually infects broadleaf plants, such as cotton, chickpea, sunflower, soybean, canola, peanut, safflower, linseed and so on and has developed resistance to numerous insecticides. As such, there is an urgent need to seek alternative pesticides. The current innovation would provide a solution to the pathogens-resistance pesticide of pesticide issue and one day could pave the way for the development of nano-pesticides that benefit sustainable agriculture.[46]

2.8 Pomegranate peel

Pomegranate, also known as *Punica granatum* is a Mediterranean shrub or a small tree. After processing the pomegranate, the peel and leaf were separated from the flesh and disposed of as biowaste.[47] Some studies have revealed that pomegranate leaves have high insecticidal activity which can cause high mortality to insects and bring to a population decrease under optimum conditions. In a previous study, Ibrahim *et al.* (2022)[18] synthesized zinc oxide nanoparticles (ZnO NPs) from pomegranate peel extract and tested them against the *Sitophilus oryzae* (*S. oryzae*) and *Sitotroga*



Scheme 6 Cobalt oxide nanoparticles derived from hibiscus flower. The prepared hibiscus extract reacted with cobalt (III) oxide to form the cobalt oxide nanoparticles after stirring for 4 hours in 100 rpm. The resulted nanoparticles were applied to the bacteria leaf blight and the disease leaf area percentage (DLA%) was reduced from 57.25% to 11.09%.

Table 1. Comparison of size and morphology of various nanomaterials derived from biowaste as pesticide and the techniques used.

Source of nanomaterials	Experimental condition for producing nanomaterials	Size of Nanoparticles (nm)	Targeted species	References
Rice Husk	20 g of rice husk added with 100 mL of 1 N HCl for 2 h under magnetic stirring. The filtrate was collected and rinsed with deionised water, dried at 100 °C for 24 h and heated at 700 °C for 3 h using a muffle furnace. Subsequently, 100 g of collected ash were grinded into fine powder and heated at 700 °C for 3 h using a muffle furnace. The obtained white powder was sent for further characterization to confirm the size and morphology of synthesized silica nanomaterials.	15	F. fujikuroi	[20]
Pongamia pinnata leaf extract	The silver nanoparticles were synthesized by reacting the leaf extract (1.0 ml) with 20 ml of 10−3 M silver nitrate at room temperature. The colour changed after 1 hour indicating the formation of silver nanoparticles which was then verified over the UV-visible spectroscopy.	20	Aedes aegypti	[13]
Cashew nut peel oil	The cashew nut shell oil nanoemulsions formed following the low-energy emulsification method. The cashew nut shell oil, surfactant mixture (Tween80, Span20) and propylene glycol were mixed together in different ratio and dropwise into a beaker containing the aqueous phase in a stirring condition at room temperature for two hours.	52 to 60	Anopheles larvae	[32]
Lantana camara leaf extract	The nanoextract was prepared from Lantana camara crude leaf that was extracted from ethanol solvent via the maceration method. Subsequently, the crude extract (0.5 wt%) was added with tween 80 (25% surfactant) and ethanol (1 litre) and subjected to ultrasonic for 1 h.	73	Spodoptera litura	[15]
Shrimp shell	About 2 grams of powered chitosan was double distilled water (100 ml). The reaction mixture was heated until boiled for 20 min. After filtration, the extract was reacted with 1 mM silver nitrate and left for stirring at room temperature. The pale yellow solution was formed indicating the formation of AgNPs derived from chitosan.	17 to 50	Aedes aegypti	[16]
Hibiscus rosa-sinensis flower extract	The cobalt oxide nanoparticles were synthesized by reacting the aqueous flower extract with cobalt oxide using 1:1 ratio (v/v) to synthesize cobalt oxide nanoparticles. The resulting mixture was left for stirring at 100 rpm for 4 hours. Pure nanoparticles were generated by rinsing the synthesized cobalt oxide nanoparticles with double distilled water and centrifuge at 10,000 g for 20 min.	21.50 to 40.90	Xanthomonas oryzae pv. oryzae	[17]
Pomegranate Peels Extract	The zinc oxide nanoparticles were synthesized by mixing stoichiometric pomegranate peels extract with zinc nitrate (1 M) and left for stirring for 2 hours. The obtained white precipitate was centrifuged at 3000 g for 15 min and the white powder was dried at 60 °C for 24 hours. Finally, The zinc oxide nanoparticles were calcinated at 350 °C.	2 to 8	S. oryzae and S. cerealella	[18]

cerealella (*S. cerealella*). Both *S. oryzae (L.)* and S. cerealella are serious pests in stored grain, such as rice, wheat, maize, barley, sorghum, beans and so on.[48] To test the toxicity of the ZnO NPs, 40 gram of wheat grain and *S. oryzae* (L.) and *S. cerealella* was placed in the container respectively. The total number of insect mortality was recorded after 1,2,3,7 and 14 days. The result shows that the mortality of the insects increased when the concentration of ZnO NPs was increased. The higher mortality for *S. oryzae (L.)* was recorded (75%) when 150 ppm was employed while for *S. cerealella* was recorded at a concentration of 150 ppm which caused 86.1% of insect mortality. In all cases, the ZnO NPs inhibited the reproduction of the *S. oryzae (L.)* and *S. cerealella* after 14 days. Moreover, the low dose of ZnO NPs used may lower the adverse effect of pesticides impacting on the environment. More research is needed in the future to assess the potentially toxic effects of these nanomaterials on human health and the environment for future nano-pesticide development in pest control.[18]

Table 1 summarizes the sizes of nanomaterials derived from biowastes and their morphology. In most cases, the sizes of the nanoparticles possess moderate to good bioassay efficacy. In the current review article, a sustainable method of producing pesticides was described which aligns to the concept of sustainable development. Moreover, the current knowledge of using nano-pesticide from biowastes will promote the concept of circular economy and sustainable agriculture, using biowastes which was once a waste in the landfill. The use of cheap and sustainable sources for making pesticide would be of interest to the industries in the future.

3. Conclusion

Nano-pesticides derived from biowastes are promising, green, sustainable and economical alternatives to the current toxic synthetic pesticides in the market. In most cases, the nano-pesticides derived from biowastes were found to possess good to excellent crop protection. Overall, the investigation and use of biowaste-based nano-pesticides is an emerging field with many promising opportunities ahead. One of the limitations identified in this review is that the use of biowaste as a source of nano-pesticide is very much dependent to the biowaste amount collected for the upscaling process. To counter this problem, close relationship and cooperation between scientists or industry farmers and local government can mitigate this problem. The current review is significant because it enables the generation of new concepts in the use of environmentally friendly and sustainable methods in crop protection against pests and weeds. This was evident when the nano-pesticides derived from biowastes showed comparable effects in comparison to commercially available pesticides. In this aspect, biowastes are definitely viable and the possibility of employing biowastes in the development of nano-pesticides to replace the commonly use pesticides possible in the future trend of crop protection for agriculture applications enabling achieving the zero hunger goal of SDGs

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

Nomenclature

nm	Nanometre
Cu	Copper
NPs	Nanoparticles
ppm	parts per million
S. oryzae (L.)	*Sitophilus oryzae (Linnaeus)*
mg/L	Milligrams per litre
SiNPs	Silicon nanoparticles
F. fujikuroi	*Fusarium fujikuroi*
Brassica sp.	*Brassica* species
pH	potential of hydrogen
mol l^{-1}	moles per litre
2,4-D herbicide herbicide	2.4 Dichlorophenoxyacetic acid
n-RH	nano rice husk
g	gram
cm	centimetre
Corylus auellana L.	*Corylus auellana linnaeus*
FAO	Food and Agriculture Organization
Xac Corylina	*Xanthamonas arboricola pv.*
EU	Eurpean Union
CNC	Callulose nano crystal
HP	Hazelnut tree pruning shoot
HS	hazelnut shells
LNP	Lignin nanoparticle
Olea Europea L.	*Olea europea linnaceus*
%	percent
w/v	weight per volume
ZnO	Zinc oxide
C. maculatus	*Callosobruchus maculatus*
μg ml^{-1}	microgram per mililitre
A. Occidentale	*Anacrdium occidentale*
Cp-Ag NPs	cashew peel nanoparticle
mg/L	milligram per liter
CNSL	cashew nutshell liquid
rpm	revolutions per minute
A.Culicifacies	*Anopheles cilicifacies*
L. camara	*Lantana camara*
A. aegypti	*Aedes aegypti*
LC_{50}	lethal concentration 50
LD_{50}	lethal dose 50
mg/cm^2	milligram per square centimeter
PFSR	post flowering stalk root
PEDC	percent efficiency of disease control
CO_3O_4 NPs	carbon oxide nanoparticle
XOO	*xanthamonas oryzae pv. Oryzae*
BLB	bacteria leaf blight
DLA %	disease leaf area percentage
H. armigera	Helicoverpa armigera
S. cerealella	Sitotroga cerealella

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