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Nanotechnology and implementation in natural products green chemistry processes

M. M. Adeyemi[1*], P. E. Omale[1], O. A. Olawuyi[1], A. Ngokat[1] and A. Bhattacharya[2]

[1]Nigerian Defence Academy, Department of Chemistry, P. M. B. 2109, Kaduna, Kaduna State, Nigeria.
[2]Nanotechnology Section, Department of Biomedical Engineering, Rajiv Gandhi Institute of Technology and Research Centre Cholanagar, R.T. Nagar Post, Hebbal, Bangalore-560 032, India.

Nanotechnology, already showing great potential for application in environmental protection has been suggested to be able to provide green and effective alternatives for the management of insect pests in agriculture and post harvest processes. This is in an effort to reduce the hazardous effects of previously used non-biodegradable substances on humans and the environment. The paper will discuss emerging nanotechnologies in antifeedant and pesticide formulations from natural products including novel photodegradable insecticide involving nanoparticles. This will include studies on synthesized nanoparticles used as larvicides, antifeedants, insecticides and pesticides. Nanoscience and nanotechnologies have offered the opportunities to combine organic constituents from natural products with elemental components in order to create complex, innovative and specific material in chemical synthesis for future and immediate use in green technologies.

Key words: Nanotechnology, green synthesis, natural products.

INTRODUCTION

Nanotechnology has been defined as the manipulation of atom-by-atom interactions in nature which can take part in chemical and biological functions and processes. Nanotechnology is becoming a revolutionary field in its integration with the green chemistry approach. The current approach involves the use of material that are effective at nanoscale such as gold and silver because of their natural and chemical characteristics. The inorganic nanomaterials exhibit well- adopted physical, chemical, and biological properties, though properties may vary in size based on their character as well as on specific pH and temperature. Nanoscale metal oxides such as TiO_2, ZnO, and Al_2O_3 dendrimers (nanosized polymers built from branched units) are performed with atom–atom interaction (Bhattacharyya et al., 2014),

Nanotechnology has found a large field of application including agricultural food production and post harvest storage, improvements in nanoporous zeolites for efficiency in the dosage and release of required quantities of water and fertilizers in plants, nano-capsules for herbicide delivery and vector and pest management and nanosensors for pest detection (Scrinis

*Corresponding author. esdupe@yahoo.com. Tel: +234-803 453 2419.

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Table 1. Plants utilized in synthesizing nanoparticles.

S/N	Synthesized nano particles	Plants utilized for the synthesis
1	Gold nanoparticles	Emblica officinalis Ocimum basilicum Psidium guajava Syzygium aromaticum Tamarindus indica Terminalia catappa
2	Silver nanoparticles [AgNPs]	Brassica juncea Camellia sinensis Coriandrum sativum Cymbopogon exuosus Ipomoea aquatic Nelumbo nucifera
3	Gold and silver nanoparticles	Parthenium hysterophorus Tanacetum vulgare

and Lyons, 2007). Nanoparticles have also been involved in the synthesis of insect repellents and deterrents, antifeedants, insecticides and pesticides (Joseph and M. Morrison, 2006). Nanoencapsulation has been defined as a process through which a chemical compound such as an insecticide is slowly but efficiently released to a particular host plant for insect pest control. This process in conjunction with nanoparticles in form of pesticides allows for proper absorption of the chemical into the plants unlike the case of larger particles (Scrinis and Lyons, 2007). This process can also deliver DNAand other desired chemicals into plant tissues for protection of host plants against insect pests (Torney, 2009). Release mechanisms of nanoencapsulation include diffusion, dissolution, biodegradation and osmotic pressure with specific pH (Vidhyalakshmi et al., 2009).

The role of nanoparticles in agriculture

Agricultural production faces the challenge of enhancing crop production and providing nutritionally adequate diets for the increasing population, under uncertain climatic extremes, water scarcity, in limited and sometimes degraded land area, and mostly with poor quality water and air, associated with rapid changes in natural biodiversity as well as trying to resolve pre- and post- harvest losses associated with pests.

The use of nanotechnology in agriculture and green chemistry practices has been mostly theoretical, but the impact of Nanotechnology in the control of insect pests in the agricultural systems is intended to enhance food production (Carmen et al., 2005). The effective use of nanotechnology in agriculture sector could be multi-directional. It involves the delivery of encapsulated pesticides, insecticides, antifeedants, etc in nanomaterials for controlled release, stabilization of bio-pesticides, slow release of nanomaterial assisted fertilizers, bio-fertilizers and micronutrients for efficient use in addition to other agrochemcial applications (Ghormade et al., 2011).

Stored nanoparticles in plants influence some of the insect-plant interaction roles and the fact that plants have been observed to have the ability to produce secondary metabolites tend to help facilitate the process. Plants which have ability to produce nano synthesizing materials are solely responsible for producing metallic nano materials. The mechanism involved in production of this eco-friendly nanoparticle have been found as effective methods for preparation of nanoformulations as the plant producing nano particles are highly acceptable, as because, it maintains uniform size and shape without aggregation or agglomeration. The utilization of this key component from plants is a crucial factor for nanopesticides production via biological processes, a pathway for future eco-friendly pesticides. There are several methods that have been reported in literature for the synthesis of plant-nanoparticle-pesticide core-shell conjugate which can be used to control agricultural insect pests. These conjugant nano particles may be in different shape, size (2-150 nm) and various forms (Sooresh et al., 2011). *Medicago sativa* (alfalfa) was the first reported plant material used in the synthesis of nanoparticles and it was credited to been capable of synthesizing gold and silver nanoparticles. This has led to several other dried plant material being screened and evaluated for nanoparticle synthesis (Gardea-Torresdey et al., 2003). Some of these are listed in Table 1.

Some of these plants have found applications as larvicides, antifeedants, insecticides and pesticides, and it has been established that plant-based green synthesis approach is one of the effective method for silver nanoparticles (AgNPs) production. Other plants that have been used in the synthesis of AgNPs include *Acalypha indica* leaves, *Murraya koenigii* (*curry*) leaves, *Nicotiana tobaccum* leaves, *Eucalyptus*, *Jatropha curcas* seeds, *Rosarugosa*, *Trianthema decandra* roots, *Ocimum sanctum* stems and roots, *Sesuvium portulacastrum* leaves, *Macrotyloma uniflorum* seeds, *Ocimum sanctum* (*Tulsi*) leaves, *Stevia rebaudiana* leaves (Burklew et al., 2012); Others include some *Acanthe phylum*, *Citrus sinensis leaves*, *Ocimum tenuiflorum*, *Solanum trilobatum*, *Syzygium cumini*, *Centella asiatica*, *Arbutus unedo* leaves, *Ficus benghalensis* leaves, Mulberry leaves, *Olea europaea* leaves and *Chenopodium album* leaves (Vadlapudi and Kaladhar, 2014). The roots and leaves of *Acorus calamus* have the ability to synthesis silver nanoparticle in addition to having antioxidant, antimicrobial and insecticidal activities (Dhanasekaran et al., 2014).

Plant mediated metal nanoparticles are presently being introduced as insect pest control in agricultural sector along with other several plants responsible for production

Table 2. Some polymers used in nanoparticles for biopesticides controlled release formulations (CRFs) production.

S/N	Polymer	Active Compound	Nanomaterial
1.	Polyethyleneglycol	B-Cyfluthrin	Capsule
2.	Polyethylene	Piperonyl Butoxide and Deltamethrin	Capsule
3.	Polyethyleneglycol	Garlic Essential Oil	Capsule
4.	Carboxymethylcellulose	Carbaryl	Capsule
5.	Alginate-glutaraldehyde	Neen seed oil	Capsule
6.	Alginate-bentonite	Imidacloprid or Cyromazine	Clay
7.	Polyamide	Pheromones	Fiber
8.	Starch-based polyethylene	Endosulfan	Film
9.	Carboxymethyl chitosanricinoleic acid	Azadirachtin	Particlea
10.	Vinylethylene and vinylacetate	Pheromones	Resin
11.	Glyceryl ester of fatty acids	Carbaryl	Spheres

of several secondary metabolites which helps agricultural insect pest control loaded with nanomaterials. Synthesis involving the use of Nanoparticle has also been considered as a means of irradiating the tobacco caterpillar, *Spodoptera litura* (Fabricius) (Lepidoptera: Noctuidae) which is a major pest of grains and pulses with high mobility and reproductive capacity (Chakravarthy et al., 2012; Bhattacharyya and Debnath, 2008; Bhattacharyya, 2009). Inorganic nanoparticles such as CdS, Nano-Ag and Nano-TiO_2 have also been used to control *Spodoptera litura* which feeds on more than 120 host plants including tobacco, cotton, groundnut, jute, maize, rice, soybeans, cauliflower, cabbage, capsicum, potato, castor etc (Chakravarthy et al., 2012). Latex of *Alstonia scholaris* and *Hevea brasiliensis*, *Calotropis gigantean*, *Musa paradisiacal* and *Achras sapota*, also posses the potential to produce green nanoparticles (Mondal et al., 2011). This was also observed when nanoparticles loaded with garlic essential oil was effective against the storage pest of maize and milled flour *Tribolium castaneum* Herbst (Yang et al., 2009).

Insecticides of synthesized natural products for vector control have been a priority in recent times. Larvicidal activity of synthesized silver nanoparticles (AgNPs) utilizing aqueous extracts from *Eclipta prostrata*, a member of the Asteraceae was investigated against fourth instar larvae of filariasis vector, *Culex quinquefasciatus* say and malaria vector, *Anopheles* subpictus Grassi (Diptera: Culicidae). The stability of the silver nanoparticles can be attributed to the formation of silver electride that may form a thin layer on the aqueous surface of the reaction mixture. It seems quite probable that the phenols play an important part in the reduction of ions to AgNPs as the concept of antioxidant action of phenol compounds is not new. Therefore, in combination with mosquito nets or other vector control measures, such plants synthesized AgNPs may have significant impact on malaria and filariasis incidence and can be potential candidates to be considered in integrated vector control programs. Plants synthesized AgNPs, being readily available and their application methods being simple and affordable may be useful in protection against malaria and filariasis. The pediculocidal and larvicidal activity of synthesized silver nanoparticles using an aqueous leaf extract of *Tinospora cordifolia* was also reported to show maximum mortality against the head louse *Pediculus humanus* and fourth instar larvae of *Anopheles subpictus* and *Culex quinquefasciatus* (Rajakumar and Abdul Rahuman, 2011).

Controlled release formulations (CRFs)

The developed controlled release formulations (CRFs) have been found useful for efficient pest management in different crops and post harvest processes. It has been suggested that when a commercial formulation for practical field applications are sought after, it must be ensured that compatible material with the proposed applications: environment friendly, readily biodegradable, not generating toxic degradation by products and low-cost are used. The use of several biopolymers, that is, polymers that are produced by natural sources, which at the same time have good physical and chemical properties and still present mild biodegradation conditions, are an interesting approach to avoid the use of petrochemical derivatives that might be another source of environmental contamination. Some of the recognized common polymers (synthetic and natural ones) used in CRFs for insecticide and antifeedant applications are listed in Table 2.

Developing new nanopesticides

Microencapsulation has been used as a versatile tool for hydrophobic pesticides, enhancing their dispersion in aqueous media and allowing a controlled release of the active compound. Serving as delivery systems, they convene more selectivity, without hindrance in the accessibility of the bioactive compounds towards the target pathogen (Peteu et al., 2010). It has been observed that some nanopesticides have already been on the market for several years too. Attempt to develop essential oil for pesticides and insecticides have been made in a variety of water- soluble formulations such as nanoemulsion incorporated with B-cypermethrin (Wang et al., 2007) and essential oil-loaded microcapsules for pest control (Moretti et al., 2002).

Many attempts have been made to manage pests and insects, an example involves the use of biological control which has a high timing rate factor. This led to the development of the controlled release systems which has been termed a viable option. The Controlled Release Formulations (CRFs) associate the active compound with inert materials. The latter are responsible for protecting and managing the rate of chemical compound release into the target site in a defined period of time. The main purpose of controlled release systems is in controlling the availability of the active compound after the application. Most of those controlled release biopesticides applications were and are still been successfully made due to the advances in nanotechnology area.

Other advantages of the use of nanoparticle insecticides are the possibility of preparing formulations which contain soluble compounds that can be more readily dispersed in solution. It reduces the problems associated with drifting and leaching, due to its solid nature, and leads to a more effective interaction with the target insect. These features enable the use of smaller amount of active compound per area, as long as the formulation may provide an optimal concentration delivery for the target insecticide for longer times. Since there may be no need for re-applications, they also decrease the costs), reduce the irritation of the human mucous-membrane, the phytotoxicity, and the environmental damage to other untargeted organisms and even the crops themselves (Cauerhff and Castro, 2013).

In summary, nanotechnology can be applied in several ways in order to enhance efficacy of insecticides in crops and for post harvest storage processes. Nanotechnology would provide green and efficient alternatives for the management of insect pests in agriculture without harming the nature. An objection to the use of previously known synthetic pesticides is still ongoing as there is a great concern regarding the fact that such chemical compounds have potential to exert hazardous effects on human and the environment (Khot et al., 2012) and when we have a nano-pesticide, it becomes a double edged weapon. However, the question that comes to mind is how safe are these Nanopesticides?

Safety of nanopesticides

Due to growing concerns, presentations were made at the EPA Pesticide Program Dialogue Committee (PPDC) meeting on the safety of the usage of Nanopesticides. The supposed potential Human Health Concerns were categorized into:

(i) Dermal absorption (so small they may pass through cell membranes)
(ii) Inhalation (go to the deep lung and may translocate to the brain that is, could cross the blood brain barrier)
(iii) Potential environmental concerns: High durability or reactivity of some nanomaterials raises issues on their fate in the environment, that is, biodegradability.
(iv) Lack of information to assess environmental exposure to already engineered nanomaterials.

Through considerations for nanotechnology-based pesticides (NBPs) exposures, researchers have found that effects of dermal exposure to pesticides may be localized at the immediate area of contact or the pesticide may be absorbed into the bloodstream, depending on a variety of factors, most notably, whether or not the active ingredient or carrier is lipid soluble.

In recommendations to assess exposure to Nanotechnology- based pesticides, reports according to the Government Accountability Office, since 2007 stated that the EPA has received a few applications for registration of various nanosilver pesticide preparations. Some of the applications have disclosed the fact the pesticide included nanomaterials, while in other cases the agency was able to determine the pesticide contained nanomaterials from the manufacturing processes.

It was also found that numerous studies and reviews will be required to address the exposure related issues. There are several lines of existing nanotechnology and pesticide research that are directly relevant to NBP exposure. While no single study will address all of the exposure-related concerns outlined above, it is evident that much of the prior research conducted on pesticides and nanomaterials would be applicable to characterize exposure to NBPs. This had led to the need to determine:

(i) If completely new active ingredients that are synthesized as NBPs are amenable to existing tests and assessment
(ii) If data from conventional active ingredients that may be reformulated into NBPs are suitable for registration purposes, and
(iii) If NBPs should be regulated under a completely different framework (Cauerhff and Castro, 2013).

Conclusion

The evolution of Nanoparticles is a resourceful and effective means for control of pests, but the deficiency of required information on how their detailed mechanisms and actions and how they can be controlled are giving regulators pause before allowing their release into the environment. Nanopesticides hold promise for reducing the environmental footprint left by conventional pesticides (Khot et al., 2012). Research on nanoparticles and insect control should be geared toward introduction of faster and ecofriendly pesticides in future. It is time therefore that leading chemical companies try to focus on formulation of nano scale pesticides for delivery into the target host tissue through nanoencapsulation. Nanoencapsulation is currently the most promising technology for protection of host plants against insect pests.

At present, the toxicological and ecotoxicological risks linked to this expanding technology ("emerging technology") cannot be assessed yet. Further developments in nanotechnology in this sector can be expected to become the main economic driving forces in the long run and benefit consumers, producers, farmers, ecosystems, and the general society at large. Over the next two decades, the Green Revolution would be accelerated by means of nanotechnology. While nanotechnology is increasingly moving into the centre of public attention, it is currently not yet linked to any great degree to concerns about health and the environment (Bhattacharyya et al., 2010; 2011).The current level of knowledge does not appear to allow a fair assessment of the advantages and disadvantages that will result from the use of some nanopesticides. It is clear that a great deal of work will be required to successfully combine analytical techniques that can detect, characterize (e.g., through size, size range, shape or nature, surface properties), and quantify the active ingredient and adjuvants emanating from nanoformulations, and also to understand how their characteristics evolve with time, under realistic conditions.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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