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Nanotechnology and insecticidal formulations

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ABSTRACT

Formulating the material as nanoparticles allows a significant increase in water solubility, dissolution rate and dispersion uniformity upon application while no chemical alteration to insecticide molecule is actually made. The conventional formulating process not only reduces efficacy but also gives rise to many secondary problems. Insecticides sensitive to light and other environmental degradation factors benefit from nano-encapsulation. Loading them into protective nanoparticles will provide controlled release and retard their fast evaporation and degradation. Various types of insecticidal compounds are being nanoformulated as nanoemulsions, nanodispersions, polymer based formulations etc. Similarly inorganic materials are nanosized or conjugated with organic active ingredient on nanoscale. In this review, various types of nanoformulated insecticides are disused with emphasis on their preparation, efficacy and application for sustainable agriculture.

Keywords: *Agriculture, Plant protection, Insecticidal activity, Nanoparticle, Insecticide formulation, Nanoemulsion, Encapsulation, Botanicals, Essential oils, Environmental fate, nanosilver.*

INTRODUCTION

Insecticides are used in different ways, based on the physical-chemical characteristics of the each chemical substance, the area that needs to be covered and the target. However, due to several degradation processes, such as leaching or destruction by light, temperature, microorganism or even water (hydrolysis), only a small amount of these chemical products reaches the target site. For this reason, repeated application of pesticides become hence necessary to efficient control of target pests, which increase the cost and might cause undesirable and serious consequences to the ecosystems, affecting human health (Gavrilescu 2005). Due to the lack of selectivity, their unrestrained use can also lead to the elimination of the natural enemies, what implies in the fast growth of plague population (Khan et al. 2015). The formulation technology tries to overcome such problems, however with variable success; nanotechnology is one promising way to do so efficiently.

Formulating the material as nanoparticles allows a significant increase in water solubility, dissolution rate and dispersion uniformity upon application while no chemical alteration to insecticide molecule is actually made. Diminishing particle size to the nanoscale boosts up saturation solubility of the material. Upon a significant reduction of the particle radii achieved by nanosizing, the surface area, tremendously increases, causing a much faster dissolution (Muller and Keck 2004). The conventional formulating process not only reduces efficacy but also gives rise to many secondary problems. Development of nanoparticles for agricultural use is much cheaper and easier compared to their application in other fields. Additional enhancement of solubility by nanosizing is achieved when utilizing nanoparticle preparation methods which lead to a partially or fully amorphous product (Margulis-Goshen and Magdassi 2012). Insecticides sensitive to light and other environmental degradation factors may also benefit from encapsulation into such porous silica nanoparticles or monolith silicon dioxide. Many essential oils, which on one hand, have insecticidal activity, but, on the other hand, are extremely volatile and sensitive to degradation, are suitable for such nano-encapsulation. Loading them into protective nanoparticles will provide controlled release and retard their fast evaporation and degradation (Oliveria et al. 2014) (Figure 1).

As per the International Organization for Standardization, ISO, materials with external dimensions or internal structures on a nanoscale are referred to as nanomaterials and the term nanoscale is generally limited to about 100 nm. Because of their nanoscale, nanomaterials exhibit properties and behaviour that differ from, or are additional to, those of coarser bulk materials with similar chemical compositions. Debate exists whether to include materials such as carriers as nanomaterials which generally have outer diameters much larger than 100 nm although the internal functional features may be smaller than 100 nm. Nanopesticides, thus may or may not fall within the definition of nanomaterials. Kah and Hoffman (2014) concluded that 'Nanopesticides may be used to describe any pesticide formulation that (a) intentionally includes entities in the nanometer size range, (b) is designated with a "nano" prefix (e.g., nanohybrid, nanocomposite), and/or (c) is claimed to have novel properties associated with the small size'. In this review, we will discuss the various types of nanopesticide formulations, their preparation, efficacy and application with brief comments on their environmental fate.

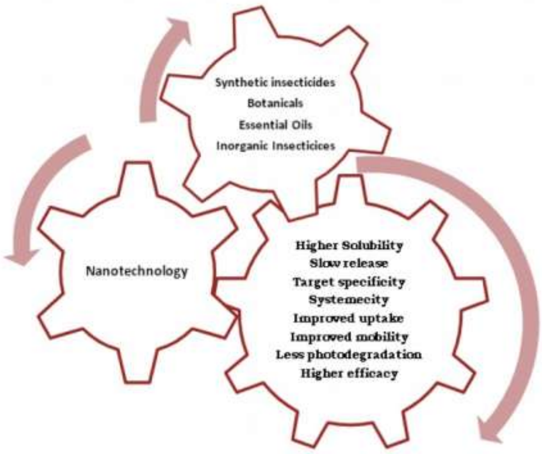

Figure 1. Potential benefits of nanoformulating insecticidal compounds.

CATEGORIES OF NANOPESTICIDE FORMULATIONS

The principal objectives of nanopesticide formulations are (a) to increase the solubility of poorly soluble active ingredients (a.i.) or (b) to release the a.i. in a slow/targeted manner and/or protect the a.i. against premature degradation. Subcategories are distinguished based on the quantities/types of adjuvants and expected discrepancies in terms of environmental fate. Many nanoformulations are a combination of several surfactants, polymers, and metal nanoparticles in the nm size range. The development of economically viable preparation and stabilization methods remains the subject of intensive research; reviewed by Gutierrez et al. (2008), Mason et al. (2006), Solans et al. (2005), and Tadros et al. (2004).

Slow/targeted release formulations are aimed at a.i. that tend to degrade under environmental insults or move away from the target. Increased water solubility is generally achieved by addition of surfactants. Now, by means of nanoparticulate formation of the a.i., possibly with a simultaneous change in solid structure e.g., metastable crystal modifications apparent water solubility is attempted (Horn and Rieger 2001). Either approach may result in an increase in the bioavailability of the a.i. Currently, the most common pesticide formulations for poorly water soluble a.i. are emulsifiable concentrates (ECs) and oil-in-water (O/W) emulsions. ECs still represented about 28% of the total number of formulations listed in the Pesticide Manual in 2007 (Knowles 2009). The main disadvantages of ECs relate to the use of organic solvents, leading to increases in the cost and flammability, as well as in dermal toxicity for the handlers and most important of all, the relatively poor stability after dilution (droplets of about 10 μm) (Knowles 2005). O/W emulsions have been proposed as an alternative to ECs. O/W emulsions generally consist of a mixture of a non-ionic surfactant, block polymers and polymeric surfactants. The drawback to O/W emulsion is that emulsification requires a high energy input with particle size ranging from 500 nm to 2 μm (Knowles 2005). Most nanoformulations aiming to increase the solubility of a.i. derive directly from these two mentioned approaches. Various types of nanoformulations attempted at achieving specific characteristics of pesticides are listed in Table 1. The major types of insecticidal nanoformulations are described as follows.

Polymer-Based Formulations

Most of the polymer-based nanoformulations are meant for the controlled release of a.i. (Kah and Hofmann 2014). Because of some polymeric support systems for the steric stabilization, nanoemulsions and polymer-based formulations are sometime classified together (ObservatoryNano 2010). Kah et al. (2013) made a distinction due to expected discrepancies in environmental fate, mainly caused by the presence of solid particles in the nm size range, and the designed slow/targeted release of the a.i. in general, two types of polymer-based nanoformulations can be distinguished: polymeric nanospheres, and nanocapsules. For the former, the distribution of a.i. is not specified, whereas the latter exhibits a core-shell structure that can act as a reservoir for a.i. dissolved in a polar or nonpolar solvent (Anton et al. 2008).

Table 1. Potential Applications of Nanotechnology in the Pesticides Sector

Function	How this can be achieved	Current examples
Enhanced apparent solubility	Nano- and microemulsions	Emulsion-based registered pesticides, Banner MAXX of Syngenta
Faster decomposition in soil and/or plant	Nanocatalyst-conjugated ai inmicrocapsules	SDS-modified TiO2/Ag conjugated with ai such as dimethomorph; imidaclopridand avermectin
Controlled release	Nanocapsules, nanospheres	Polymeric stabilized bifenthrin; nanocomposite 2,4-D; porous hollow Siencaged validamycin
Targeted delivery	Nanocapsules	Nanoenapcsulated glyphosate or sulfonylurea herbicide
Protection against premature degradation	Nanocapsules with catalyst aiconjugate	TiO_2-M262 polymer metaflumizone; porous hollow Si-encaged validamycin
Enhanced uptake/efficacy	Nano- and microemulsions,nanospheres	Nanopermethrin; nanosphere insecticides
Enhanced toxicity to target organism (lower dose)	Nanodispersions; nanosuspensions	Nanodispersed triclosan
Nanoparticle as ai	Nanometals and nanoclays	registered Nano-Ag biocide; Nano-Si

(after Kookana et al. 2014)

Nanocapsules have several advantages over larger capsules e.g., stability of the spraying solution, increased uptake, increased spraying surface, and reduced phytotoxicity owing to a more homogeneous distribution. However, designing capsules in the low nm size range while keeping the amount of a.i. sufficiently high relative to the amount of polymer forming the core-shell structure is challenging. In addition, no studies have suggested that nanosized capsules would provide a more controlled release than microcapsules. Boehm et al. (2000) compared the properties of nanospheres prepared with various amounts of poly(epsilon-caprolactone) to improve the delivery of a.i. to plants. The release of the a.i. was immediate and followed a release profile similar than that of a classical suspension. Although the addition of surfactants did not directly influence the formation of nanospheres; a stability test showed that surfactants were necessary in order to prevent crystallization of the a.i. over a two-month period. Boehm et al. (2003) later tested the efficacy of similar nanospheres loaded with insecticide (average particle size of 135 nm and 3.5% loading rate) on cotton plants infested with aphids. The speed of action and sustained release showed no improvement over a classical suspension, but the small size of the nanospheres was shown to enhance the penetration of a.i. in the plants and consequently to improve the systemicity of the a.i. (Boehm et al. 2003).

Liu et al. (2008) reported a method to produce polymer-stabilized bifenthrin nanoparticles using a multi-inlet vortex mixer to reach high supersaturation followed by rapid nucleation and growth of nanoparticles (named the Flash Nanoprecipitation Process). Kumar et al. (2010) and Shakil et al. (2010) recently proposed a self-assembly preparation method using poly(ethylene glycol) and various copolymers for the controlled release of insecticides. The diffusion controlled release rate of a.i. could be adjusted by changing the proportions and molecular weights of the polymers. Several studies have also proposed the use of polymeric nanospheres for the release of various fungicides for treating wood, using conventional pressure treatment methods (Liu et al. 2002a; 2002b; 2002c; Liu et al. 2001; Salma et al. 2010). Polymer nanoparticles can serve as a protective reservoir and diffusion-controlled release carrier. The biocide can thus be released at the minimum rate required to protect the wood, which results in longer protection and a reduction in losses due to leaching. Salma et al. (2010) recently reported the development of a novel approach aiming to tackle the weaknesses of the previously developed formulations (by providing lower-cost ingredients, a single preparation step, and optimization of delivery and release rates). Chang et al. (2010) developed a novel nano particle synthesis method wherein contrary to the most recognizable whiskers of slender parallelepiped rods, unique nanoparticles of about 50–100 nm were obtained from chitin after consecutive acid hydrolysis and mechanical ultrasonication treatments. Bhan et al. (2014) encapsulated temephos and imidacloprid within biodegradable and biocompatible, polyethylene glycol in different ratios by using melt-dispersion method. They reported that the non-capsulated temephos and imidacloprid were more effective as compared to their encapsulated forms however, the mortality rate remained same after encapsulation. Roy et al. (2009) developed biopolymer microspheres of sodium alginate and starch were prepared by employing $CaCl_2$ as a crosslinker loaded the microspheres with an insecticide, chlorpyrifos. It is found that whereas 50% release occurs in one day only when the pesticide is applied directly to the soil while it taken 5 days for the same extant of release when release occurs through swelling and eroding loaded biopolymeric beads. Kang et al. (2012) studied the effects of two chitosan based nano types of pyrifluquinazon and a non-nano type of pyrifluquinazon on mortality of the green peach aphid, *Myzus persicae*. According to the bioassay both types of pyrifluquinazon at all concentrations were effective for controlling *M. persicae*. However, the nano type pyrifluquinazon exhibited a more effective controlled-release feature than that of the other types. Kumar et al. (2014) synthesised imidacloprid loaded sodium alginate nanoparticles. Transmission electron micrographs (TEM) confirmed the size of pesticide-loaded nanoparticles in the range of 50–100 nm. Entrapment efficiency and pesticide loading was estimated to be 98.66%and 2.46% respectively. Sodium alginate nanoparticles because of their biodegradability, biocompatibility, better stability, low toxicity, simple and mild preparation methods, offer a valuable tool to pesticide delivery systems.

Solid lipid nanoparticles (SLNs) have been intensively investigated for the formulation of pharmaceuticals as they combine the advantages of emulsions and liposomes with those of polymer nanoparticles, while simultaneously avoiding some disadvantages (e.g., possibility of slow release and reduced stability/toxicological problems (Torchilin 2006). Whilst exhibiting similar insecticidal activity, SLNs of γ -cyhalothrin were shown to be less toxic towards fish and daphnia than an EC formulation (by a factor 10 and 63, respectively (Frederiksen et al. 2003). In addition, the particle size of the SLN formulations had only a slight effect on the biological activity (Frederiksen et al. 2003). Lai et al. (2006) showed that SLN formulations can remain stable over a two-month period and significantly reduce the loss of a.i. by evaporation when compared to classical emulsions (prepared with a maximum 5% surfactant, water, and homogenized under high pressure). SLNs can cover an extremely wide range of sizes (up to 100 μm in Frederiksen et al. 2003; from about 200–300 nm in Lai et al. 2006). A second-generation of lipid nanoparticles has recently been developed, incorporating liquid lipids into the solid matrix of solid lipid nanoparticles in order to increase the payload and slow release of the a.i. The preparation of coated liposomes for the slow-release of insecticide was first described by Bang et al. (2009). Two studies have since tested the insecticidal efficacy of such formulations and demonstrated the prolonged or delayed activity of the nanoformulations relative to that of the pure a.i. (Hwang et al. 2011; Kang et al. 2012). Two papers have recently been published on the potential of such formulations to protect deltamethrin from photodegradation (Nguyen et al. 2012a,b). Both direct and indirect photodegradation were reduced for the formulated a.i. relative to the pure a.i., but relatively high losses were still observed.

A number of polymer-based nanoformulations in the form of nanogels, or nanofibers have recently been proposed for this purpose. Nanogels may be superior to nanospheres (or microspheres) because they are insoluble in water and thus less prone to swelling or shrinking with changes in humidity (Bhagat et al. 2013), and they can significantly improve the loading and release profiles (limited the occurrence of bursts or potential leaks (Paula et al. 2011). Recently, nanogels have been proposed for use in plant protection products as a possible way to meet organic farming standards, with pheromones, essential oils, or copper as the a.i. Pheromones are considered to be highly specific and eco-friendly biological control agents, Bhagat et al. (2013) proposed the immobilization of pheromones within a nanogel. Evaporation of the pheromones in the nanogel was significantly reduced compared to the evaporation of the pure a.i., extending their effectiveness for up to 33 weeks compared to only three weeks for the pure a.i. The efficacy of the nanoformulation was also demonstrated in an open orchard during an adverse season. The efficacy of a nanogel formulation of essential oil extracted from *L. sidoides* was also shown to be superior to that of the free oil (Bhagat et al. 2013). Brunel et al. (2013) proposed the use of pure chitosan nanogels to improve the performance of antifungal treatments based on copper. Formation of the copper(II)–chitosan complex is pH dependent, and since most fungi tend to reduce the pH of their surrounding environment, it is also suggested that the release of copper(II) may be triggered by the growth of the pathogen. When testing the formulations (over 7 days) a strong synergistic effect was observed between chitosan and copper in inhibiting the growth of *Fusarium graminearum*. The potential mechanism remains unclear (Brunel et al. 2013).

Nanofibers obtained by electrospinning have recently been investigated for plant-protection applications (Persano et al. 2013). The potential advantage of such nanofibers over spheres or capsules lies in their ability to avoid the release bursts that occur when the a.i. is not homogeneously distributed within the polymer matrix (Xiang et al. 2013). Hellman et al. (2011) demonstrated the possibility of efficiently incorporating pheromones into nanofibers made of polyamide or cellulose acetate, and of achieving an almost linear release over several weeks. The authors proposed that nanofiber webs could be distributed across the fields to be protected in order to allow a uniform release of pheromones. A similar nanofiber network composed of poly(lactic acid) and cellulose nanocrystals has been presented by Xiang et al. (2013). The fibers loaded with thiamethoxam were efficient against whitefly over a 9 day period in a glass house experiment, at 50% of the recommended dosage for the pure a.i. (Xiang et al. 2013). However, no comparisons with commercial formulations or with the pure a.i. were performed and it is therefore not possible to draw any conclusions on possible reductions in application rates.

In a series of experiments, insecticide formulations with polyethylene glycol (PEG) based amphiphilic copolymers were studied by Shakil et al. 2010. Release of the a.i. in water was significantly slower than from commercial formulations for a variety of a.i. including imidacloprid (Adak et al. 2012), thiamethoxam (Sarkar et al. 2012), carbofuran (Pankaj et al. 2012), thiram (Kaushik et al. 2013) and β-cyfluthrin (Loha et al. 2011). The release rates increased with increasing PEG molecular weight, potentially allowing the availability to be tuned to the optimum period. Another formulation based on PEG with acephate as a.i. (Choudhury et al. 2012) was shown to have both a greater efficacy against target organisms and a lower toxicity to non-target organisms than its commercial counterpart (Pradhan et al. 2013). The greater efficacy could be explained by a slower rate of release and consequent protection of the relative labile a.i., but as with the nanoemulsions, the reasons for the lower toxicity to non-target organisms have yet to be elucidated. Hill et al. (2015) developed pH responsive nanoparticles from polysuccinimide to capitalize on the higher pH of plant phloem for the design of a site-specific delivery system to plants. It was found that above pH 7, the hydrophobic succinimidyl units of nanoparticles hydrolyzed to release encapsulated materials. Plant toxicity studies showed that the polymer materials exhibit little to no toxic effects at biologically relevant concentrations.

Many recent works using polymer-based nanoformulations have shared the common objective of developing less harmful plant-protection products through the use of biodegradable polymers and/or a.i. of natural origin. The types of polymers considered for nanopesticides consist mainly of polysaccharides (e.g., chitosan, alginates and starch), polyesters (e.g., poly-ε-caprolactone, and polyethylene glycol) etc. Recently, there has been an increase in the use of biodegradable materials of biological origin such as beeswax, corn oil, or lecithin (Nguyen et al. 2012a,b), or cashew gum (Abreu et al. 2012). Table 2 provides a list of the commonly used polymers for nanoformulating the insecticides. In addition to being viewed as more eco-friendly, it is conceivable that such matrix material, when associated with a.i. of natural origin, could be considered for use in organic crop production.

Table 2. Major examples of polymers often used in the nanoparticle production.

Polymer	Active Ingredient	Nanomaterial
Lignin-polyethylene glycol-ethylcellulose	Imidacloprid	Capsule
Polyethylene glycol	B-Cyfluthrin	Capsule
Chitosan	Etofenprox	Capsule
Polyethylene	Piperonyl Butoxide and Deltamethrin	Capsule
Polyethylene glycol	Garlic Essential Oil	Capsule
Poly(acrylic acid)-b-poly(butyl acrylate) ;Polyvinyl alcohol; Polyvinylpyrrolidone	Bifenthrin	Capsule
Acrylic acid-Bu acrylate	Itraconazole	Capsule
Carboxymethyl cellulose	Carbaryl	Capsule
Alginate-glutaraldehyde	Neem Seed Oil	Capsule
Alginate-bentonite	Imidacloprid or Cyromazine	Clay
Polyamide	Pheromones	Fiber
Starch-based polyethylene	Endosulfan	Film
Methyl methacrylate and methacrylic acid with and without 2-hydroxyethyl methacrylate crosslinkage	Cypermethrin	Gel
Lignin	Aldicarb	Gel
Lignin	Imidacloprid or Cyromazine	Granules
N-(octadecanol-1-glycidyl ether)-O-sulfate chitosanoctadecanol glycidyl ether	Rotenone	Micelle
Polyethyleneglycol-dimethyl esters	Carbofuran	Micelle
Carboxymethyl chitosan-ricinoleic acid	Azadirachtin	Particle[a]

Polymer	Active Ingredient	Nanomaterial
Chitosan-poly(lactide)	Imidaclopride	Particle[a]
polyvinylchloride	Chlorpyrifos	Particle[a]
Cashew gum Extract	*Moringa Oleifera*	Particle[a]
Chitosan-angico gum	*Lippia Sidoides* essential oil	Particle[a]
Polyvinylpyrrolidone	Triclosan	Particle[a]
Anionic surfactants (sodium linear alkyl benzene sulfonate, naphthalene sulfonate condensate sodium salt and sodium dodecyl sulfate)	Novaluron	Powder
Vinylethylene and vinylacetate	Pheromones	Resin
Glyceryl ester of fatty acids	Carbaryl	Spheres
Poly(ε-caprolactone) Active	Ingredients[b]	Spheres
Poly(methyl methacrylate)-poly(ethylene glycol) Polyvinylpyrrolidone	Carbofuran	Suspension

[a] The authors do not mention which active compounds they encapsulated in the nanospheres;
[b] The authors do not mention if the particles are spheres or capsules.
(after Perlatti et al. 2013)

Nanoemulsions

The interest in nanoemulsions has experienced a continuous increase in the last years, this enormous interest is triggered by the wide range of applications, namely in the pharmaceutical, cosmetic, food, chemical, etc. industries (Solans and Solé 2012). Nano-emulsions have advantages over conventional emulsions due to their small droplet size which confers them stability against sedimentation or creaming and a transparent or translucent optical aspect (similar to that of microemulsions). However, nano-emulsions, in contrast to microemulsions which are thermodynamically stable, are non–equilibrium systems which may undergo flocculation, coalescence and/or Ostwald ripening. Nevertheless, with an appropriate selection of system components, composition and preparation method, nano-emulsions with high kinetic stability can be achieved. It is generally accepted (Taylor 1998) that nano-emulsion main breakdown process is Ostwald ripening (diffusion of molecules of the disperse phase from small to big droplets, through the continuous phase, as a consequence of their different Laplace pressure). Nanoemulsions are often said to be metastable as they may possess a relatively high kinetic (meta-) stability (e.g., several years, Gutierrez et al. 2008). However, flocculation may be a possible breakdown mechanism for nano-emulsions formulated with mixed nonionic-ionic surfactants (Wang et al. 2009).

The misconception in the scientific literature between nanoemulsions and microemulsions is widespread; two recent reviews; Anton and Vandamme (2011) and McClements (2012) are illustrative of the effort in clarifying the differences and similarities of these colloidal dispersions. Nanoemulsions (also called as miniemulsions, ultrafine emulsions, and submicron emulsions (Anton et al. 2008; Lawrence and Warisnoicharoen 2006; Song et al. 2009) are emulsions with a droplet size that can overlap with those of microemulsions. Nanoemulsions are produced by methods requiring high-energy input e.g., requiring high-shear stirring, high-pressure homogenizers, or ultra-sound generators. Recent research has therefore focused on developing a variety of reproducible low-energy emulsification methods like spontaneous emulsification methods and phase inversion temperature methods (Anton et al. 2008). Nanoemulsions contain lower concentration of surfactants (5–10%) than microemulsions (about 20%) and many preparation methods include a step that consists of diluting a microemulsion. The range of droplet sizes typically quoted is 20–200 nm. Distinct properties of nanoemulsion include a possible higher efficacy (Anjali et al. 2010; Yang et al. 2009), reduced hydrolysis (Song et al. 2009), and reduced volatilization of the a.i. (Yang et al. 2009). Tadros et al. (2004) suggested that wetting, spreading, and thus penetration, may be enhanced due to the low interfacial tension of the droplets. Recent work has indicated higher uptake of a.i. as well (Anjali et al. 2010; Kumar et al. 2013). Wang et al. (2007) showed that no precipitation occurred in the nanoemulsion formulation of β-cypermethrin within 24 hr of dilution, in contrast to a commercial microemulsion. Since precipitation may reduce the bioavailability of the a.i., the authors suggested that nanoemulsion may thus allow the application rate to be reduced. Zeng et al. (2008) observed a slightly slower release of β-cypermethrin from a nanoemulsion than from a commercial EC. Results from two recent studies support the hypothesis of enhanced uptake by the formulating insecticides as nanoemulsions. Experiments on a series of nanoemulsions of neem oil showed that the LC_{50} decreased with droplet size, which was interpreted as indicating an increased uptake of smaller droplets (Anjali et al. 2012). In the second study, the efficacy of a nanoemulsion of permethrin was significantly higher than that of the pure a.i., which was again interpreted as indicating an increased uptake of the nanoformulated a.i. (Kumar et al. 2013). The effects on non-target organisms (i.e., soil bacteria and plants) were reduced (Kumar et al., 2013), but the reasons for the different effects on target and non-target organisms are yet to be elucidated.

The general aim of nanoemulsions of insecticides is to increase the apparent solubility of poorly soluble a.i., while keeping the concentration of surfactants lower than that in microemulsions. Once formulation design is established, microemulsions form spontaneously upon addition of water and gentle stirring (unlike classical emulsions where preparation requires large energy input (Lawrence and Warisnoicharoen 2006; Pratap and Bhowmick 2008). The determination of the best proportions of each ingredient (while keeping costs as low as possible) may be challenging as found for various pesticides (e.g., novaluron, Elek et al. 2010; cyhalothrin, Feng et al. 2010; dufulin, Hu et al. 2009; dimethyl dichlorovinyl phosphate, Shen et al. 2009; abamectin, Wei et al. 2009; cyhalothrin, Zhao et al. 2009). The particle size in microemulsions may be about 250 times smaller than typical pesticide particles (ETC 2004) and several reports have suggested diameters of less than 100 nm (ETC 2004; Knowles 2005; ObservatoryNano 2010). Droplet sizes reported in the literature range from 6 nm in a microemulsion of novaluron, up to 50 nm for a microemulsion of chlorpyrifos (Huang et al. 2006).

Compared to other formulations (e.g., ECs) the advantages of microemulsions may include improved tank mix compatibility, improved stability, reduced wear on equipment and low flammability (due to low solvent content in a continuous water phase (ETC 2004; Knowles 2005; ObservatoryNano 2010). It has also been suggested that microemulsions can enhance herbicidal efficacy due to the improved penetration or uptake of the a.i. that result from the high solubilizing power of surfactants (Green and Beestman 2007; Knowles 2005). Disadvantages of microemulsions include a low a.i. content (<30%), a high concentration of surfactants (usually in the region of 20%, Lawrence and Warisnoicharoen 2006; Tadros et al. 2004), and the limited number of suitable surfactant systems. Finally, provided an enhanced uptake is confirmed microemulsion formulations may also present phytotoxicity and handler toxicity issues (Knowles 2005).

Nanodispersion

Dispersion of nanocrystals in liquid media leads to the formation of nanodispersions, also called nanosuspensions, having similar properties to solutions (Muller and Junghanns 2006). The nanocrystals may be crystalline or amorphous particles but consist of 100% a.i. The primary objective is to maximize the surface area in order to increase the dissolution velocity and solubility saturation of poorly water soluble a.i. The addition of surfactants or polymeric stabilizers is sometimes necessary (Muller and Junghanns 2006). The greatest increase in solubility is expected for crystals <50 nm (Muller and Junghanns 2006). Commonly adopted methods for preparing organic nanoparticles including dry/wet milling, extraction precipitation, and solvent evaporation from emulsions are used (Elek et al. 2010). Dispersions of nanocrystals are widely used in the food industry e.g., for the incorporation of bioactive compounds such as carotenoids, phytosterols, and natural antioxidants (Muller and

Junghanns 2006). Elek et al. (2010) described a method that rapidly converted a microemulsion of novaluron into powders consisting of a.i. and surfactants. The nanoparticles obtained were 200±50 nm and consisted of aggregates of smaller nanoparticles (30–100 nm). However, insecticidal activity was not improved (Elek et al. 2010). Amorphous particles are more soluble than crystalline particles (Hancock and Parks 2000) and could thus be indicative of improved bioactivity. A nanodispersion of the antimicrobial agent triclosan prepared by combining a processing technique of modified emulsion templating and freeze-drying resulted in the formation of stable dry powder composites that formed a nanodispersion upon addition of water (Zhang et al. 2008). A higher biocidal activity was observed for the nanodispersion of triclosan than for an ethanol/water system (minimum inhibitory concentration was eightfold lower for the nanodispersion (Zhang et al. 2008).

Inorganic Nanoparticles as Active Ingredients

Silver

Silver (Ag) is known for antimicrobial properties and several *in vitro* studies have demonstrated that nano-Ag can significantly inhibit the growth of plant pathogens (Nowack et al. 2011; Chun et al. 2010; Jung et al. 2010). Jo et al. (2009) showed that preventive application of both ionic and nano-Ag can significantly reduce the development of fungal diseases on Ryegrass (*in vitro* and growth chamber experiments at concentrations of 100–200 mg L^{-1}). Jung et al. (2010) carried out greenhouse experiments and showed that a weekly application of nano-Ag solutions to the roots of cultivated green onions efficiently inhibited the development of white rot (average particle size 7–25 nm, 7 mg L^{-1}). Other suggested applications of nano-Ag as a replacement for synthetic organic bactericides include the coating of fruit bags to efficiently control the development of black stain on fruit (Chun et al. 2010) and the treatment of cut flower stems to extend vase life (Liu et al. 2009; Solgi et al. 2009).

Kim et al. (2009) conducted a successful evaluation of the antifungal activity of three different forms of silver nanoparticles against ambrosia fungus *Raffaelea* sp. which has been responsible for the mortality of a large number of oak trees in Korea. Likewise, successful reduction of sclerotium-forming fungi was achieved in a dose-dependent manner when silver nanoparticles (AgNPs) were used (Min et al. 2009).

Lamsal et al. (2011a) evaluate the possibilities of using silver nanoparticles instead of commercial fungicides for the management of Pepper anthracnose caused by *Colletotrichum* sp. The application of 100 ppm concentration of silver nanoparticles produced maximum inhibition of the growth of fungal hyphae as well as conidial germination in comparison to the control *in vitro*. In field trials, the inhibition of fungi was significantly high when silver nanoparticles were applied before disease outbreak on the plants. In another study, Lamsal et al. (2011b) evaluated the effect of silver nanoparticles against powdery mildew under different cultivation conditions *in vitro* and *in vivo*. Scanning electron microscope results indicated that the silver nanoparticles caused detrimental effects on both mycelial growth and conidial germination. Zahir et al. (2012) synthesized silver nanoparticles by using aqueous leaves extracts of *Euphorbia prostrata* as a simple, non-toxic and ecofriendly green material against the adult of *Sitophilus oryzae* L. The nanoparticles were rod in shape and size of 25-80 nm with an average size of 52.4 nm. The LD_{50} values of aqueous extract, $AgNO_3$ solution and synthesized Ag NPs were 213.32, 247.90, 44.69 mg/kg^{-1}; LD_{90}=1648.08, 2675.13, 168.28 mg/kg^{-1}, respectively. These results suggest that the leaf aqueous extracts of *E. prostrata*, and synthesized Ag NPs have the potential to be used as an ideal eco-friendly approach for the control of the *S. oryzae*. Suman et al. (2013) synthesised silver nanoparticle from the aqueous aerial extract of *Ammannia baccifera* as reducing agent and investigated the larvicidal activity of synthesized Silver nanoparticles against two mosquitoes species *Anopheles subpictus* and *Culex quinquefasciatus*. LC_{50} of 257.61 ppm against the larvae *A. subpictus* and 210.88 ppm against the larvae *C. quinquefasciatus* was recorded for the former while as the synthesized silver nanoparticles showed significantly higher toxicity against the larvae of *A. subpictus* with an LC_{50} of

29.54 ppm and 22.32 ppm against *C. quinquefasciatus*.

Possible benefits of nanosilver over synthetic fungicides e.g., reductions in human toxicity, in plant protection related costs, and in pollution, have been suggested but none have yet been demonstrated.

Aluminium

Nanostructured alumina dusts have great potential for the protection stored grains. Preliminary experiments showed insecticidal activity at rates comparable to those recommended for commercially available insecticidal dusts (summarised by Shah and Khan 2014). Stadler et al. (2010) determined the toxicity of nanoalumina against two storage pests *Sitophilus oryzae* L. and *Rhyzopertha dominica* (F.), Both species experienced significant mortality after 3 days of continuous exposure to treated wheat. It was found that the nanoalumina performed better than commercial dusts and at lower cost. Stadler et al. (2012) further compared the activity of nanoalumina to that of the most effective diatomaceous earth formulation on the market. Results showed that nanoalumina was equally effective as, or more effective than the commercial formulation. Buteler et al. (2015) synthesized three unique types of alumina dust through multiple solution based synthesis routes utilizing standard aluminum salt precursors. These were compared with regards to morphology, particle size and surface area using electron microscopy and dynamic light scattering particle size analysis. Insect toxicity to *Sitophilus oryzae* and *Rhyzopertha dominica*. By the dust synthesized using a modified glycine nitrate combustion process consistently yielded greater mortality rates, and all dust types were more effective on *S. oryzae* than on *R. dominica*, although the difference varied across dust types. This study suggests that pesticide dusts can be engineered through modified synthesis to better target different insect species.

Nanoalumina may thus be a good alternative to or complement the products based on diatomaceous earth. However, the mode of action of nanoalumina is yet to be elucidated and further research is required to optimize the product in terms of the mineral composition, type of formulation, efficacy for a range of insect species under a range of storage conditions.

Silica

Silicon (Si) has long been known to enhance plant tolerance of various abiotic and biotic stresses (e.g., metal toxicity, water stress, and fungal attack; Fauteux et al. 2005; Zargar et al. 2010) and the application of non nano forms of Si (e.g., potassium silicate) is common practice. Surface modified hydrophobic nano-Si particles have been suggested as a potential candidate for the control of a range of agricultural insect pests (Nair et al. 2010; Barik et al. 2008). The efficacy of combined Si and Ag nanoparticles stabilized with polymers has been tested in greenhouse experiments on green squash plants infected with powdery mildew (Park et al. 2006). The antifungal effects of nano- Si-Ag were observed almost immediately after application at 3 mg L^{-1}, and symptoms of infection had completely disappeared after three weeks.

Debnath et al. (2011) reported higher insect mortality from treatment with silica nanoparticles (15–30 nm) than with bulk silica (100–400 nm). The similar efficacy of nanoparticles with different coatings e.g., with no coating or with hydrophobic, hydrophilic, or lipophilic coatings, indicated a mechanical mode of action that could be enhanced for smaller particles. Another study, however, indicated that silica nanoparticles coated with 3-mercaptopropyl triethoxysilane were more efficient than those coated with hexamethyl disilazane (Debnath et al. 2012), and in this case the effect was not related to size since the former nanoparticles (29–37 nm) were larger than the latter (15–20 nm). Further research is therefore required to elucidate the mode of action involved. In another study, Rouhani et al. (2013) conducted laboratory trials to determine the effectiveness of silica nanoparticles (SNP) and silver nanoparticles (AgNP) on larval stage and adults of *Callosobruchus maculatus* on cowpea seed. Result showed that, the both nanoparticles (silica and silver) were highly effective on adults and larvae with 100% and 83% mortality, respectively.

Titanium dioxide

The antimicrobial activity of titanium dioxide is well recognized and several studies have suggested that applying titanium dioxide to crops can suppress bacterial and fungal pathogens (Norman and Chen 2011). Photocatalytic nanoscale titanium dioxide was used, either alone or doped with silver or zinc, against the causal agent for bacterial spot disease in tomatoes (Paret et al. 2013b) and roses (Paret et al. 2013a). Greenhouse and field trials showed that using titanium dioxide/zinc could result in significantly reduced bacterial spot severity. The overall efficacy was better than, or on a par with, the standard treatments for management of the diseases. Leaf phytotoxicity (5% to 10% leaf area) was observed after repeated applications, but this may be avoided by using electrostatic instead of conventional sprayers (Paret et al. 2013b). The main advantage of the titanium dioxide/zinc formulation presented is its potential to lower ecological and toxicological risks, compared to currently used copper-based treatments at the application rates investigated.

Copper

Mondal and Mani (2012) reported that a nanoformulation of copper could suppress the growth of bacterial blight on pomegranate at concentrations of 0.2 mg/L, four orders of magnitude lower than that usually recommended for copper oxychloride (2500–3000 mg/L). This result are comparable to Gogos et al. (2012), who reported an 8% increase in efficiency compared to a formulation of copper hydroxides salts currently in use. The tests by Mondal and Mani (2012) were carried out *in vitro* and no details of the formulation were provided.

Inorganic Materials Associated with Organic a.i.

Such formulations involve (i) use of mesoporous silica as a carrier for slow release, or (ii) incorporating TiO_2 in a polymer matrix to catalyze the photodegradation of the organic a.i. (Kah et al. 2013). These studies demonstrate the effectiveness and tunability of an environmentally friendly sustained release system for insecticide, which has great potential for broader agricultural applications with minimal environmental risks. Cao et al. (2005) reported a nanoformulation of chlorfenapyr containing nanoTiO_2. The results showed that chlorfenapyr nanoformulation and suspension concentration degradation in soil and in cabbage coincided. They concluded that Chlorfenapyr nanoformulation was safer than suspension concentration as its harvest interval and dosage could attain a high level. Similarly, Guan et al. (2011; 2010; 2008) incorporated different proportions of nano-Ag and nanoTiO_2 in polymer-based microcapsules loaded with insecticide (imidacloprid and avermectin). The aim of these nanoformulations was to promote the photocatalysis of the a.i. after release, with the objective of reducing residues on plants and in the soil. Nanoformulations were slightly more efficient than an aqueous formulation when applied directly on adult stage *Martianus dermestoides* kept in the dark (for avermectin, 96h-LC_{50} were 11.45 and 14.58 mg/L, respectively, Guan et al. 2011; for imidacloprid, 142h-LC_{50} were 9.86 and 13.45 mg/L, Guan et al. 2008). Sooresh et al. (2011) proposed a novel synthetic scheme to produce metal nanoparticle-pesticide conjugates, to be used as agents against arthropod vectors. Nano-Ag cores surrounded by deltamethrin (15–20 nm, characterized by electron microscopy and Fourier-transform infrared spectroscopy) were tested against mosquitoes in 24 hr bioassays. The efficacy of the nanoformulation was slightly lower than the pure a.i. At higher concentrations, mosquito mortalities provoked by the two formulations were comparable, demonstrating that the conjugation process did not completely inactivate the pesticide. By using silica (Mingming et al. 2013; Song et al. 2012) or calcium carbonate (Qian et al. 2011) nanoparticles as carriers for the slow release of an organic a.i., all three of these nanoformulations increased the activity of the a.i. Both laboratory and field tests demonstrated that that the insecticidal activity of chlorfenapyr associated with silica nano particles was twice as high as that of chlorfenapyr associated with microparticles (Song et al. 2012). Formulations with silica nanoparticles were also shown to improve the performance of a plant growth regulator when compared to results obtained using the pure a.i. which is probably related to the slow release (i.e., over 10–20 weeks) of an a.i. that is toxic when applied at high concentrations (Mingming et al. 2013). Similarly, the prolonged activity of validamycin when formulated with calcium carbonate nanoparticles can be explained by the sustained release of the a.i. over 14 days (Qian et al. 2011). Chen et al. (2010) prepared a slow release formula of

Pyoluteorin by using nanophase material of silicon dioxide loading drugs, synthesized by a highly ordered monolith method. This formula could continuously release 85.13 ± 2.03 % of the pesticide within 28 days. A bioactivity experiment showed that it authentically prolonged the antifungal effects.

Wibowo et al. (2014) reported a new biocompatible oil core silica shell nanocapsule for sustained release of fipronil insecticide. Sustained release of fipronil *in vitro* was tunable through control of the silica shell thickness (i.e., 8–44 nm). *In vivo* laboratory tests showed that the insecticidal effect of the fipronil encapsulated silica nanocapsules against economically important subterranean termites could be controlled by tuning the shell thickness. Janatova et al. (2015) tested the antifungal activity against *Aspergillus niger* of seven volatile essential oil components from plants—allyl isothiocyanate, carvacrol, cinnamaldehyde, diallyl disulfide, eugenol, thymol, and thymoquinone. Significant antifungal activity was verified in five out of the seven tested substances. These results were correlated with the evaporation rate of pure and encapsulated substances. It has been proven that by encapsulating selected volatiles, excluding sulphur compounds, their long-term effectiveness is ensured by controlled release and easy handling, with positive effects for their antifungal activity.

Researchers from China have investigated the potential of hollow silica nanoparticles to be used as carriers for the controlled release and UV shielding of avermectin and validamycin (Li et al. 2007; Li et al. 2006; Liu et al. 2006). The rate of release was influenced by temperature, pH, and shell thickness. Although Li et al. (2007) mentioned the encapsulation of avermectin, the release profile exhibited a multistage pattern which was interpreted as being due to the release of a.i. located in different parts of the particles (i.e., external, in pore channels, and in the internal core). Prado et al. (2011) recently reported a method to modify hexagonal mesoporous silica with carboxyl acids. The nanospheres synthesized were <50 nm (determined by thermogravimetry) and had a mean pore diameter of 10 nm (derived from N_2 sorption isotherms). Hussain et al. (2013) studied the uptake and distribution of mesoporous silica nanoparticles functionalised with amine crosslinked fluorescein isothiocyanate by wheat, lupin and *Arabidopsis*. The preparation of these particles at room temperature enabled the synthesis of 20 nm particles that contained a network of interconnected pores around 2 nm in diameter. The nanoparticles did not affect seed germination in lupin and there was no phytotoxicity. Following germination they were found within cells and cell walls of the emerging root and in the vascular transport elements, the xylem, and in other associated cells. In leaves and roots of *Arabidopsis* the nanoparticles were found to be taken up by the entire leaf and they were principally found in the intercellular spaces of the mesophyll but also throughout much of the root system. This study demonstrates that MSNs could be used as a novel delivery system for small molecules in plants. Sun et al. (2014) synthesized monodispersed mesoporous silica nanoparticles, having a size of 20 nm, for uptake by plant organs, tissues and cells. There were no negative effects of MSNs on seed germination or when transported to different organs of the four plant species tested in the study. Results showed that MSNs penetrated into the roots via symplastic and apoplastic pathways and then via the conducting tissues of the xylem to the aerial parts of the plants including the stems and leaves. The translocation and wide scale distribution of MSNs in plants will enable them to be used as a new delivery means for the transport of different sized biomolecules into plants.

NANOFORMULATING BOTANICAL INSECTICIDES

Botanicals offer an environmentally benign solution for the management of insect pests, however their application is limited due to their low stability in environment (Forim et al. 2013; Gogos et al. 2012a; Khater 2011). Therefore, Investigations have focused on the development of nanoformulations of botanicals that could make a significant contribution (Gogos et al. 2012a,b; Scott and Chen 2012). Although synthetic organic pesticides have adverse environmental impacts, their specificity towards the targeted pests is high. Therefore, the botanical insecticides must be rigorously standardized to a degree that ensures a certain level of effectiveness in the final use so that it could compete with their synthetic counterparts (Tramon 2014, Isman 2006; Tramon 2014). A well designed controlled-release system may enhance their target specificity and optimizing the action (Risch and Reineccius 1995). Nanotechnology offers great promise in this direction and nanoformulations can be used to improve both the stability and effectiveness of these natural products (Ghormade et al. 2011; Perlatti et al. 2013). Many different matrices can be used to produce nanostructured systems, including biodegradable polymers, and a variety of preparation techniques have been reported (Gogos et al. 2012b; Kumar et al. 2010; Perlatti et al. 2013). Oliveira et al. (2014) reviewed the nanostructured products that have been developed for use with active agents isolated from plants, as well as the essential oils.

Nanostructured Systems Containing Active Agents Isolated From Plants

Table 3 lists the main studies that have been published concerning botanical insecticides isolated from plants and encapsulated using micro- and nanoparticulate systems.

Table 3. Main bioactive compounds, their sources and carrier systems employing micro- and nanotechnology.

Bioactive compound	Source	Carrier system	Reference
Azadirachtin	Mainly extracted from the species Azadirachta indica (Meliaceae) Insecticidal and acaricidal activity.	Microcapsules of poly(vinyl acetate), Capsules of sodium alginate / glutaraldehyde, Nanoparticles of carboxymethyl chitosan/ ricinoleic acid, Spheres of sodium alginate, Polymeric nano/microparticles, Polymeric nanocapsules	Riyajan and Sakdapipanich (2009), Riyajan and Sakdapipanich (2009), Feng et al. (2012), Jerobin et al. (2012), Forim et al. (2013), Da Costa et al. (2014)
Rotenone	Found in species of the genera Derris, Lonchocarpus, and Tephrosia (Fabaceae) Insecticidal and pesticidal activity	Nanoparticles of chitosan, Polymeric microparticles	Lao et al. (2010), Martin et al. (2013)
Carvacrol	Found in the essential oils of oregano and thyme. Insecticidal and bactericidal activity.	Nanoparticles of chitosan Chitosan/β-cyclodextrin	Keawchaoon and Yoksan (2011), Higueras et al. (2013)
Thymol	Found in the essential oils of thyme and pepper-rosmarin, amongst others. Insecticidal and bactericidal activity.	Film of nanoclay, Polymeric microparticles, Zein nanoparticles	Lim et al. (2010), Guarda et al. (2011), Zhang et al. (2014)
Eugenol	Present in the essential oils of clove, cinnamon, myrrh, and sassafras. Insecticidal, nematicidal, and bactericidal activity.	Cyclodextrins, Solid lipid nanoparticles ,Chitosan/β-cyclodextrin, Chitosan nanoparticles	Choi et al. (2009), Garg, Singh (2011), Sajomsang et al. (2012), Woranuch, Yoksan (2013)
Curcumin	Active component of turmeric (*Curcuma longa* Zingiberaceae). Insecticidal action.	Zein nanoparticles, Nanoparticles of hydroxypropylcellulose	Gomez-Estaca et al. (2012), Bielska et al. (2013)

Azadirachtin

Azadirachtin active compound from *Azadirachta indica* (Meliaceae) (neem), is widely used in agriculture to combat insects, nematodes, fungi, and bacteria. However, due to light and temperature sensitivity, and degradation by microorganisms, it bioefficacy is reduced (Khater 2011). Using capsules of sodium alginate reticulated with glutaraldehyde and coated with natural rubber, encapsulation efficiency greater than 90% was achieved for azadirachtin, and the release profile in aqueous medium was modified, with the microcapsules coated with rubber providing slower release, compared to uncoated microcapsules (Riyajan and Sakdapipanich 2009). Jerobin et al. (2012) prepared particles of alginate and evaluated the effects of coating agents starch and PEG, and the release profile of the active agent. The average encapsulation efficiency was 80%, and was lower when the coating agents were used. The release profile of azadirachtin was modified following encapsulation, with the coated particles showing slower release, compared to the uncoated particles, and the release rate was proportional to the encapsulation efficiency. Forim et al. (2013) developed a new technique for the preparation of poly(ε-caprolactone) nanoparticles containing azadirachtin, as well as the preparation of a powdered form of this system using spray drying. Encapsulation efficiency of around 98% was achieved, and the best formulation showed an average size of 245 nm. The release of the active agent was due to relaxation of the polymeric chains or erosion of the polymer. Bioassays showed that the nanoparticles containing azadirachtin (5000 mg/kg) were effective in combating *Plutella xylostella*, with 100% mortality of the larvae. Da Costa et al. (2014) prepared different types of formulations viz., nanocapsules, microparticles, and emulsion concentrates containing azadirachtin. It was found that the nanocapsule formulation was more stable to degradation by UV radiation. The unencapsulated compound was completely degraded within seven days, while the encapsulated azadirachtin showed only 20% degradation after 14 days.

Rotenone

Rotenone is obtained from the roots or rhizomes of leguminous plants of the genera *Derris*, *Lonchocarpus*, and *Tephrosia*. The use of rotenone is limited by its sensitivity to UV, extreme toxicity to fish and low water solubility (Chen et al. 2009; Isman 2006). Lao et al. (2010) prepared and characterized an amphiphilic derivative of chitosan, N-(octadecanol-1-glycidyl ether)-O-sulfate chitosan, which was used as a carrier for rotenone. The insecticide was successfully encapsulated in the nanomicelles at a concentration 26 mg/mL with 13,000 times higher solubility of rotenone in water. The use of *in vitro* release assays revealed that the micelles slowed down the release of rotenone in relation to free compound. Martin et al. (2013) investigated the encapsulation of rotenone by biodegradable polymers using the supercritical assisted atomization process. Three types of polymer were tested viz., polyethylene glycol (PEG), polyvinylpyrrolidone and sodium alginate. The best encapsulation was achieved for the alginate/rotenone (~100%) and PEG/rotenone (98%) systems. So far, no comparisons has been documented regarding the activities of nanoformulations containing rotenone relative to the free compound (Oliveira et al. 2014).

Eugenol

Eugenol is an insecticidal compound in the essential oil of clove (*Syzygium aromaticum*) and other plants of the Myrtaceae family (Amiri et al. 2008; Isman, 2006). Choi et al. (2009) encapsulated the the compound using molecular inclusion in β-cyclodextrin (β-CD) and 2-hydroxypropyl-β-cyclodextrin (2-HP-β-CD), while the emulsion–diffusion method was employed for its encapsulation in polycaprolactone (PCL) nanoparticles. The average sizes of the nanoparticles containing eugenol were in the region of 320 nm, encapsulation efficiencies of eugenol in the PCL, β-CD, and 2-HP- β-CD nanoparticles were 100, 90.9, and 89.1%, respectively. In stability studies, greater resistance to eugenol oxidation during storage was achieved using the emulsion–diffusion method. Garg and Singh (2011) prepared solid lipid nanoparticles of eugenol using stearic acid and liquid caprylic triglyceride. Both formulations showed release profiles that were slower than obtained for free eugenol in solution. They also reported an improvement in the antifungal activity of eugenol when it was administered in the form of SLNs. Sajomsang et al. (2012) prepared and characterized water soluble derivatives of chitosan combined with β-cyclodextrin (DC–CD) as carriers of eugenol. It was also found that the DC–CD eugenol inclusion complex showed greater antimicrobial activity against compared to DC–CD alone. Woranuch and Yoksan (2013) obtained spherical nanoparticles with average diameters of 80–100 nm prepared from chitosan/tripolyphosphate (TPP) loaded with eugenol. The addition of a thermoplastic agent increased the thermal stability of encapsulated eugenol in relation to eugenol only. The results suggested the possibility of using chitosan nanoparticles of eugenol in plastics for food packaging, in addition to agricultural applications.

Curcumin

Curcumin is a phenolic compound found in several different plant species, notably turmeric, *C. longa* L. (Zingerberaceae). Gomez-Estaca et al. (2012) prepared nanoparticles of zein using the electrodynamic atomization technique. Nanoparticles of zein could be obtained using zein concentrations of between 2.5 and 15% (w/w), with particle sizes varying from 175 to 900 nm and increasing when higher concentrations of polymer were used. Encapsulation efficiencies of 85 and 90% were achieved using curcumin : zein ratios of 1: 500 and 1:10, respectively. After three months of storage, there were no significant changes in the size or morphology of the nanoparticles and the curcumin contents remained unaltered. Two different polymeric derivatives of hydroxypropyl cellulose (HPC), either cationic or anionic were synthesized by Bielska et al. (2013). The particles were spherical, with diameters in the range of 150–250 nm and the size and surface charge of the nanoparticles could be controlled by means of the polycation/polyanion ratio and temperature. Curcumin was encapsulated with an efficiency of approximately 67%, and the release profile was temperature dependent. Nonetheless, the use of curcumin as a possible agent to control pests still requires further evaluation using the existing as well as new formulations. It remains necessary to demonstrate that satisfactory effects on target species can be achieved, without causing significant harm to non target organisms such as not to produce phytotoxicity to plants and toxicity to human health. Commercial production technology also needs to be realised.

Nanostructured Systems for Essential Oils

The use of essential oils as insecticidal principles is often limited by their solubility and the need to disperse them in such a way as to ensure their effective action. However, advantages of the use of essential oils include the presence of other components that might have synergistic effects with the main active agents in the oil (Jiang et al. 2009). Table 4 lists the principle studies aimed at nanoformulating insecticidal essential oils.

Table 4. Principal studies reported in the literature involving the association of plant essential oils and carrier systems employing nanotechnology (After Oliveira et al. 2014).

Source of essential oil	Carrier system	Reference
Artemisia arborescens L. (Asteraceae)	Solid lipid nanoparticles	Lai et al. (2006)
Garlic	Polyethylene glycol (PEG) nanoparticles	Yang et al. (2009)
Lavender	Polymeric microspheres	Varona et al. (2010)
Peppermint	Polymeric microcapsules	Dong et al. (2011)
Lippia sidoides (Verbenaceae)	Chitosan/cashew gum nanogel	Abreu et al. (2012)
Oregano	Chitosan/TPP nanoparticles	Hosseini et al. (2013)
Eucalyptus staigeriana (Myrtaceae)	Chitosan hydrogel	Ribeiro et al. (2013)
Various sources	Cyclodextrins	Hill et al. (2013)
Citrus	Film of chitosan/locust bean gum	Aloui et al. (2014)
Rosemary	Polymeric microparticles	Fernandez et al. (2014)
Marjoram, clove, and cinnamon	Film with nanocomposites of alginate/clay	Alboofetileh et al. (2014)
Thyme	Polymeric film	Jouki et al. (2014)

Lai et al. (2006) prepared solid lipid nanoparticles (SLNs) containing the essential oil of *Artemisia arborescens* (tree wormwood) employing two types of surfactant (Poloxamer 188 and Miranol Ultra C32) and a high-pressure homogenization process. Both formulations showed high stability at different storage temperatures over a period of two months. The average particle size was around 200 nm, and the size of the nanoparticles loaded with the essential oil showed no change during storage. Release assays conducted *in vitro* demonstrated that the SLN acted to reduce the evaporation rate of the essential oil, compared to reference emulsions. Yang et al. (2009) used polyethylene glycol (PEG) nanoparticles as a carrier for the essential oil of garlic (*Allium sativum* (Liliaceae)), against *T. castaneum* (Tenebrionidae). The nanoparticles were prepared by the fusion–dispersion method, and showed an encapsulation efficiency of 80%. After five months, the formulation showed 80% effectiveness against beetles, which was probably due to the slow release of the active components from the nanoparticles. Polymeric microcapsules have been used as carriers for the essential oil of lavender. Varona et al. (2010) employed two different types of polymer (PEG and modified starch), and two methods were used to prepare the particles. Release of the active principle from the microspheres prepared using the SG method was slower than from the particles prepared using the SG-D technique, due to the absence of crystals. The formulations prepared using SG therefore showed potential as carriers for the essential oil of lavender in special as an insect repellent. The coacervation technique has been used to prepare microcapsules of gum arabic/gelatin, using transglutaminase as a hardening agent (Dong et al. 2011). Particle morphology, encapsulation and release of the essential oil of peppermint were investigated. There was a strong influence of the nucleus/wall ratio on particle size and encapsulation efficiency, with thin walls favouring high encapsulation efficiency and a faster rate of release in hot water, while larger particles showed slower release rates. Abreu et al. (2012) investigated the use of nanogels based on chitosan/cashew gum for encapsulation of the essential oil of pepper rosmarin (*L. sidoides*). An encapsulation efficiency of 70% was achieved using an oil/gum/chitosan mass ratio of 10:1:1. Release assays conducted *in vitro* showed that the oil encapsulated in the nanogels was released in a slower and more sustained fashion, compared to the unencapsulated oil. At a mass ratio of 10:1:1, 75% mortality was observed after 48 h against *Aedes aegypti*, and over 90% mortality was achieved after 72 h. In another work, Hosseini et al. (2013) obtained spherical nanoparticles, with a homogeneous size distribution (average sizes of between 40 and 80 nm), from chitosan using the water/oil emulsion method and ionic gelification of chitosan with sodium tripolyphosphate. The encapsulation efficacy for the essential oil of oregano was between 21 and 47%. Release assays conducted *in vitro* showed that an initial rapid release was followed by a slower release of the active principle, and that the release process was influenced by the oil/chitosan ratio employed. Fernandes et al. (2014) investigated the microencapsulation efficacy of different polymeric matrices containing gumarabic, modified starch, maltodextrin, and inulin for the essential oil of rosemary (*Rosmarinus officinalis)*. The average size of the particles was 14.5 µm. The presence of inulin improved the wettability but decreased the encapsulation efficiency, while a mixture of modified starch and maltodextrin (1:1, m/m) was cost-effective and also provided good encapsulation efficiency. Another advantage of these formulations was that they presented the high glass transition temperatures that are important for successful storage. Alboofetileh et al. (2014) incorporated essential oils derived from different plants (clove, coriander, cumin, cinnamon, marjoram, and caraway), into films and reported that the antibacterial activity of the essential oils was maintained. Aloui et al. (2014) evaluated the use of chitosan or carob gum polymeric matrices with different citrus essential oils against *Aspergillus flavus*. Both oils significantly reduced spore germination @ 2% (v/v), with reductions of 87 and 90% for the bergamot and orange oils, respectively. Coatings based on chitosan incorporating citrus essential oils reduced fungal degradation of infected fruits by 52–62% after 12 days with no undesirable flavors or odors. In another recent work, Jouki et al. (2014) formulated essential oil of thyme in films based on the mucilage of quince seeds. The quince seed mucilage exhibited antioxidant activity, which was significantly improved with addition of the essential oil.

ENVIRONMENTAL FATE OF INSECTICIDE NANOFORMULATIONS

The effects nanoformulation on the fate of an a.i. may be multiple and depend on the combination under consideration. The objective of many of the nanoformulations attempted is to achieve the slow release of an organic a.i. and/or to protect it from premature degradation. The data summarized in Table 1 show that a number of products have achieved this objective. Klaine et al. (2008; 2012) have reviewed the state of knowledge with regard to fate and risk assessments of inorganic (mainly metallic) engineered nanoparticles. That of insecticidal nanoformulations has been reviewed by Kah et al. (2013) and Kah and Hofmann (2014). The principles of environmental fate of nanofomulations have been laid by Kah and Hofmann (2014) as the study of release profiles, followed by transport, bioavailability and finally the fate of the carrier. A summary of the environmental behaviour of various types nanoformulations is given in Table 5.

Table 5. Environmental fate of various nanoformulations reported in the literature.

Type and AI	Fate of the nanoformulation	References
Microemulsion		
Literature review	Increased or decreased sorption of the a.i. depending on concentration and type of surfactant	Katagi (2008)
Literature review	Slower or faster degradation depending on a.i. and type of surfactant	Katagi (2008)
Emamectin-benzoate	Better retention on rice crop leaves (15% lower surface tension and from 10 up to 100% higher residues on leaves)	Fan et al. (2010)
Nanoemulsion		
Riazophos technical grade	Reduced hydrolysis (by up to 35%)	Song et al. (2009)
Free garlic essential oil	Reduced volatilization (stable over 5 months storage)	Yang et al. (2009)
beta-cypermethrin	Slower release (60 min)	Zeng et al. (2008)
Polymer-based		
Terbuconazole	Reduced leaching from treated wood (2 up to 6-fold less concentrated leachates) / aqueous solution of	Salma et al. (2010)
Ethiprole	Enhanced penetration in plants / classical suspension of ethiprole (demonstrated indirectly through the comparison of contact and systemic efficacy)	Boehm et al. (2003)
Carbofuran	Release of a.i. can be adjusted by changing the proportions and molecular weight of the polymers	Shakil et al. (2010)
Imidacloprid, Thiamethoxam, Carbofuran, Thiram, Beta-cyfluthrin	Slower release in water than commercial formulation (e.g., for β-cyfluthrin, time for 50% release was 1.4–20.5 d and 4–5 d, respectively) More rapid release with increasing PEG molecular weight	Adak et al. (2012); Kaushik et al. (2013); Loha et al. (2011, 2012); Pankaj et al. (2012); Sarkar et al. (2012)
Thiamethoxam	Slower release in soils compared to commercial formulation (time for 50% release was 3.5–6 d and 1.3 d, respectively)	Sarkar et al. (2012)
Emamectin	Enhanced photostability compared to commercial formulation (half-life of about 6 and 1 d, respectively)	Qing et al. (2013)
Lansiumamide B	Enhanced photostability compared to pure AI	Yin et al. (2012)
Paraquat	Weaker sorption than pure AI	Silva et al. (2011)
Pheromones	Reduced volatilization compared to pure AI (prolonging activity from 3 to up to 33 weeks)	Bhagat et al. (2013)
Solid lipid nanoparticle		
Artemisia arborescens L essential oil	Lower evaporation (after 48 hr, cumulative losses by evaporation was reduced by half) / emulsion of *Artemisia arborescens* L essential oil	Lai et al. (2006)
Deltamethrin	Decreased direct and indirect photodegradation compared to pure AI (relatively high losses still observed for the nanoformulation)	Nguyen et al. (2012a;b)
Porous hollow silica nanoparticles		
Avermectin	Slower degradation due to UV-shielding (20% a.i. remaining after 720 min) / free a.i. and similar formulation using SiO2 nanoparticles as carrier for avermectin (complete photodegradtion within 120 min)	Li et al. (2006; 2007)
2,4-dichlorophen-Oxyacetate, Alpha-naphthalene acetate	Slow release following first order, second order, power equation, or multistage pattern kinetic and influenced by	bin Hussein et al. (2002; 2005; 2009a; 2009b), Park et

Type and AI	Fate of the nanoformulation	References
	pH, temperature	al. (2010), Qui et al. (2009)
Layered double hydroxides and clays		
Cinnamic acid, Atrazine	Prolonged persistence (e.g., DT50 of cinnamic acid in soil were 6 d for an aqueous solution and 17 d when formulated with layer double hydroxides) Similar bioavailability in soil (mineralization rate) / free atrazine	El-Nahhal et al. (1999); Maqueda et al. (2009), Park et al. (2010)
Diuron	Reduced leaching (up to 5 times smaller total amount leached) but similar persistence for an organoclay formulation of diuron / commercial formulation	Trigo et al. (2010), Trigo et al. (2009)
Metal and organic a.i.		
Chlorfenapyr	Similar half-life in plant and soil / suspension concentrate of chlorfenapyr	Cao et al. (2005)
Imidachlorprid	Faster degradation / suspension concentrate of imidachlorprid in soil (half-lives of 2.8 and 6.2 days, respectively) and in soya bean plants (1.9–4.5 days	Guan et al. (2010)

(modified after Kah et al. 2013; and Kah and Hofmann 2014)

CONCLUSIONS

The principal objectives of nanopesticide formulations are to increase the solubility of poorly soluble a.i. or to release the a.i. in a slow/targeted manner and/or protect the a.i. against premature degradation. Tremendous research efforts are directed towards the development of various nanoformulations. The major issues that remain to be addressed include the demonstration of the clear cut efficacy of the formulations over traditional ones under field conditions. The commercial production is yet to be realised at comparable price. Data on the effects on non-target organisms is scarce. 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. Investigations into the environmental fate of nanopesticides remain scarce, and have generally only focused on the particular processes targeted by the formulation (e.g., degradation, in a formulation aiming to protect the a.i. from premature degradation). As a prerequisite for such assessment, the development of robust analytical methods for the quantification and characterization of nanopesticides will be required in order to reduce the uncertainty associated with classically applied protocols. However, the current level of knowledge is very encouraging.

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Conflicts of Interest

The authors declare no conflict of interest.