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NANO-DELIVERY SYSTEMS OF PESTICIDES ACTIVE AGENTS FOR AGRICULTURE APPLICATIONS - AN OVERVIEW

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Abstract

Agricultural protection agents used in soil and crops, when applied conventionally, may have their activity impaired against pests and vectors due to their volatilization, photodegradation, leaching, and other unwanted occurrences caused by weather conditions. These problems cause economic and environmental damage due to the high volume of applications necessary for the farmer to achieve the desired results. The indiscriminate use of free pesticides causes high environmental pollution because these compounds are cumulative in soil, water and vegetation, sometimes causing air contamination, which can cause health issues in local workers and the death of animals. In contrast, nanopesticides are an alternative emerging technology that allows the controlled release of active compounds, improving pest control performance and turning it more sustainable and in line with the concept of precision agriculture. The use of nano-delivery systems for pesticide agents uses nanostructures capable of altering the release kinetics of these compounds, providing the plantation with an adequate amount for pest elimination. This paper presents an overview of nanopesticides, addresses some current concepts of sustainability, reviews and analyzes the latest developments regarding these nanomaterials, and provides an update on their advantages and disadvantages.

Keywords: nanopesticides, controlled release, precision agriculture, emerging technologies, sustainable agriculture.

1. Introduction

Pesticides are a group of chemical compounds widely used in agriculture for pest control (Chart 1). Without them, crops would be devastated by opportunistic organisms that would eliminate or limit food production on a large scale (BAPAT *et al.*, 2016; CAROLIN *et al.*,

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2020). Pesticide agents play a fundamental role in maintaining agricultural production, however, their indiscriminate use, in addition to being dangerous to the health of rural workers, can be highly harmful to the environment causing damage to the local biome and even to the soil (AKTAR; SENGUPTA; CHOWDHURY, 2009; CAROLIN *et al.*, 2020).

Chart 1. Classification of pesticides most used in agriculture, their target organisms, and some examples of products used in the field.

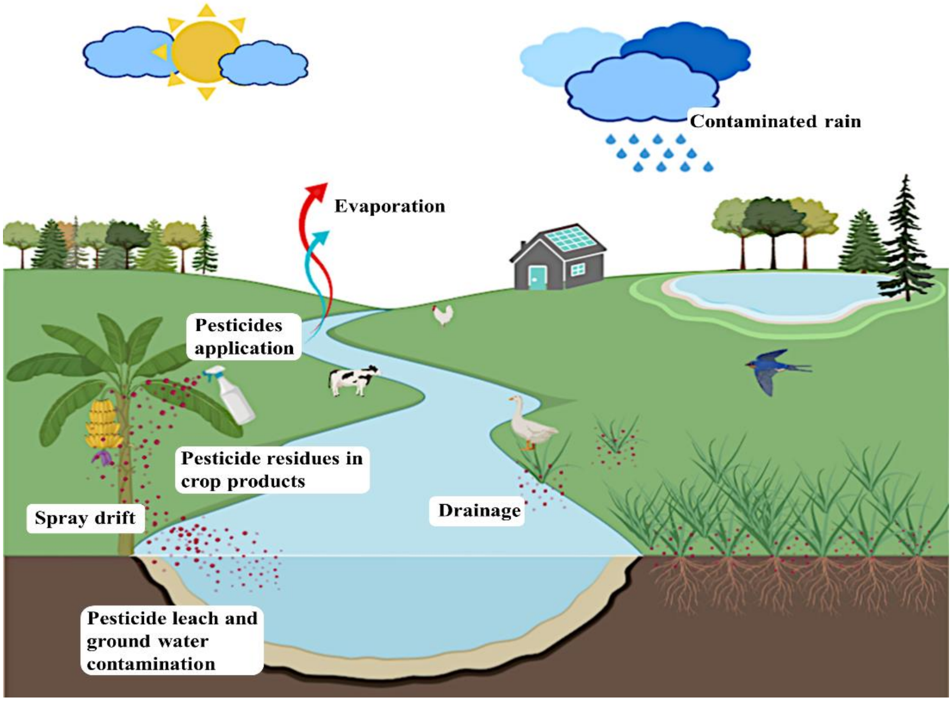
Function	Target organism	Compound examples
Acaricide	Mites and ticks	Dicofol, Carbamate, DDT, organophosphates
Algicide	Algae	Simazine, Dichlone, Benzalkonium chloride
Fungicide	Fungi	Metalaxyl, Hexaconazole, Cymoxanil
Herbicide	Weeds	Atrazine, Paraquat, Oxadiazon, Linuron
Insecticide	Insects	DDT, Lindane, Thiacloprid, Clothianidin, Endosulfan
Nematicide	Nematodes	Fenamiphos, Methyl bromide, Chlorpyrifos
Rodenticide	Rats	Zinc phosphide, Bromadiolone, Coumachlor, Coumatetralyl, Warfarin
Synergists	Several pests	Piperonyl butoxide

Source: Adapted from (SHARMA *et al.*, 2020)

Research has shown that the number of bee colonies in the USA on agricultural land decreased from 4.4 million to 1.9 million between 1985 and 1997, due to the direct and indirect effects of pesticides, capable, for example, of weakening the immune system of bees against natural diseases and mites (HORRIGAN; LAWRENCE; WALKER, 2002). In the province of Quebec in Canada, a study on the Saint-Laurent River correlated problems in the development of local amphibious life with the presence of pesticides in the water, including body deformities, such as the growth of extra legs in places such as the abdomen and back and poorly developed limbs (OUELLET *et al.*, 1997). Other studies have shown immune system impairment in dolphins, seals, and whales exposed to contaminated waters. In humans, direct exposure to organophosphate pesticides can lead to the appearance of lymphomas (KOUTROS *et al.*, 2019). Organochlorine pesticides are highly carcinogenic and generate oxidative stress and mitochondrial cell malfunction (SCHMIDT *et al.*, 2017), while carbamates lead to apoptosis (cell self-destruction) and the development of tumor cells in the central nervous system (PIEL *et al.*, 2019). The widespread and poorly administered use of pesticides has increased the resistance of certain plant species to herbicides. Approximately 262 weed species (152 dicots and 110 monocots) are no longer responding to conventional herbicide active principles attacks worldwide. Currently, 513 unique cases in the world have been reported in 92 cultures in 70 countries according to Heap (2020).

The pesticide compounds, when applied conventionally, are released into the environment, directly reaching the soil, plants, water sources, and/or nearby vegetation, part of which are volatilized, contaminating the air, as shown in Figure 1. Until they reach the target (pests), pesticides find these barriers where they are retained and accumulated, thus requiring greater frequency and volume/concentration of application so that they can protect the crop at the expense of environmental poisoning (KUMAR *et al.*, 2019).

Figure 1. Schematic illustration of possible routes of environmental contamination caused by the conventional application of pesticides.



Source: Authors.

Considering that commercial pesticide formulations when applied conventionally, require large volume and frequency of applications to combat pests with unwanted environmental accumulation, the good use of pesticide agents applied to the field has become the main issue when it comes to optimizing a more safe and conscious agricultural production. It is estimated that for all pesticides applied to crops, only about 0.1% reach the target pests, leaving 99.9% of these chemical agents accumulated in the environment, raising serious environmental issues (HORRIGAN; LAWRENCE; WALKER, 2002; PIMENTEL, 2009).

In 2024 it is estimated that the global population will reach 8 billion inhabitants (ROSER; RITCHIE; ORTIZ-OSPINA, 2013). Population growth triggers an increase in the demand for food, and therefore it is safe to say that the current farming system, which is already considered unsustainable, will become unbearable if it keeps the same growth rate. The growth of the pesticide market is evident, the global pesticide market moved around $32 billion in 2007, $56 billion in 2012, movements of around $71 billion are expected in 2021, and it is estimated that between 2025 and 2026 it will exceed $100 billion (CPCM, 2016; SHARMA *et al.*, 2017; TILMAN *et al.*, 2001). The high discharge of pesticides into nature has bioaccumulative effects, which is why global research efforts on the use of these substances in the field are almost always to reduce the quantities of products applied without causing financial losses and reduced productivity (LECHENET *et al.*, 2017).

Among the most promising scientific fields is nanotechnology, which has the potential to allow, at the same time, reduced use of pesticides, increased inhibition of pests in crops, increased or maintained production levels and less exposure of users to active agents during pesticides application (IRFAN *et al.*, 2018). Since 2003, nanotechnology has been introduced in the agricultural and food industries. Initially, its applications were in food preparation and conservation, monitoring and sensing of environments and improvement of animal feed, however, it has advanced to applications in the field in the search for increased productivity through the use of nanofertilizers. More recently, it has advanced in combating pests and environmental protection with the use of nanopesticides and nanoparticles for the extraction, detection, and degradation of pesticides accumulated in the soil (BAPAT *et al.*, 2016; HE; DENG; HWANG, 2019).

Concerns about the environment led science to find more sustainable alternatives for the application of agrochemicals in the environment, from these needs the concept of precision agriculture was originated. Precision agriculture is an innovation that follows three principles: (i) economic viability; (ii) profitability with increased production; and (iii) reduction in environmental impacts; it is recognized as a management strategy that uses information technology capable of providing accurate data for decisions associated with production in the field (ALLAHYARI; MOHAMMADZADEH; NASTIS, 2016; MONDAL; BASU, 2009; ZHANG; WANG; WANG, 2002). Nanotechnology is a tool that can improve the delivery systems of agrochemicals in cultivations in a controlled way, and also monitor the needs of the culture regarding the control of nutrients and pests through nanosensors, capable of feeding information to a system of agricultural management. Precision agriculture has spread rapidly in developed countries, research in the area began in the USA, Canada, Australia and Western Europe in the 1980s and is now worldwide (ALLAHYARI; MOHAMMADZADEH; NASTIS, 2016; MONDAL; BASU, 2009; ZHANG; WANG; WANG, 2002).

Nanostructured systems can be used as carriers of active compounds, maintaining their chemical stability against the effects of oxidation, humidity and other environmental factors, in addition to allowing their release into the environment in a controlled, continuous and prolonged manner (IRFAN *et al.*, 2018). In this case, these nanometric supports doped with pesticide agents act as nano-delivery systems and can be called nanopesticides. The phenomenon of delivery of compounds *in-situ* occurs by mass transfer, the actives contained within the nanoparticulate support migrate by diffusion from the nucleus to the shell and, when in contact with the external environment, they can reach local pests through optimization of targeted delivery of compounds to specific target sites (ABRAHAM; PILLAI, 1996; CHEN *et al.*, 2008; IRFAN *et al.,* 2018; NI *et al.*, 2011).

Generally, nano-delivery supports are prepared from biodegradable polymers such as polysaccharides (cyclodextrins, chitosan, xanthan and carboxymethylcellulose), alginic acids used to release herbicides, natural polypeptides (collagen, gelatines and amino acids), poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(ε-caprolactone) (PCL), bacterial polyesters such as polyhydroxyalkanoates (PHAs), poly(β-hydroxybutyrate) (PHBs), poly(β-hydroxy-valerate) (PHV), and poly(hydroxybutyrate-co-valerate) (PHB-V), among others (DE OLIVEIRA *et al.*, 2019; FRANCHETTI; MARCONATO, 2006; GRILLO *et al.*, 2014; KUMAR *et al.*, 2015; MARUYAMA *et al.*, 2016; OLIVEIRA *et al.*, 2018). For the reasons stated above, nanopesticides are seen as a promise of advancing agricultural technologies to make products that are less polluting, safer and more effective.

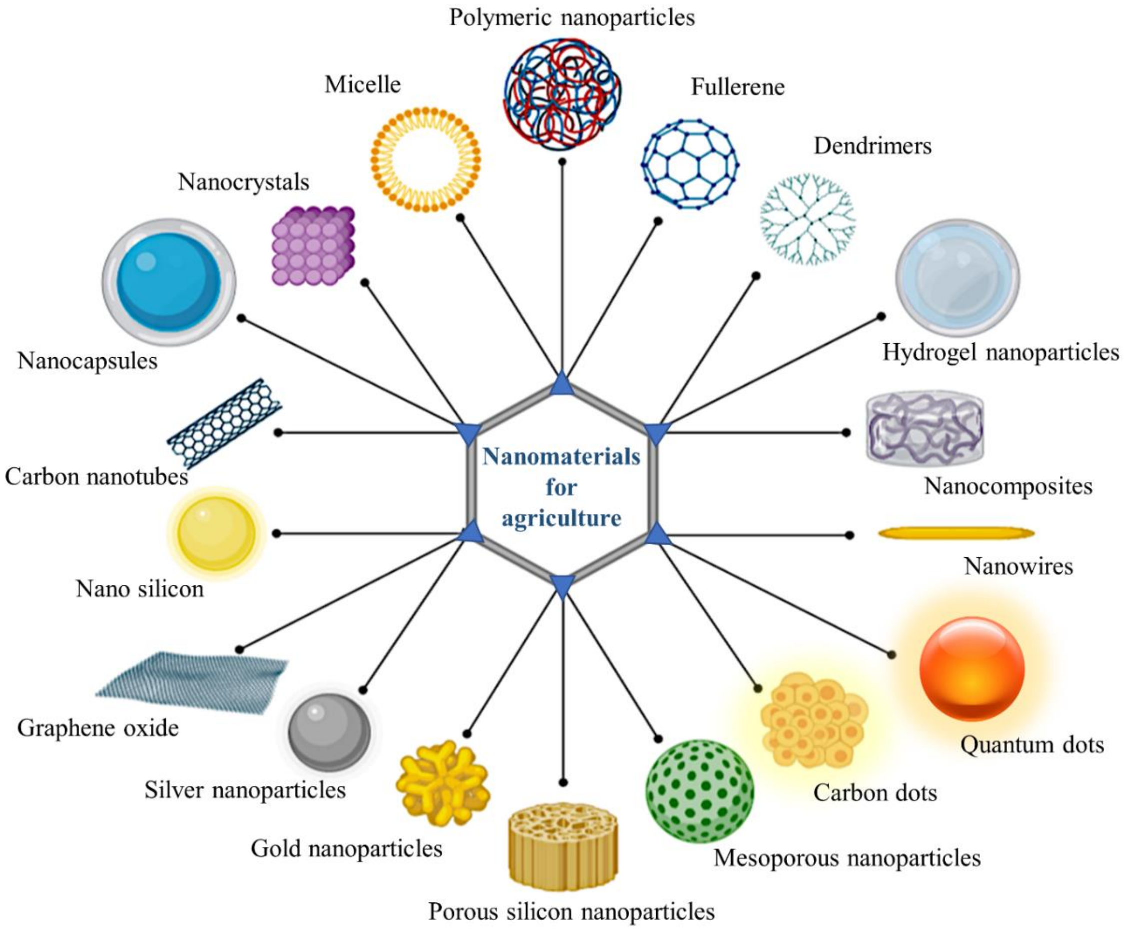
Based on the issues discussed above, the present work consists of an overview of the nano-delivery systems of active pesticide compounds used in agriculture, addressing topics related to the methods of obtaining, mechanism of action, advantages and disadvantages of these nanomaterials. Since the subject of this review is a novelty and there are few studies related to the theme in the literature, this work also sought to address current developments in the sector that may gather important information for professionals and scholars in the field.

2. Nano-delivery systems (nanocarriers) of pesticide agents

Conventional distribution systems are important for the application of pesticides in agriculture, these systems need to focus on improving product efficiency and managing spray diversion. A promising alternative for solving these problems is the adequate use of controlled delivery systems. The controlled delivery technique consists of releasing the pesticide compounds in adequate quantities, according to the needs of the crop, without exceeding the sufficient amounts of agrochemicals that the crop needs to overcome the target pest (TSUIJI, 2001).

Nanotechnology has been widely considered in the adaptation and updating of conventional systems for the application of agrochemicals in the environment, searching for the global consolidation of precision agriculture (MA, 2019). Nanotechnology is the scientific and technological knowledge that uses, develops, studies, controls and/or applies materials of the order of nanometers, which structure has a diameter or at least one of its dimensions in the order of 100 nm or less, called nanomaterials (AUFFAN *et al.,* 2009). Nanostructured systems can consist of nanoparticles (nanocapsules, nanospheres, nanocrystals, nanocomposites, nanotubes, nanoneedles, etc.), micro/nanoemulsions, fullerenes and biomimetic systems, which make up a wide subject to be explored in the agricultural area (GHORMADE; DESHPANDE; PAKNIKAR, 2011), as illustrated in Figure 2.

Figure 2. Some types of nanomaterials used to combat pests in agriculture.



Source: Authors.

Nanomaterials in agriculture can be used for crop protection (nanopesticides), plant nutrition (nanofertilizers), management of agricultural practices (nano[bio]sensors) and remediation (pollutant remediation nanostructured systems) (GHORMADE; DESHPANDE; PAKNIKAR, 2011). Nanostructured systems can act as transport agents for chemical compounds for cultivation, which deliver/release these substances in a slow and controlled manner, due to their small size, high surface/volume ratio, packaging of actives in a core-shell diffusion system and unique optics properties.

Several scientific researches have proven that the use of nanostructures containing active compounds behave as excellent controlled release systems for these actives. Research with particles considered to be micrometric (10 - 100 µm), sub-micrometric (1 - 10 µm) and nanometric (<1 µm) used as support for controlled delivery of agrochemicals reported that the nanometric ones have advantages over the others because they have greater surface area per unit volume, easy fixation and accelerated mass transfer (GHORMADE; DESHPANDE; PAKNIKAR, 2011). Several materials can be used as nanoparticles or compose nanostructured systems for applications in the field such as quantum dots, metal oxides, biopolymers (synthetic or natural), clay minerals, emulsions, lipids, peptides, dendrimers, among others (PUOCI; *et al.*, 2008).

2.1. Mechanisms of action and release of active compounds

For a chemical product of crop protection to be successful, it must remain active in the environment regardless of weather (cold, rain, heat, sun, etc.) as well as reach and penetrate the target organism (insects, phytopathogens, etc.). It must also resist the defense mechanisms of the pest, must be benign to the soil and the cultivation, inactive in non-target organisms, have profitable manufacture and offer good economic return (SMITH; EVANS; EL-HITI, 2008).

In addition to transport vehicles, nanocarriers in many cases act as a protective container for active components against adverse external conditions (high temperature, radiation, high humidity, oxidation, among others), increasing their physical and chemical stability. The nano-delivery systems must follow an intelligent principle of controlled release of the chemical compound at the destination site in a manner appropriate to the specific needs (COOPER, 2010; FLORES-CÉSPEDES *et al.*, 2015; MARUYAMA *et al.*, 2016). The main functions of the nanocarriers, in this case, are (i) to retain/protect the active compounds without release or loss before they reach the target; (ii) to improve the dissolution of the compounds when they reach the target, for example, improving the penetration in the plant tissues of the weeds; and (iii) to change/control the active release functions in neighboring environments. These functions depend directly on the size, shape, and material from which the nanocarrier is made (COOPER, 2010; FLORES-CÉSPEDES *et al.*, 2015; MARUYAMA *et al.*, 2016).

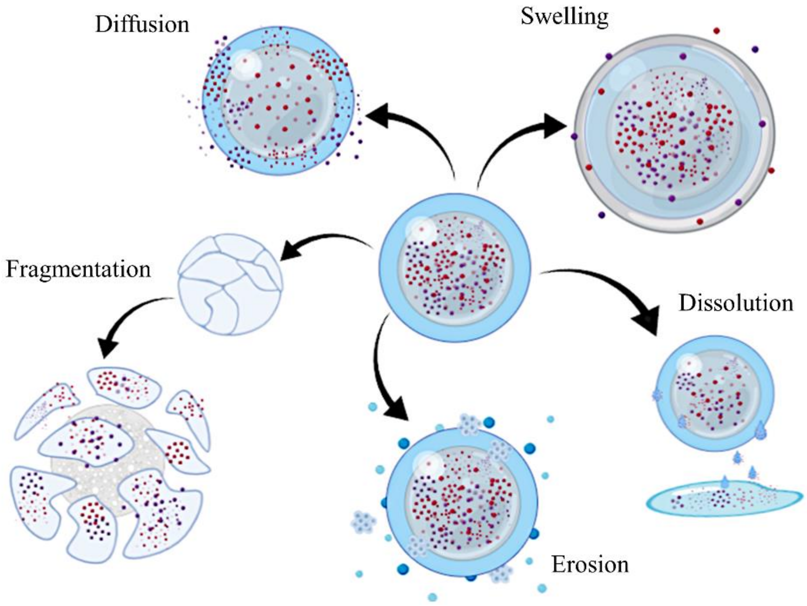
Various materials can be applied in the preparation of nanopesticides: from polymers (natural and synthetic), waxes/lipids, proteins/peptides to oxides and clay minerals (IRFAN *et al.*, 2018; LI *et al.*, 2007). The geometry of the nanostructures is related to the surface area per unit of volume, and therefore the shape of the nanocarrier is extremely important in defining the release and protection profile of the actives. These nanomaterials can be designed for (i) slow-release; (ii) quick release; (iii) selective release; (iv) moisture release; (v) release by heat; (vi) release by pH; (vii) release by ultrasound; (viii) magnetic release; and (ix) release by DNA profile (LI *et al.*, 2007).

Polymeric nanocapsules are the supports most commonly used as nanocarriers, mainly biodegradable polymers such as chitosan, alginate, gelatin, collagen, carboxymethylcellulose, polyethylene glycol (PEG), among others (KUMAR *et al.*, 2018; RANI *et al.*, 2017). Nanocapsules consist of a shell or membrane structure that surrounds the active compound and retains it in its core. Numerous factors can interfere with the delivery mechanisms of the nanocapsules, in general, the release occurs through the diffusion of the active compound contained in the nucleus through the polymeric membrane until it reaches the shell (surface), where it is finally exposed to different stimuli from the external environment (IRFAN *et al.*, 2018). Some of the important factors that can significantly affect the controlled release mechanism of these nanostructures include the mechanical properties and level of biodegradability of the coating material, the thickness of the coating, the density of the actives, the physiology and water content of the soil (IRFAN *et al.*, 2018). The complexity of the phenomena can include the transport of water through the coating, the condensation of water in the nucleus of the nanocapsule, the development of osmotic pressure, the dilution of the active compounds, the swelling of the granule, the modification of the micropores, among others (IRFAN *et al.*, 2018).

In addition to the general mechanisms for releasing active compounds from their matrices, different strategies for applying these nanostructures can also be studied to improve the effectiveness of pest control *in situ*. Sharma *et al.* (2017) synthesized copper selenide nanoparticles decorated in graphene nanoparticles doped with chlorpyrifos (insecticide) for foliar application in vegetable culture. The authors developed a hydrophobic material with adhesive properties, which when applied to the leaves do not leach easily with rain. When the nanomaterial applied to the leaves comes in contact with the body of the larvae of *Pieris rapae* (worm), the nanopesticide adhere to the insect and slowly poison it until its death. The authors report that graphene acts as an adhesion support, while the pesticide agent acts by poisoning the animal organism. Copper selenide nanoparticles act in three ways: poisoning when ingested by the insect, assisting the daytime release of the insecticidal compound due to its photothermal activity, and helping in the degradation of the pesticide that remains in the leaves left in the field after the time of cultivation. The authors reported that the nano-support developed showed resistance to bad weather, controlled release, and increased larval mortality by more than 35%.

The release of agrochemicals from a colloidal nanoparticle system is similar to that of other active compounds released from nanostructures. The delivery of pesticide agents incorporated and/or adsorbed on nanocarriers can occur through different mechanisms, among which it is possible to mention the release by (i) diffusion; (ii) dissolution; (iii) erosion; (iv) fragmentation; and (v) swelling, which may occur alone or together (BAKER, 1987; LIECHTY et al., 2010; PEPPAS et al., 2000), as shown in Figure 3.

Figure 3. Some of the most common mechanisms for releasing active compounds from nanocarriers.



Source: Authors.

2.1.1. Diffusion

In this case, the release of the active compound (solute) occurs by molecular diffusion, through the matrix (support). The particle matrix can remain intact or with few changes throughout the diffusion process, or it can undergo considerable changes due to its dissolution/fragmentation, for example (MCCLEMENTS, 2017). In this mechanism, the release rate of the actives depends on several factors, such as the chemical properties of the solute (polarity, molecular weight, volatility, among others), physical-chemical properties of the matrix (density, rheology, polarity, physical state, cross-linking state, and others), the physical characteristics of the particle (size, shape, crystallinity, etc.) and the gradient of contraction of the solute through the matrix in the core-shell direction (BAKER, 1987; LIECHTY et al., 2010; PEPPAS et al., 2000).

2.1.2. Dissolution

This active delivery/release mechanism occurs when the nanostructure comes in contact with specific environmental solutions or conditions capable of causing its dissolution (BAKER, 1987; MCCLEMENTS, 2017). In cases where the nanocarrier is the active compound itself, its release occurs in the medium as it dissolves. When the matrix is soluble, the active agent contained within it is released as the carrier matrix dissolves. In these cases, the release rate of the actives depends on the particle composition and the magnitude, the type and the duration of the environmental conditions that cause the dissolution (temperature, pH, ionic strength, humidity, etc.) (BAKER, 1987; LIECHTY et al., 2010; PEPPAS et al., 2000).

2.1.3. Erosion

In this case, the pesticidal compounds are released as the carrier matrix erodes due to specific environmental conditions. Erosion is a process of molecular chemical degradation of the matrix, which can occur in mass (in the whole particle) or only on the surface (outside the particle). Erosion is a phenomenon that can occur due to chemical (*e.g.* pH or the presence of strong acids/bases), physical (*e.g.* high/low temperature), and/or biological factors (*e.g.* enzyme action) (MCCLEMENTS, 2017). In this type of mechanism, the release rate depends on the speed and the erosion profile. For this mechanism, as well as for the others, other phenomena can occur simultaneously, for example, secondary processes of fragmentation and dissolution can interfere in the main erosion process, in which case the release rate will be influenced by these additional variables (BAKER, 1987).

2.1.4. Fragmentation

In this case, the release of pesticide actives is dependent on the fragmentation rate of the carrier matrix. Fragmentation is a process in which the nanostructure acquires fractures caused by physical disturbances of climatic, mechanical, chemical, physical, or enzymatic origin (BAKER, 1987). Due to the stresses suffered, the cracked nanostructure starts to fragment, pieces are loosened and released continuously in the medium in smaller and smaller sizes until complete degradation (BAKER, 1987; MCCLEMENTS, 2017).

2.1.5. Swelling

This mechanism includes the system for releasing actives that occur from the swelling of the matrix, caused by solvents and environmental conditions. In this case, the particles find favorable conditions for their swelling in the environment in which they are exposed. The swelling of the particles occurs due to an increase in the internal pore size. When the pore size reaches a value similar to the molecular size of the active compound, it becomes an escape route for this compound to the external environment. In this mechanism, the pesticide release rate will depend mainly on the swelling rate and the diffusion time through the matrix (BAKER, 1987; LIECHTY et al., 2010; PEPPAS et al., 2000).

2.2. Developments, applications and results: some current approaches

This section presents an update on new developments in the field of nano-based agricultural protection, in which some works were briefly presented. Table 2 shows some relevant research carried out in the last 5 years, in which the authors developed, applied, and evaluated the use of nano-delivery systems (nanocarriers) of pesticide agents for agriculture.

Maghsoudi and Jalali (2017) investigated the performance of graphene oxide nanosheets as photoprotectors of *Bacillus thuringiensis* against solar UV radiation. *B. thuringiensis* is a gram-positive spore-forming bacterium widely used in crops as a biopesticide since the 1940s. Although ecologically correct, the effectiveness of this bacterium in combating pests is sometimes impaired due to its low stability to environmental factors, such as natural UV radiation that is capable of causing its death. The team tested the larval resistance for 96 h under radiation in the isolated presence of graphene oxide, olive oil, olive oil mixed with graphene oxide, and free spores. The authors observed that larval mortality was 56%, 47%, 69%, and 40%, respectively, indicating that graphene oxide and olive oil achieved better results when applied together. The authors also mentioned that the results found exceed some results in the literature that use other photoprotection agents, such as molasses.

Suriyaprabha *et al.* (2014) used silica nanoparticles (20 - 40 nm) to treat *Fusarium oxysporum* and *Aspergillus niger*, two species of fungi that attack vegetables and legumes. The authors tested the application of nanosilica for the treatment of corn, and observed that a greater expression of phenolic compounds (2056 mg/mL) and less expression of stress-responsive enzymes (743 mg/mL) were found in leaf extracts from treated plants. The authors reported that the treated corn expressed greater resistance to *Aspergillus niger*, and that the same treatment carried out with silica in bulk did not present significant results in comparison to the results with nanosilica in terms of disease index and total phenol, peroxidases, polyphenol oxidase, and phenylalanine ammonia-lyase content. Therefore, they concluded that the silica nanoparticles had excellent antifungal properties and therefore can be considered as an alternative to combat phytopathogens.

Kumar *et al.* (2015) developed nanocapsules containing acetamiprid, a pesticidal agent. The nanocapsules were prepared by complexing alginate and chitosan polyelectrolytes and tested for controlled *in vitro* release under three different pH conditions. To obtain the nanocapsules, the team prepared two independent aqueous solutions of chitosan in acetic acid and alginate, with a corrected pH of 4.6 and 4.9 respectively. The pesticidal compound was ultrasonicated in the alginate solution and then a solution of calcium chloride was slowly added to the mixture. Under constant agitation, the chitosan solution was added slowly to the previous mixture. The recovery of the nanocapsules occurred after washing and centrifugation (14,000 rpm). The results revealed that the maximum release occurred at pH 10, and the lowest release at pH 4, and that the nanoparticles showed a controlled release of the insecticide for up to 36 h.

Maruyama *et al.* (2016) studied the nanoencapsulation of the herbicides imazapic and imazapyr in nanoparticles of alginate-chitosan and chitosan-tripolyphosphate, obtained by ionotropic gelation. For the preparation, they used a solution of sodium alginate in which the herbicidal compounds were added. After preparation, a solution of calcium chloride was added dropwise to obtain a pre-gel after 30 min of stirring. Then a solution of chitosan in acetic acid was added to the mixture and kept for 12 h under vigorous stirring to obtain the nanoparticles. For the preparation of chitosan-tripolyphosphate nanoparticles, the team prepared a solution of chitosan in acetic acid and later added the herbicidal compounds. Then a tripolyphosphate solution at pH 4.5 at 8 °C was added, and the mixture was kept under stirring for 12 h. The nanoparticles had an average size of 400 nm and showed excellent stability stored at room temperature for 30 days. In the end, they found that the nanoencapsulated herbicides showed greater efficiency and less genotoxicity when compared to the results of free compounds.

Yang *et al.* (2009) developed nanoparticles from polyethylene glycol (PEG) loaded with garlic essential oil to assess insecticidal activity against adult *Tribolium castaneum* (brown beetle). The nanoparticles prepared by the fusion dispersion method had a rounded shape and good size distribution with an average diameter of 240 nm. The authors tested the application of free and encapsulated oil and observed that the efficacy against *T. castaneum* remained over 80% even after five months when the nanoparticles were applied, while the application of free garlic oil reached only 11% of efficacy using the same concentration. Finally, they attributed the success of the application to the controlled release of the active garlic compound into the environment.

Campos *et al.* (2018a) used cyclodextrins to functionalize chitosan using a nano complexation method. The obtained mixture was used to encapsulate carvacrol and linalool, which are two phenolic monoterpenes extracted from herbs with insecticidal and repellent properties. The nano complexation of the biopolymers allowed an increase in the product's life due to the greater control of release and volatilization of the encapsulated essential compounds. The same group used zein, a protein obtained from the endosperm of corn kernels to encapsulate citronella, eugenol, geraniol oils, and cinnamaldehyde, which are natural compounds used in insect control (DE OLIVEIRA *et al.*, 2019).

Kumar, Kumar, and Dilbaghi (2017) prepared chitosan-pectin nanoparticles loaded with carbendazim (active pesticide) to combat *Fusarium oxysporum* and *Aspergillus parasiticus*. Chitosan-pectin nanoparticles were obtained by ionic interaction method. The authors separately made the dilution of chitosan in acetic acid and pectin in distilled water, under adequate sonification. Aqueous solutions of carbendazim dissolved in acetic acid, and sodium dioctyl sulfosuccinate (surfactant) were prepared. During 3 hours under vigorous stirring, the authors slowly dripped the pectin, carbendazim, and sulfosuccinate solutions simultaneously into the chitosan solution. After the reaction, the medium containing the nanoparticles was centrifuged for 1 hour at 10,000 rpm, the decanted was washed several times and lyophilized with mannitol (cryoprotectant). The authors obtained nanoparticles between 70 and 90 nm that showed 100% inhibition of fungi at concentrations of 0.5 and 1 ppm, while for pure carbendazim they observed 80 and 97% for the same concentrations, respectively. Based on the many tests carried out, the authors concluded that nano-formulated carbendazim is more effective and safer for the germination and root growth of *Cucumis sativa* (cucumber) seeds than the compound applied directly.

Shyla, Natarajan, and Nakkeeran (2014) chemically synthesized nanoparticles of titanium dioxide (TiO_2), zinc oxide (ZnO) and silver (Ag), and tested their effectiveness in combating *Macrophomina phaseolina*, a soil fungus that causes the root and stem rot of many plants, until their death. The synthesized nanoparticles showed an excellent average size distribution of 35-45, 20-80, 85-100 nm, for ZnO, Ag, and TiO_2 respectively. The best result was obtained by the application of silver nanoparticles and in lower concentrations than those used for the others. Sidhu, Barmota, and Bala (2017) produced copper sulfide nano-aquaformulations by the sonochemical method, followed by microwave irradiations in the presence of capping agents (polyvinylpyrrolidone, 4-aminobutyric acid or tri-sodium citrate). The authors tested the colloidal system *in vitro* for antifungal action in rice seeds. Studies have shown multiple efficacy against *Alternaria alternata*, *Drechslera oryzae*, and *Curvularia luneta*. The team also observed a significant reduction in seed rot and pest content in the seedlings, in addition to favorable effects on seed germination and plant growth.

Oliveira *et al.* (2015) prepared poly(ε-caprolactone) (PCL) nanocapsules with an average diameter of 241 nm containing atrazine as an active pesticide. The authors tested the post-emergence herbicidal activity of nanocapsules for target plant species. The herbicidal activity was noticed even after 72 h in *Brassica juncea*; the team also observed lower toxicity of encapsulated atrazine compared to the application of the free herbicide. Guo *et al.* (2015) developed silica microcapsules cross-linked with carboxymethylcellulose and epichlorohydrin, containing emactite benzoate as an insecticidal agent. The authors obtained capsules with an average size of 1 and 3 µm using the emulsion polymerization method, and their insecticidal action was tested against *Myzus persicae*. The authors observed excellent cellulase-responsive property, high efficacy against *M. persicae*, and less genotoxicity with *Allium cepa*.

Chart 2. Some relevant researches on the development, application and evaluation of nanocarrier systems of pesticide agents, from the last 5 years.

Nanocarrier / (average size)	**Pesticide Agent**	**Preparation method**	**Application**	**Results**	**Reference**
Nanoparticles of mesoporous silica and trimethylammonium / (423 nm)	2,4-dichlorophenoxy acetic acid	Sol-gel and nanosilica graft post	Herbicidal action against dicot plants	Electrostatic interactions were the driving forces that induced the loading of pesticides, and regulated the compound release by decreasing leaching in the soil.	(CAO *et al.*, 2018)
Silica gel microparticles loaded with ZnO and copper nanoparticles / (600 nm - 1.1 μm)	---	Chemical reaction in aqueous dispersion	Antimicrobial action against *Xanthomonas alfafae*, *Pseudomonas syringae*, and *Clavibacter michiganensis*	Excellent antimicrobial activity and high effectiveness in the control of citrus canker in Ruby grapefruit.	(YOUNG *et al.*, 2018)
2-nitrobenzyl-carboxymethyl-chitosan succinate micelles / (140 nm)	Diuron	Graft of side chains and method of conjugation	Photo-controlled pesticide release	High rate of photo-controlled release (96.8%) for up to 8 h (at pH 7) under solar radiation stimulus.	(YE *et al.*, 2015)
Hollow TiO_2 nanoparticles doped with Ag / (< 50 nm)	---	Chemical reaction in alcoholic dispersion	Fungicidal action against *Fusarium solani* and *Venturia inaequalis*	Excellent fungicidal activity under natural lighting (visible light).	(BOXI; MUKHERJEE; PARIA, 2016)
Chitosan and gum arabic nanoparticles / (~ 226 nm)	Carvacrol e Linalool	Ionic gelation	Insecticidal action against *Helicoverpa armígera* and *Tetranychus urticae*	Excellent insecticidal action and increased mortality rate. The compounds applied together showed better results than when applied alone.	(CAMPOS *et al.*, 2018b)
Zein nanoparticles / (278 ± 61.5 nm)	Neem oil	Anti-solvent precipitation	Investigation of toxicity to non-target organisms	The nanocapsules showed less genotoxicity to *Allium cepa* than free Neem oil, there was no change in soil biota, and safe application for *Caenorhabditis elegans*.	(PASCOLI *et al.*, 2019)
Microspheres of vinyl polyacetate (PVA) / (320 nm)	Emamectin-benzoate (EMB)	Microemulsion polymerization	Slow and controlled release pesticide action	Excellent photoprotective capacity of active agents, good stability of microspheres under natural conditions, and gradual EMB release over 200 h.	(WANG *et al.*, 2017)

Source: Authors

3. Disadvantages in the use of nanopesticides: a critical view

Throughout the review on the use of nano-delivery systems in agriculture, it became clear that nanotechnology is undoubtedly an ally in the development of solutions for cultivation. Its gains, advantages, and benefits have been exhaustively exemplified, but it has not been mentioned what are the real challenges encountered for the wide use of these nanomaterials, the risks offered, and the disadvantages they can cause. It is clear that for many specific applications, normally under controlled conditions, the results of the use of nanocarriers have shown an increase in application effectiveness and levels of preservation of the environment never seen before (DANG *et al.*, 2010; KIM *et al.*, 2018). The results of serious and reputable scientific researches have indicated that the use of pesticide nano-delivery systems in the field is a viable, promising and more sustainable alternative when compared to the conventional pesticide application system, which occurs due to the indiscriminate spillage of free agrochemicals in crops and soil, most often by direct spraying (DANG *et al.*, 2010; KIM *et al.*, 2018). Virtually all studies are concerned with only developing some technology that shows signs of positive and sustainable results, but there is no concern with studying the financial viability and economic consequences of its use (DIMKPA; BINDRABAN, 2018).

In recent decades, a large number of patents have been issued for works related to the development and application of nanomaterials containing pesticide agents for agriculture. However, the commercialization of these materials is extremely limited due to numerous challenges and knowledge gaps around their use (KIM *et al.*, 2018). Some of the challenges for advancing the use of nanotechnology include low investments in teaching and research/development infrastructure, the high cost of producing nanomaterials, low agricultural financial return, the resistance of the agricultural sector in the implementation of nanomaterials in the field, among other limitations that delay progression (HUANG *et al.*, 2015; PARISI; VIGANI; RODRÍGUEZ-CEREZO, 2015). Several technical restrictions in the scope of industrial production of nanopesticides limit the advance in the use of these materials, for example, the high energy demand of the processes involved (DIMKPA; BINDRABAN, 2018). Due to their size, nanoformulations tend to form clusters, or even dissolve the matrix, which alters their surface chemical properties. The aggregation of nanoparticles transforms them into non-nanological formulations, which is contrary to their main creation objective (DIMKPA; BINDRABAN, 2018). Other obstacles that the advancement of the use of these nanomaterials face are the unknown risks that the absorption and accumulation of nanomaterials in foods can present. The presence of more resistant agrochemicals in food can contaminate the food chain creating imminent health hazards for humans and animals, and even for the environment (MANCHIKANTI, 2019; PENG et al., 2017; VILCHEZ-ARUANI et al., 2020).

4. Final Considerations

Nanopesticides are a class of materials used to combat and control pests harmful to food and crops. These materials are based on nanometric systems for the actuation and/or delivery of active compounds in the field. Thus, nano-delivery systems for pesticides have been widely studied in an attempt to find effective solutions to current problems of environmental pollution, low efficiency of conventional application systems, and less toxicity to users and food. Numerous advantages have been reported in the literature in the use of these nanomaterials, and a very promising and more sustainable future can be expected from these nanostructures compared to traditional agriculture. However, some issues that slow the advance of the use of nanopesticides in the agricultural sector have limited the evolution of industrial production and the consolidation of these materials in the market. Another worrying factor is that little is known about the possible risks that these nanoformulations can cause. Therefore, further studies and more consolidated concepts are needed regarding health safety in the use of nanomaterials, their mechanisms of action, bioaccumulation behavior, cost of processing, the economic viability of production, marketing logistics, the stability of nanoformulation stock, ways of application in the field, and financial return to the producer. For these reasons, nanopesticides are still considered an emerging, revolutionary technology, in wide expansion and very promising if treated with awareness.

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