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Nanotechnology-Based Delivery Systems: Highlights in Agricultural Applications

**Jhones L. de Oliveira^a,
Estefânia V.R. Campos^a, Marcela C. Camara^a,
Lucas B. de Carvalho^a, Renata A. Monteiro^a,
Renata de Lima^b and Leonardo F. Fraceto^{*a}**

^aLaboratory of Environmental Nanotechnology
São Paulo State University (UNESP)
511 Avenida Três de Março, Sorocaba,
São Paulo, 18087-180, Brazil

^bUniversity of Sorocaba
km 92.5 Rodovia Raposo Tavares,
Sorocaba, São Paulo, 18023-000, Brazil

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Due to the excessive use of chemical agents in agriculture, numerous problems have arisen, such as contamination of the environment, intoxication of non-target organisms and the development of resistance mechanisms by pests. To overcome these challenges, several sustainable technological approaches are being explored, and nanotechnology is one of them. This review aims to provide insights into the use of nanotechnology related to the agricultural sector. Articles were selected using the Web of Science and Science Direct databases; more than 50 manuscripts between 2015 and 2019 were reviewed. This review includes systems based on nanotechnology, in particular, for the sustained release of active ingredients for pest control, nutrition and plant growth. Nanoparticle-based formulations have great potential to increase agricultural productivity and reduce health and environmental impacts. However, there are certain technological challenges that must be addressed to allow the adoption of this technology for wider use in agri-food production.

Keywords: nanotechnology-based delivery systems, sustained release, nanoparticles, sustainable agriculture, herbicides, insecticides, hormones and nutrients.

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* Corresponding author E-mail address: leonardo.fraceto@unesp.br

ORCID: 0000-0002-9664-0349 (Oliveira J.L. de); 0000-0002-9420-7461 (Campos E.V.R.); 0000-0002-3630-3455 (Camara M.C.); 0000-0002-1956-0580 (Carvalho L.B. de); 0000-0002-4118-2491 (Monteiro R.A.); 0000-0001-8712-1144 (Lima R. de); 0000-0002-2827-2038 (Fraceto L.F.)

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Основные характеристики наноразмерных систем доставки, предназначенных для применения в сельском хозяйстве

**Дж.Л. де Оливейра^а, Э.В.Р. Кампос^а,
М.К. Камара^а, Л.Б. де Карвалью^а,
Р.А. Монтейро^а, Р. де Лима^б, Л.Ф. Фрасето^а**

^аГосударственный университет Сан-Паулу (UNESP)
Институт науки и техники Сорокабы (ICTS)
Бразилия, 18087-180, Сан-Паулу, Сорокаба,
Аvenida Трес де Марш, 511

^бУниверситет Сорокабы
Бразилия, 18023-000, Сан-Паулу, Сорокаба,
Родовия Рапосо Таварес, км 92,5

Чрезмерное использование химических веществ в сельском хозяйстве привело к возникновению множества проблем, в частности загрязнению окружающей среды, токсическому воздействию на организмы, не являющихся мишенями, а также к развитию механизмов устойчивости у вредителей. Для преодоления этих вызовов изучается ряд устойчивых технологических подходов, одним из которых выступает нанотехнология. Данный обзор призван дать представление об использовании нанотехнологий применительно к сельскохозяйственному сектору. Статьи отбирали с помощью баз данных Web of Science и Science Direct; было проанализировано более 50 рукописей за период с 2015 по 2019 год. Обзор описывает нанотехнологические системы, в частности, для замедленного высвобождения активных ингредиентов для борьбы с вредителями, для питания и роста растений. Препараты на основе наночастиц имеют большой потенциал для повышения продуктивности сельского хозяйства и снижения воздействия на здоровье и окружающую среду. Тем не менее остаются определенные технологические проблемы, которые должны быть решены для более широкого использования этих технологий в производстве продуктов питания.

Ключевые слова: наноразмерные системы доставки, замедленное высвобождение, наночастицы, устойчивое сельское хозяйство, гербициды, инсектициды, гормоны и питательные вещества.

Introduction

Agribusiness has proven to be one of the most important sectors of the world economy. The growing demand for food caused by population growth, as well as by the scarcity of productive regions, puts pressure on this sector (Bruinsma, 2017). The so-called green revolution has led to great progress in agribusiness. However, it was based mainly on the use of agrochemicals and fertilizers and the mechanization of production. This resulted in poor management practices, in particular, excessive use of agrochemicals, which caused environmental contamination. With the growing concern of the harm caused by chemical methods of crop protection, it is of paramount interest to make considerable technological, economic and commercial advances in environmentally friendly agricultural technologies that will allow for gradual improvement in the sector (Shiva, 2016).

In this context, applications of nanotechnology in the agricultural and food sectors deserve special attention. Nanotechnology is viewed as a breakthrough approached “in basic research, development

of technologies and new materials production” (He et al., 2019). Nanotechnology has great potential to revolutionize agriculture and food systems throughout the agricultural chain. It is currently an important tool for increasing agricultural productivity that complements conventional agriculture technologies. Unlike the conventional delivery of agrochemicals, which require several applications to obtain the effective dose, nanotechnology-based delivery systems are able to perform a sustained release of active compounds in the dosing interval between the minimum effective concentration and maximum safe concentration (Fig. 1). Thus, nanotechnology-based delivery systems reduce the amount of active compounds required for a biological response and decrease environmental contamination risks, energy consumption and labour costs. Nanotechnology can provide greater safety for agricultural crops and for non-target organisms, such as pollinators (Fraceto et al., 2016; Kremer, 2019; Shukla et al., 2019).

Therefore, promoting the growth of food production and thereby contributing to the development of sustainable agriculture

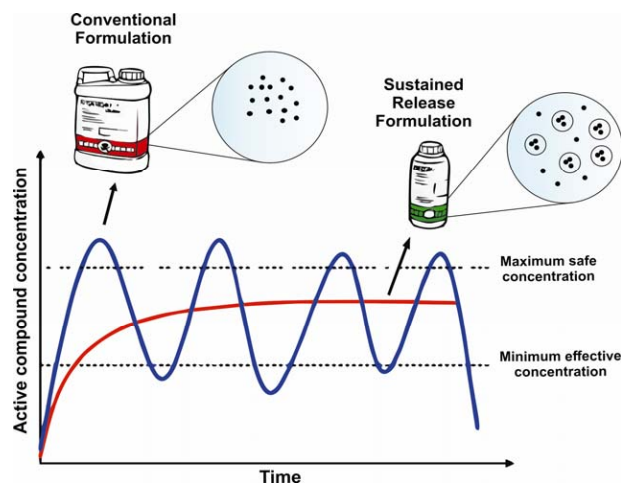


Fig. 1. Schematic representation of a conventional system and a sustained release system for agricultural applications. The effectiveness and concentration of an active compound in a conventional system decreases as a function of time, requiring new applications. The sustained release system, however, maintains the concentration of the active compound in an effective range of action

and improving food security investments in developing nanotechnology in agriculture is important.

Nanoparticle-based formulations for agricultural applications

Agricultural formulations are based mainly on active components that act against different types of pests and diseases (insects, fungi, rodents, plants, etc.). However, in recent years, the agricultural market has been increasingly interested in formulations that affect crop growth and development (hormones and nutrients). Researchers have tried to address these demands using nanotechnology in the agricultural sector. Due to the growing concern about environmental impacts, molecules and compounds derived from natural matrices are also being widely studied (Fig. 2). Below, we outline some advances in nanocarrier systems for active ingredients used in agriculture.

Herbicides

Herbicides are a class of substances that belong to agricultural pesticides and are

specifically used to control weeds. Weeds are considered to be invasive plants because they compete with cultivated plants for light, moisture and nutrients. In addition, weed species possess great rusticity, resistance to pests and a capacity to produce large numbers of seeds, which increases their propagation rate (Cobb and Reade, 2010; Zimdahl, 2018). Herbicides are widely used because of their numerous advantages, such as high speed of action, flexibility of treatment schedule and suitability for application on large areas. Herbicides can be classified according to their selectivity, chemical structure, mechanism of action and mode of application (pre- or postemergence pesticides) (Prosser et al., 2016). Table 1 presents a number of papers on the use of nanotechnology-based carrier systems for herbicidal compound applications.

Maruyama et al. (2016) used combinations of imazapyr and imazapic encapsulated in chitosan-based nanoparticles (chitosan/alginate, CS/ALG, and chitosan/tripolyphosphate, CS/TPP) to control weeds. According to the authors, the encapsulation efficiency for the CS/ALG and CS/TPP nanoparticles was

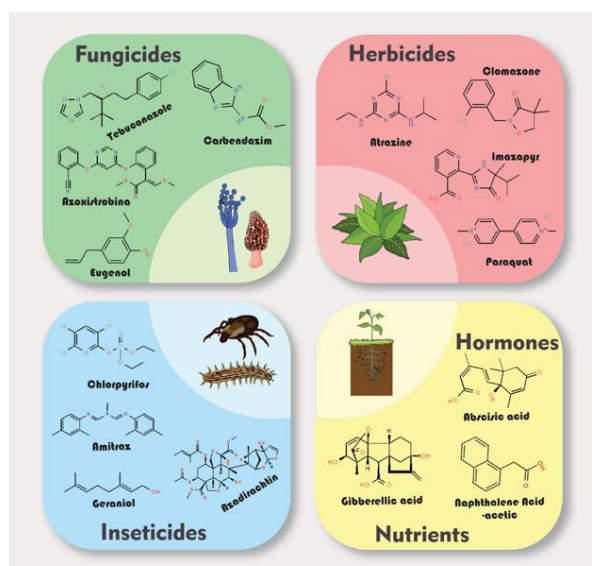


Fig. 2. Formulae of some active ingredients for agricultural applications

Table 1. Sustained release systems based on micro/nanotechnology for herbicide application. The table contains information on carrier systems, particle characterization and main results.

Matrix	Carrier system	Carrier properties	Active compound	Main results	Reference
1	2	3	4	5	6
Poly(epsilon-caprolactone)	Nanoparticles	Mean diameter 483.1 ± 2.5 nm; Polydispersity index < 0.2; Zeta Potential -22.8 ± 2.2 mV; Encapsulation efficiency > 95%	Atrazine	The nanoparticle formulation of atrazine was stable (60 days). Genotoxicity tests using <i>Allium cepa</i> demonstrated that nanoparticle systems were able to reduce genotoxicity of the herbicide. The mobility of atrazine in the soil was also reduced after encapsulation. Plant tests were performed with target (<i>Brassica</i> sp.) and non-target (<i>Zea mays</i>) species, and nanoparticle formulations were effective for the control of target species	Pereira et al., 2014
Lignin	Microparticles	Spherical morphology; Mean diameter of 25.3 ± 6.7 µm; Encapsulation efficiency 77.5 ± 2.5%	Atrazine	The release assays showed that approximately 98% of atrazine was released within 48 h. Soil leaching experiments showed that approximately 80% of the free atrazine was leached in 37 days, while 65% were leached when encapsulated in the microparticles	Taverna et al., 2018
Poly(methylmethacrylate)	Nanoparticles	Mean diameter 20-200 nm; Spherical morphology; Surface pores; Encapsulation efficiency > 70%	Haloxyfop R Metiliter	The formulation of nanoparticles containing the active compound showed stability as a function of time. The authors evaluated the toxicity of the system against non-target plant species (<i>S. polyrhiza</i>). The systems were shown to be less toxic to the non-target species compared to the non-encapsulated compound	Torbati et al., 2018
Carboxymethyl chitosan/ Glutathione	Nanoparticles	Mean diameter 250 ± 2.2 nm; Polydispersity index 0.31 ± 0.10; Zeta potential -34.2 ± 4.2 mV; Efficiency of encapsulation 83 ± 2.2%	Diuron	The formulations showed storage stability for three months. <i>In vitro</i> release studies have shown that diuron can be released from the nanoparticles in a sustained way and the percentage released depends on the concentration of glutathione. Herbicidal activity (pre-emergence) trials with target species (<i>Echinochloa crus-galli</i>) showed the effectiveness of the encapsulated herbicide in relation to the non-encapsulated herbicide. Non-target species (<i>Zea mays</i>) showed that encapsulated diuron did not affect plant growth	Yu et al., 2015

Continuation Table 1

1	2	3	4	5	6
Poly(3-hydroxybutyrate)	Microparticles Granules Pellets	The granules had a size of 2.5-3 mm and an encapsulation efficiency of 95-100%. Pellets had a diameter of 13 mm and a mass of 200 ± 0.15 mg, of which 25% consisted of metribuzin. The microparticles had a diameter of 2-17 μ m, a zeta potential of -30 mV and an encapsulation efficiency of 80%	Metribuzin	All formulations prepared showed stability over storage time (49 days). The release profile of metribuzin was altered when encapsulated in the different formulations. It is also noted that by varying the form of the formulations it was possible to control the release time of metribuzin	Volova et al., 2016
Rice husk	Nanoparticles	Mean diameter <100 nm; Zeta potential 40 mV	2,4-Dichlorophenoxyacetic acid	Monolayer sorption was observed for the formulations. Sustained release and reduction of the leaching property of the nanof ormulation was achieved. In addition, a better herbicidal activity against the target species (<i>Brassica</i> sp.) compared to that of the commercial 2,4-D was observed	Abigail et al., 2016
Chitosan/ Tripolyphosphate	Nanoparticles	Mean diameter ~ 200 nm; Polydispersity index <0.2; Zeta potential 30.1 ± 3.8 mV; Encapsulation efficiency ~ 80%	Paraquat	The encapsulation of the herbicide resulted in changes in its diffusion and release, as well as soil sorption. Cytotoxicity and genotoxicity assays showed that the nanoencapsulated herbicide was less toxic than the pure compound. The evaluation of herbicidal activity showed that the efficacy of paraquat was preserved after encapsulation	Grillo et al., 2014

between 50% and 70%; the nanoparticles had an average size of 400 nm and remained stable for 30 days at room temperature. Sustained release of the herbicides was observed, and the toxicity of the encapsulated herbicides was lower in comparison with the non-encapsulated herbicide.

In another study, Abigail et al. (2016) used rice husks to produce nanoparticles as a carrier for 2,4-D herbicides. The authors observed that due to the transformation of rice husks into particles of nanometric size, an increase in adsorption potential occurred. In addition, nanoformulations showed a higher herbicidal activity against the target plant *Brassica* sp. than commercial 2,4-D. The authors also observed a reduction in soil leaching after the encapsulation of herbicides.

Grillo et al. (2015) prepared polymeric nanoparticles of chitosan/tripolyphosphate loaded with herbicide paraquat and described their characteristics. They also investigated the effect of aquatic humic substances on the stability of nanoparticles and their toxicity to the environment. The results showed that the toxicity of paraquat was significantly reduced when the herbicide was encapsulated in nanoparticles, and the interaction of the nanoparticles with the humic substances also allowed a reduction of herbicide genotoxicity.

The search for new technologies for obtaining safer formulations of herbicides is important mainly due to the negative impacts of herbicides on the environment, including human health (workers, their families and consumers) and non-target species, such as pollinators. Because of the ease of application and the effectiveness of conventional herbicides, many farmers have abandoned more sustainable agricultural techniques. Thus, excessive use of herbicides puts human health at risk and interferes with the biological processes in

ecosystems (Abouzienna et al., 2016). In addition, such practices have led to the emergence of herbicide-resistant weeds, erosion and infertility of soils, and crop susceptibility to pathogens and diseases. Consequently, farmers use an increasing amount of herbicides to combat new pests. New technologies, such as nanotechnology, have been developed as tools to decrease the adverse effects of excessive herbicide application (Pérez-de-Luque, 2017).

Insecticides

Insects are highly specialized animals that are easily adaptable to highly varied and harsh living conditions. They belong to the phylum Arthropoda, comprising more than one million described species (Rechcigl and Rechcigl, 2016). In agriculture, these organisms play an important role as pollinators, but they can also act as agricultural pests. Agricultural pests are one of the main factors in reducing crop productivity around the world. They can cause losses in the field and during storage (pre-harvest and post-harvest losses) (Guedes et al., 2016).

Insecticides are currently the main means of controlling these organisms. They can fight adult insects as well as eggs and insect larvae (Mulé et al., 2017). Insecticides may have a synthetic or natural origin (when derived from secondary metabolites of plants). Throughout history, several types of natural materials have been used against insects, such as nicotine and tobacco (Oliveira et al., 2018). Insecticides can act through different mechanisms, such as inhibition of oviposition and feeding, promotion of mortality, and the induction of developmental disorders, and they also function as repellents (Mulé et al., 2017).

Although compounds with insecticidal activity are used to control diverse pests, their efficiency is decreasing due to developed resistance in pests caused by years of intensive use (Bass

Table 2. Sustained release systems based on micro/nanotechnology for insecticide application. The table contains information on carrier systems, particle characterization and main results.

Matrix	Carrier system	Carrier properties	Active compound	Main results	Reference
1	2	3	4	5	6
Poly(butyl acrylate-co-styrene)	Microcapsules	Mean diameter 88.3 – 101.8 µm; Encapsulation efficiency of 96.5%	Chlorpyrifos	The infrared and thermogravimetric analyses showed the encapsulation of chlorpyrifos in the microparticles. The release assays show that the release kinetics of chlorpyrifos were modified after encapsulation. Increased concentration of the crosslinking agents decreased the release of the active compound. According to the mathematical modelling, the release of chlorpyrifos from microcapsules obeyed the diffusion-controlled process	Wang et al., 2015
Sodium olysioxane carboxylate	Microparticles	Mean diameter approximately 3.5 µm and coating thickness of 285 nm; Encapsulation efficiency of 50.8%, spherical morphology and smooth surface	Chlorpyrifos	Microparticles containing chlorpyrifos were successfully synthesized by the coacervation method. Microparticles loaded with chlorpyrifos showed remarkable sustained release properties, since the release kinetics were altered as a function of the different crosslinking agents tested	Dai et al., 2017
Mesoporous silica/copper and alginate	Nanoparticles	Mean diameter <100 nm; Zeta potential of 30 mV and Encapsulation efficiency > 60%	Chlorpyrifos	The release of chlorpyrifos through the synthesized system presented a significant response to pH. Under pH ≤ 7 condition, the release rate decreased with increasing pH. The release rate under weakly basic conditions was slightly higher than that under weakly acidic conditions. The release rate of chlorpyrifos was also affected by differences in ion concentration. The mathematical modelling showed that the release curves adjusted to the sustained kinetic model could be described by the Korsmeyer-Peppas equation	Huayao et al., 2016
Chitosan and alginate	Nanocapsules	The nanoparticles presented spherical morphology, sizes in the range of 226.4 to 786.6 nm, and a zeta potential in the range of -21.3 to + 45.5 mV. The encapsulation efficiencies for essential oils of saffron and lemon balm were 71.1% and 86.9%, respectively	Essential oils of saffron and lemon balm	The best nanoparticles for saffron and lemon balm essential oils were obtained using 0.3 mg/mL alginate and 0.6 mg/mL chitosan, which resulted in the smallest particle size. Sustained release was evaluated at pH 1.5 and 7.4. For safflower oil, approximately 90% and 70% of the oil were released at pH 7.4 and 1.5, respectively, after 48 h. For the lemon balm oil, there was a release of 42% and 38% of the oil at pH 7.4 and 1.5, respectively. High cell viability was observed in the presence of carriers containing essential oils, indicating that they were non-toxic	Natrajan et al., 2015

Continuation Table 2

1	2	3	4	5	6
Zein	Nanoparticles	Nanoparticles loaded with geraniol had a mean diameter of 172.3 ± 3.8 , a polydispersity index of 0.351 ± 0.032 and a zeta potential of -18.8 ± 1.02 mV. The nanoparticles loaded with R-citronellal had an average diameter of 142.5 ± 9.3 , a polydispersion index of 0.330 ± 0.052 and a zeta potential of -12.8 ± 0.98 mV	Geraniol and R-citronellal	The botanicals were successfully encapsulated in nanoparticles (> 90%). The systems exhibited good physicochemical stability in addition to protecting the assets from UV degradation. Both cytotoxicity and phytotoxicity assays showed reduction in toxicity. The biological activity (repellency) in <i>Tetranychus urticae</i> Koch showed that the nanoparticle systems containing the botanical compounds presented high repellency	Oliveira et al., 2018b
Chitosan and gum arabic	Nanoparticles	Nanoparticles containing geraniol showed a mean diameter of approximately 200 nm. The zeta potential was positive at 32.1 ± 2.1 mV and the polydispersity index was approximately 0.4. The nanoparticles remained stable for 90 days and showed spherical morphology	Geraniol	The nanoparticles of chitosan/gum arabic containing the active compound geraniol showed good colloidal properties and were also able to protect the active compound against degradation by UV radiation. The biological results with whitefly (<i>Bemisia tabaci</i>) showed that the formulation of nanoparticles containing geraniol showed significant attraction activity and can be used in trap systems	Oliveira et al., 2018a

et al., 2015). Many conventionally formulated insecticides have several environmental incompatibilities (Moradi et al., 2019) and affect non-target organisms. They may exert toxic effects through different mechanisms of action and may even be lethal. There are reports on the negative impacts of insecticides on important species that collectively contribute to ecosystem integrity, such as pollinators, decomposers, and predators (Chagnon et al., 2015).

New strategies to circumvent pesticide resistance in harmful organisms to protect crops and improve vector control tools are invaluable to agriculture and public health. The use of compounds in a rotational approach is a more sustainable management practice of mitigating insecticide resistance and is, along with the minimization of chemical dependence and the development of eco-friendly technologies, one of the most favoured tactics (Bass et al., 2015). Table 2 provides references to a number of papers that describe nanotechnology-based carrier systems used for the application of insecticidal compounds.

The use of carrier systems improves insecticidal activity through targeted and sustained release of the active compound, as demonstrated in studies of formulations containing the λ -cyhalothrin pesticide (Zhang et al., 2019). Uniform particles of 800 nm, a zeta potential of +29.1 mV and a loading efficiency of 31% λ -cyhalothrin were produced with dopamine-conjugated silica encapsulation. The sustained release from this system responded to pH variations with a higher percentage released in a more alkaline environment, which was in accordance with the Fickian diffusion model. The nanocapsules improved the stability of the pesticide, showed high activity against *Helicoverpa armigera* and reduced the genotoxicity of λ -cyhalothrin to non-target organisms.

Nanoparticles formed by encapsulation of the insecticides λ -cyhalothrin and imidacloprid in chitosan-coated nanoliposomes showed a positive surface charge (ZP = + 31 mV), with a size of 69 nm, a polydispersity index (PDI) of 0.25 and an encapsulation efficiency of 93% and 51%, respectively (Moradi et al., 2019). The chitosan coating may aid in crossing through nonpolar substances, such as cuticular waxes and cellular membranes, and in the movement through polar substances such as water. The study showed that the concentration of chitosan influenced the thickness of the lipid layer, prolonged the residual activity of the insecticides and influenced the peak time of *Myzus persicae* mortality (Moradi et al., 2019).

In nanoparticle formulations with less stable active compounds, such as essential oils, the limiting characteristics of these compounds (degradation with UV light) can be circumvented, as is the case for the leaf oil of *Zanthoxylum rhoifolium*. The leaf oil was encapsulated in polycaprolactone (PCL) with 96% efficiency, which gave rise to particles smaller than 500 nm with a zeta potential of -20 mV (Christofoli et al., 2015). The encapsulation promoted effective protection of the active ingredients against degradation with UV light, and their insecticidal effect on populations of *Bemisia tabaci* resulted in a 95% reduction in the number of eggs and nymphs. The release profile of the encapsulated insecticide was characterized by a rapid initial release followed by slow release for more than 12 h.

Hormones and nutrients

Nutrients are chemical elements extracted by plants from the soil and water by absorption through roots. Nutrients are vital in metabolic processes to ensure satisfactory growth and productivity (Fageria, 2016). These compounds are divided into two main groups, macronutrients

Table 3. Sustained release systems based on micro/nanotechnology for nutrient and hormone application. The table contains information on carrier systems, particle characterization and main results

Matrix	Carrier system	Carrier properties	Active compound	Main results	Reference
1	2	3	4	5	6
Starch/Alginate	Spheres / Hydrogels	-	Phosphorus	FTIR peaks showed the successful interaction between O-H stretch bonds in starch with COO- in alginate. In addition, the phosphorus was successfully encapsulated in the synthesized formulation. The crosslinking with sodium chloride showed that it was able to improve the surface morphology of the prepared hydrogels. Hydrogels with high CaCl ₂ content have low thermal stability. The calcium chloride content also significantly influenced the rate of release, swelling and dissolution. After 30 days, the formulation presented 7% phosphorus release with 40% swelling and 80% dissolution	Phang et al., 2018
Carboxymethyl cellulose	Nanocomposites	Highly porous morphology	Nitrogen Phosphorus Potassium (NPK)	The superabsorbent nanocomposite was prepared by <i>in situ</i> polymerization. The characterization results showed that NPK was successfully incorporated. The fertilizer release behaviour through the NPK-loaded hydrogel nanocomposite was in accordance with the European Standard Committee standard, indicating its excellent slow-release property. These characteristics prove that the formulation of hydrogel nanocomposite fertilizer can be used in agricultural and horticultural applications	Olad et al., 2018
Mesoporous silica	Nanoparticles	Mean diameter <50 nm; Zeta potential 28 mV	Abscisic acid	The authors investigated the encapsulation of abscisic acid in mesoporous silica nanoparticles. In addition to the preparation and characterization, the authors evaluated the biological effect in <i>Arabidopsis thaliana</i> . According to the authors, the system caused a reduction of water stress, a reduction of leaf stomatal opening and a reduction of water loss	Sun et al., 2018
Mesoporous silica/Gold	Nanoparticles	Mesoporous nanostructures range from 40 to 60 nm, 10-15 nm gold core	2,4-Dichlorophenoxyacetic acid	After biotechnological application in plant culture cells (<i>Linum usitatissimum</i> L.) the authors observed increased occurrences of ploidy and embryogenesis and an induction of methylation levels	Kokina et al., 2017

Continuation Table 3

1	2	3	4	5	6
Chitosan	Nanoparticles	Average particle size of 326 nm and a zeta potential of 22.1 mV. Slow release of copper with the presence of chitosan	Copper	Evaluation of biological activity in <i>Zea mays</i> . The authors observed effects on growth such as height increase, stem diameter, root length, number of roots, chlorophyll content and an increase in yield. Additional biological effects were also observed, such as defence responses against the <i>Curvularia</i> leaf spot	Choudhary et al., 2017
Chitosan	Nanoparticles	Mean diameter of 88.21 nm and a zeta potential of -29 mV	Copper	The authors observed that <i>Eleusine coracana</i> seed treatment and foliar applications with the prepared system improved development and increased the production of the plants. An increase in the defence enzymes was observed in addition to the suppression of blastic disease	Sathiyabama and Manikandan, 2018
Chitosan	Nanoparticles	Mean diameter of 59 nm and a zeta potential of 24 mV	Silver	After characterization of the system, the authors observed the biological activity in <i>Cicer arietinum</i> L. The authors observed that the treatment of the seeds increased the germination rate, the length of the seedlings and the dry weight. There was also an increase in the activity of α - and β -amylase, ascorbate peroxidase, peroxidase and catalase, and an increase in chlorophyll content was also observed	Anusuya and Banu, 2016

and micronutrients, which plants need at high and low concentrations, respectively. Macronutrients are major constituents of the most important plant substances; for example, phosphorus and nitrogen are essential components of nucleic acids (Xu, 2018). In contrast, plant hormones, or phytohormones, are natural substances of plant metabolism that regulate the physiological processes of growth and development (Ordaz-Ortiz et al., 2015). These molecules work as chemical messengers, transported from the production site to the target cells, and modulate gene expression and protein activity there (Khan et al., 2014). Table 3 presents some examples of studies that describe the encapsulation of hormones and nutrients in sustained release systems.

As shown in Table 3, different strategies have been employed to encapsulate plant fertilizers and hormones in an effort to control the release of nutrients into soil to promote plant growth, their resistance to unfavourable conditions and their protection from diseases. The use of chitosan as a matrix was investigated by different authors because it is known for its biocompatibility, biodegradability and economic viability (Anusuya and Banu, 2016; Choudhary et al., 2017; Sathiyabama and Manikandan, 2018). Choudhary et al. (2019) also used chitosan to synthesize zinc-chitosan nanoparticles to improve plant nutrition and development. The authors obtained highly bioactive positively charged nanoparticles with a spherical shape, porous structure and mean size of 387.7 nm. A faster release was achieved at acidic pH (1 to 3), reaching 86.98% of zinc release after 144 h. Zn-chitosan nanoparticles showed strong antifungal activity against *Curvularia lunata* and stimulated maize plant defence enzymes, increasing the activities of SOD (2.0-fold), PAL (3.0-fold), PPO and POD (up to 17.24-49.37% compared to that of the control). Seed and leaf treatments with the nanoparticles also increased plant height (1.3-1.6-

fold), stem diameter (1.6-3.3-fold), root length (1.0-1.6-fold) and grain yield (by approximately 40%). Chitosan was also successfully used in encapsulation of S-nitrosoglutathione (GSNO) by the ionotropic gelation method (Silveira et al., 2019). GSNO-chitosan nanoparticles had an average size of 104.8 nm and a positive zeta potential (17.5 mV). These nanoparticles were efficient in controlling stress in sugarcane caused by water deficiency. Due to the controlled release features of nanoparticles, an increase in leaf CO₂ assimilation was observed under the water deficit, as well as a 5.8-fold increase in shoot dry mass after encapsulated GSNO treatment when compared to that of the treatment with free GSNO.

Some studies have investigated the encapsulation of plant growth-promoting bacteria (PGPB) or rhizobacteria (PGPR). These microorganisms are responsible for plant stimulation through a wide variety of mechanisms, such as phosphate solubilization, nitrogen fixation and plant hormone production (Paul and Lade, 2014). Li et al. (2017) reported that the controlled release of bacterial fertilizers has a promising application in agroindustry. The authors produced microcapsules of *Pseudomonas putida* from a mixture of sodium alginate and bentonite using the external gelation technique. Spherical microcapsules ranging from 25 to 100 µm with high encapsulation efficiency and yield of approximately 90% were obtained. In addition, the study showed that the matrix preserves cell viability under different pH conditions. He et al. (2017) showed that cotton seed treatment with sodium alginate-bentonite microcapsules loaded with *Pseudomonas putida* improved seed germination and plant development and efficiently alleviated salt stress at low salt concentrations (0.5 – 1%).

Water, fertilizer deficit and other abiotic stresses are the main factors that limit plant

growth and affect agricultural production worldwide (Silveira et al., 2019). Therefore, the development of environmentally friendly particles that could release nutrients slowly, reduce water consumption and increase crop yield is an emerging field extensively explored today. However, the wide production and commercialization of nanoparticles is still limited by certain obstacles (Mahanty et al., 2017; Choudhary et al., 2019), such as (i) the absence of well-developed techniques that are adaptable to large-scale commercial use for the production and application of biofertilizers, (ii) the lack of awareness of technology involved in nanoparticle products, especially among farmers, (iii) distrust of the formulations that do not pose any risks to the environment and health in both the general public and regulatory agencies worldwide, (iv) high costs of nanoparticle-based products having to compete with commercially available chemical products and (iv) insufficient knowledge of biofertilizer toxicity to the soil environment and the biofertilization interaction with soil microflora.

Conclusion

Nanotechnology is recognized as an important tool in the development of sustained release systems for agricultural applications. There is a large body of evidence that sustained release systems can be successfully employed to control agricultural pests as well as to improve plant nutrition and crop growth. However, there

are still few commercial products available on the market. This is mainly due to the regulatory divergences that still exist in nanotech products as well as the scarcity of information regarding the relationship between the effectiveness of these new systems and their safety for non-target organisms and the environment. Overall, this review summarizes works related to sustained release systems developed based on nanotechnology for agricultural applications. Part of the works reviewed presented systems as promising for use in agriculture without presenting the results on their biological activity. Despite this fact, in general, the review demonstrates that the use of nanotechnology allows the reduction of the amounts of active compounds used. It is also worth noting that nanoparticle-based products have high associated costs, so research is still needed to make them economically feasible with costs that are competitive with conventional formulations.

In conclusion, we emphasize that although a major breakthrough has been achieved in the field of nanoparticle-based formulation development for agricultural applications, further research is required to address the remaining gaps in technology.

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