Chapter 4. Potential use of polymeric particles for the regulation of plant growth

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Abstract

Plant growth regulators (PGRs) are molecules widely applied in the agriculture, leading to increased crop yield and improved quality of agricultural products. These compounds act as plant hormones, affecting the plant hormonal homeostasis, and thus control plant growth and development. Recently, the development of polymer-based modified release systems for PGRs has emerged as a promising alternative for increasing the efficacy of these compounds. This review will focus on polymeric particles that are used as carrier systems for PGRs, allowing their controlled release and protecting them from degradation. Successful examples include the phytohormone gibberellic acid (GA_3)-loaded nanoparticles, which showed higher efficacy than the non-nano active ingredient in promoting seed germination and seedling growth, andsalicylic acid (SA) and nitric oxide (NO)-releasing nanoparticles as effective plant protection agents against stresses. Polymeric nanomaterials *per se* such as chitosan (Cs) can also alter plant signaling pathways and promote plant growth and development. Despite their great potential in improving the plant production with less damage to the environment, relatively few studies have focused on the use of these nanomaterials for the development of modified release systems for PGRs. In this scenario, this review discusses on the major advances and obstacles in the area.

Keywords: Carrier system; Chitosan; Nanoparticles; Plant growth regulator.

5.1. Introduction

Currently,agrochemicalsare of extreme importance in the agriculture, especially for their large production and uses(Prasad et al. 2017b). However, the excessive use of these compoundshascausedenvironmental damage, resulting in soil degradation and contamination of natural resources(Mishra et al. 2017).These negative factors present major challenges for today's agriculture and also open some questions, such ashow agricultural practices could increase global production without causing damage to the environment(Ciura and Kruk 2018).

In this context, new technologies for the controlled release of agrochemicals can revolutionize the agricultural sector(Mishra et al. 2017; Duhan et al. 2017).They include the development of microparticles and nanoparticles as active substance carrier systems in order to improve their biological action and reduce environmental impact(Chen and Yada 2011; Ghormade et al. 2011; Khot et al. 2012; de Oliveira et al. 2014; Campos et al. 2015; Grillo et al. 2016; Fraceto et al. 2016; Athanassiou et al. 2017).

Several advantages are associated with the use of micro and nanoparticles, among them, greater protection against premature degradation, slower release of the active ingredient, extension of its duration of action, and improved uptake of the active ingredient by target species (Kah et al. 2013; Kah and Hofmann 2014; Valletta et al. 2014; Nguyen et al. 2016; Tripathi et al. 2017; Prasad et al. 2017a). These micro and nanoparticle characteristics allow reductions not only in the dosage of the active ingredient but also on the application frequency, decreasing also the environmental contamination and the risk of harming non-target organisms (Kah et al. 2013; Kah and Hofmann 2014).

Among the active ingredients used in the agriculture, we have the plant growth regulators (PGRs), which are natural or synthetic substances that are applied exogenously to alter plant hormonal homeostasis and/or signaling (Rademacher, 2015). Phythormones (also called plant hormones) may be used as PGRs, as well as their precursors and synthetic analogues. PGRs also include compounds that inhibit the biosynthesis, the translocation or the signaling pathway of phytohormones(Basra 2000; Rademacher 2015). Phytohormones are substances of plant metabolism that act at low concentrations to regulate physiological processes of plant growth, development and responses to the environment(Ordaz-Ortiz et al. 2015; Rademacher 2015). According to their chemical structure and functions in plant physiology, nine major groups of phytohormones are found in plants: auxins, cytokinins, gibberellins, ethylene, abscisic acid, brassinosteroids, jasmonic acid, SA and strigolactones (**Fig.5.1**). Recently, other signaling substances with functions similar to those of plant hormones have been described. An important example is NO, a gaseous signaling molecule that acts in many developmental processes and in plant responses to biotic and abiotic stresses (Lindermayr and Durner, 2018).

PGRs have wide applications in agriculture and horticulture, being applied from seed germination and seedling production to grain filling and fruit ripening (**Table 5.1**). Therefore, PGRs provide important benefits that include enhanced crop yield and quality, facilitated crop management and extended storage of perishable products (Basra 2000; Rademacher 2015). However, despite the high number of studies regarding PGRs and their systematic agricultural use since the 1930s, PGRs currently represent a relatively small portion of the agrochemical market, especially if compared with pesticides (Rademacher 2015). One factor that hinders the application of PGRs is their degradation when exposed to field conditions of light and temperature, which compromises their biological activities (Silva et al. 2013; Dong et al. 2016; Yang et al. 2018). In addition, when applied at supra-optimal concentrations, PGRs may exert phytotoxic effects thereby acting as an herbicide rather than a hormone (Skůpa et al. 2014). Another aspect is the poor water solubility of some PGRs, which may hamper their applications (Ambrogi et al. 2006; Ge et al. 2011; Yang et al. 2018).

This review was focused on the major advances and obstacles regarding the use of polymeric micro and nanomaterials for the development of modified release systems for PGRs. Although there are multiple publications reporting the synthesis and physico-chemical characterization of micro and nanocarriers of PGRs particularly in the chitosan (Cs) polymeric matrix with a potential use in agriculture, few studies have demonstrated their mode of action andbiological effects in plants. This important issue constitutes a challenge for the next years. The actions of some polymers *per se* especially Cs in altering plant signaling pathways and promoting growth will alsobe discussed.

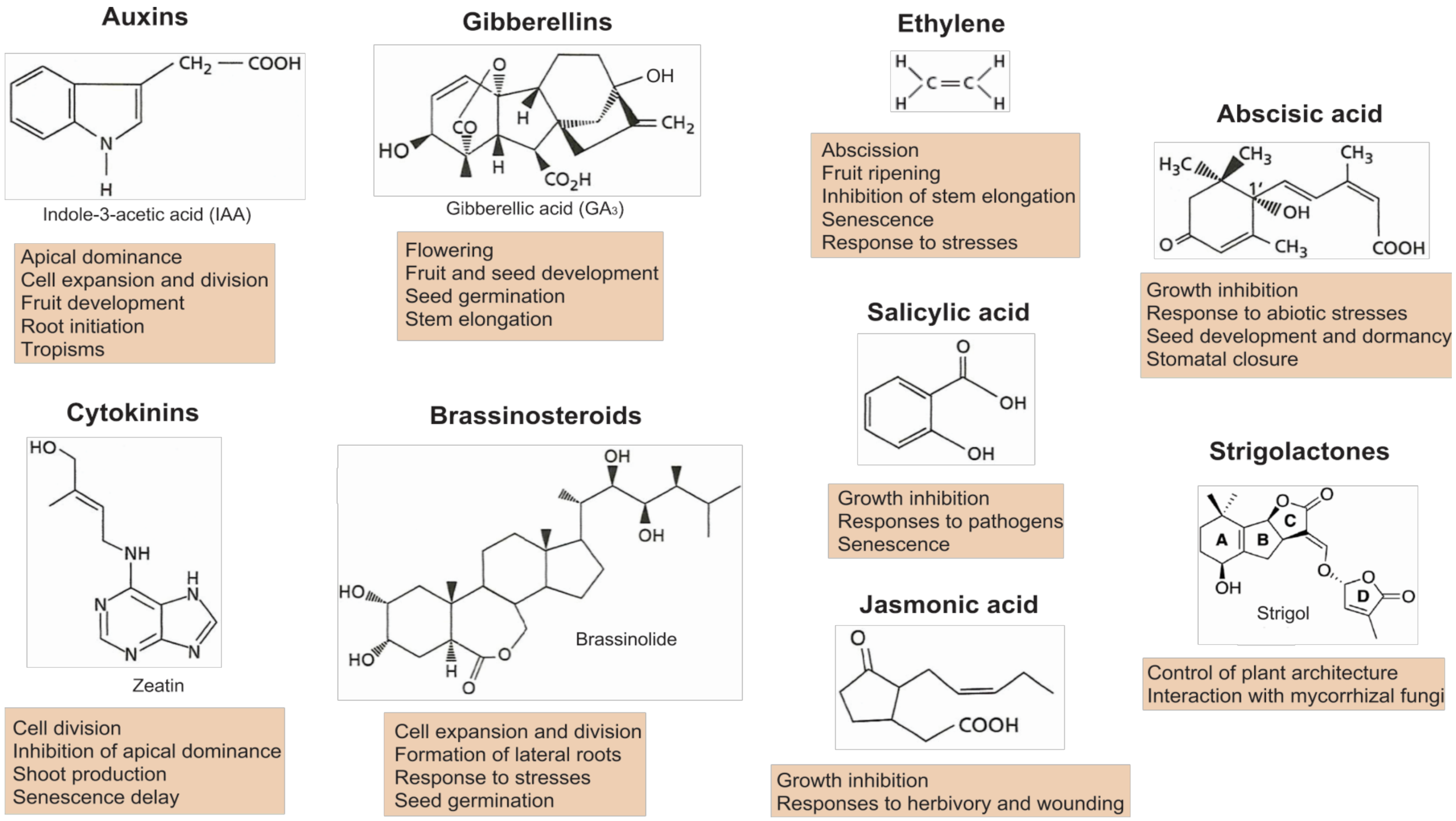

Fig.5.1. Major groups of phytohormones. Chemical structure of a representative compound from each group and some of their respective physiological functions are indicated.

Table 5.1. Major PGR types foragricultureapplications.

PGR types	Examples	Applications	References
Auxins	2,4-D, indole acetic acid (IAA), naphthalene-1-acetic acid (NAA)	Induction of rooting of cuttings, cell culture, herbicide	Cardoso et al. 2011; Dibax et al. 2013; Schulz and Segobye 2016
Cytokinins	Kinetin,6BA	Cell culture	Dibax et al. 2013
Ethylene releaser	Ethephon	Induction of fruit ripening and flowering	Hussain et al. 2015; Espinosa et al. 2017
Ethylene inhibitor	AVG, 1-MCP	Delay of senescence and fruit ripening	Petri et al. 2007; Steffens et al. 2009; Grozeff et al. 2010
Gibberellin	GA_3	Induction of flowering, seed germination and fruit growth	Peixoto et al. 2011; Cardoso et al. 2012; Camara et al. 2018
Gibberellin inhibitor	Trinexapac-ethyl, Calcium proexadione, Clormequat chloride, Mepiquat chloride	Reduction of shoot height	Rodrigues and Fioreze 2015
NO donor	Sodium nitroprusside, *S*-nitrosothiols	Tolerance to abiotic stress	Oliveira and Seabra 2016
JA	n-Propyl dihydrojasmonate	Improvementoffruitquality	Kondo 2010

5.2. Production of polymeric nanoparticles

The development of nanoparticles becomes a valuable strategy in the field of active ingredientvectorization. Nanoparticles allow a wide variety of molecules to be targeted to different parts by releasing them in a controlled manner over time, protecting them from degradation, increasing their half-life and decreasing its toxicity. **Fig.5.2** shows the possible structure for polymeric nanoparticles.

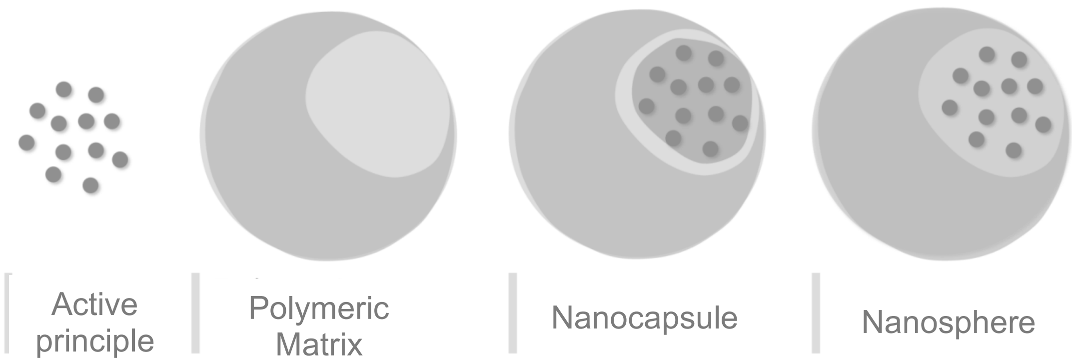

Fig.5.2. Possible structures of a polymeric nanoparticle. The nanocapsules show a core-shell structure and nanospheres present a polymeric matrix.

5.2.1. Biodegradablepolymersused as activeprinciplecarriers

During the past decades, significant advances have been made in the development of biodegradable polymeric materials as active principle vehicles. Degradable polymeric biomaterials are preferred candidates for developing carriers. A wide range of natural or synthetic polymers are being investigated for agricultural applications. Biodegradable polymers can be derived from different sources. The number of such materials that are used in or as adjuncts in delivery has increased dramatically over the past decade. The different kinds of biodegradable polymers used as vehicles are summarized in **Fig. 5.3**.

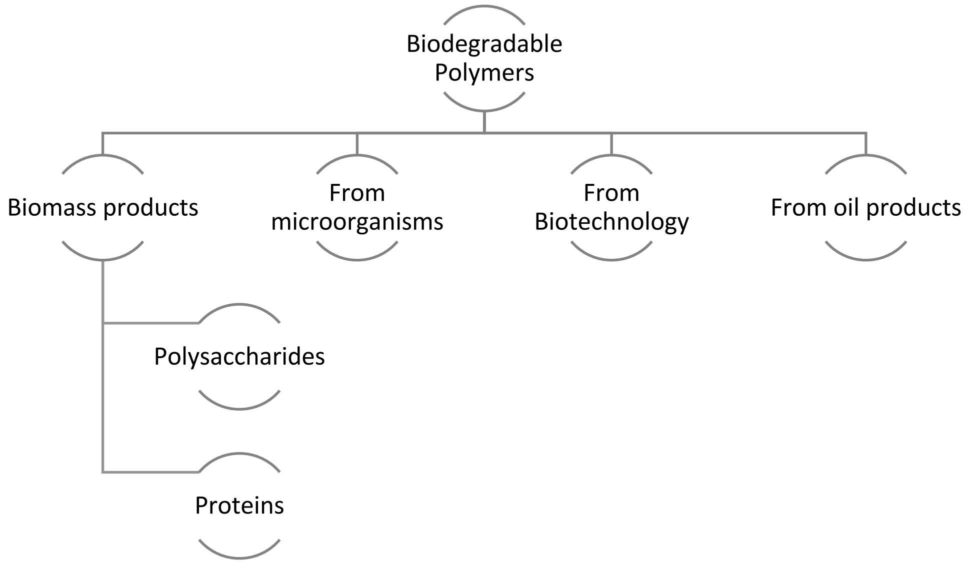

Fig.5.3. Different kinds of biodegradable polymers used as vehicles of active ingredients. The main sources of biodegradables polymeric materials come from biomass products (polysaccharides and proteins), from microorganisms or obtained from biotechnology routes and oil byproducts.

Many biopolymers such as alginate, Cs, cellulose, pectin and cellulose have been used to the development of carriers systems for agrochemicals (Campos et al. 2015) as well as to the coating of metallic nanoparticles (Navarro et al. 2015; López-Moreno et al. 2018). The most widely used polymer for the development of nanocarrier systems has been Cs(Kashyap et al. 2015). Cs is a polysaccharide derived from chitin. It has great characteristics including the biodegradability and biocompatibility as well as fungicidal properties, Cs has been also use in the pharmaceutical, cosmetics and food fields (Zargar et al. 2015; Malerba and Cerana 2016). In the case of biopolymers used as a stimulator for plant development, Cs has been one of the most cited in order to promote plant growth resulting in increased production.

In addition, many types of polymers and agents can be used for the coating nanoparticles such as lactate, polyvinylpyrrolidone, polyethylene glycol, gelatin, sodium dodecyl benzenesulfanate, citrate, dexpanthenol and carbonate (Navarro et al. 2015). When these systems are coated, their properties such as size, zeta potential are altered, as well as the biological effects on plants. Thus, this issue opens up a wide field in the design of new nanoparticles or nanocarrier systems in order to increase the biological activity of a nanoparticle system or even reduce toxic effects on plants.

Depending on the mode of degradation, polymeric biomaterials can be classified as: hydrolytically and enzymatically degradable polymers. It is important to remark that most of the naturally occurring polymers undergo enzymatic degradation.

5.2.2. Common techniques to prepare polymeric nanoparticles

There are numerous methods for producing polymeric nanoparticles carrying hydrophobic or hydrophilic molecules, simple or complex (Rao and Geckeler 2011). These methods can be classified into two categories: those that involve polymer synthesis or those that involve preformed polymers. Among the methods involving polymer synthesis, mention may be made of polymerization/emulsion(Thickett et al. 2007) and interfacial polymerization (Crespy et al. 2007). Considering the methods that use preformed polymers, simple(Solans et al. 2005; Fryd and Mason 2012)or double (Hanson et al. 2008; Iqbal et al. 2015) emulsion with subsequent evaporation of solvent, and nanoprecipitation(Hornig et al. 2009; Martín-Saldaña et al. 2016, 2017).The simple emulsion method with subsequent solvent evaporationis the most widely technique used to accommodate hydrophobic active principles in nanoparticulate polymer matrix systems. It consists in forming a stable emulsion from two immiscible phases: an aqueous or continuous phase provided with an appropriate stabilizing agent and an organic dispersed phase containing the drug and the matrix polymer. In most cases, an ultrasound probe is responsible for generating an emulsion that guarantees nanometric droplets composed of the dispersed phase. Then, the polymer contained in the droplets precipitates in the form of nanoparticles trapping the drug as a result of the evaporation of the organic solvent, which must naturally be volatile. The main advantage of this method is the high efficiency of encapsulation of hydrophobic active ingredients (Gómez-Gaete, 2014).

Differently, double emulsion is a strategy to house hydrophilic molecules in hydrophobic polymeric nanoparticles. Emulsions are a type of dispersed phase systems, depending on the type of dispersion the emulsions are classified as those of the water in oil (w/o) or oil in water (o/w) type. It is possible to obtain more complex dispersions for more specific purposes, such as multiple emulsions of the w/o/w or o/w/o type, which require, first, the formation of a stable primary emulsion and then its dispersion in the phase external by dispersing two immiscible liquid phases, which have a high attraction force between their own molecules, a large interface area is generated producing a thermodynamically unstable system, which entails the breakdown of the emulsion in a certain time. To stabilize the dispersed systems or emulsions, an agent having interfacial activity must be added, which allows decreasing the interfacial tension and the attractive interactions between the droplets that are dispersed. These agents that are called surfactants, are amphipathic chemical species, which by various mechanisms prevent the collapse of the droplets, preventing their coalescence or flocculation. Double emulsions are complex systems in which the droplets of the dispersed phase contain one or more types of smaller scattered droplets(Iqbal et al. 2015).

Double emulsions have the potential to transport both hydrophobic and hydrophilic active principles. However, this technique is more commonly used to encapsulate hydrophilic molecules, which suffer from a low loading efficiency due to the rapid partition of the drug in the external aqueous phase when using simple emulsions (Iqbal et al. 2015).

5.3. Polymeric nanoparticles as carrier systems for PGRs

Polymeric nanoparticles have been developed as carrier systems for different types of PGRs (**Table 5.2**). Liu et al.(2013) developed the first reported material for the controlled delivery of GA_3, which is the most representative gibberellin. GA_3 is not dissolved in water and is easily degraded under neutral and alkaline conditions as well as by light and temperature, properties that affect its efficiency in formulations for the use in the field (Kah and Hoffman 2014). Hence, GA_3-Cs conjugate efficiently protects the phytohormone from photo and thermal degradation. Itsrelease properties can be achieved by controlling pH, temperature and UV irradiation. Pereira et al. (2017a,b) described the properties of Cs nanocarrier systems forGA_3. These particles showed a sustained release of 58% of GA_3 in two days and enhanced properties compared with free GA_3 hormone in the promotion of seed germination, root and leaf development and also, increased the photosynthetic pigments in *Phaseolus vulgaris*.

Quiñones et al.(2010) described the encapsulation of two synthetic brassinosteroid analogues (DI31 and S-7) in tripolyphosphate (TPP)- Cs microparticles. Higher loading capacity and release from microparticles were obtained when the steroids were dissolved in ethanol. Both steroids show a sustained and constant release rate for the first 10 h.Until now the biological activity of these microparticles has not been assayed in plants (Quiñonez et al. 2010).

Table 5.2. Nanoparticle and nanocarrier systems for PGRs for crop applications. The table contains information about the nanoparticle or nanocarrier systems, nanoparticles characterization, target organism and biological effects.

	Nanoparticle/Microspheres/polymer	PGRs	Characterization	Target plant	Biological effects	Author
Carrier systems for plant growth regulators	Cs/alginate and Cs/tripolyphosphate nanoparticles	**GA_3(Gibberellin)**	Spherical nanoparticles, nanoparticles of alginate/Cs with average size of 450nm, zeta potential of -29 mV, and Cs/tripolyphosphate with 195 nm, zeta potential of -27 mV. Sustained release of the PGR	***Phaseolus vulgaris***	The effects depend on the concentration. Increase of plant growth and of the content of photosynthetic pigments	Pereira et al. 2017b
	Cs/polyglutamic acid nanoparticles	**GA_3**	Spherical nanoparticles with average size of 117 nm, zeta potential of -29 mV. Sustained release of the PGR	***Phaseolus vulgaris***	Increase of seed germination and root development	Pereira et al. 2017a
	GA3-Cs conjugate	**GA_3**	Conjugate with 60% w/w modification degree forCs and good solubility in water at pH 6.Sustained release of the PGR.	***No evaluation***		Liu et al 2013
	Cs microparticles	**IAA and NAA (Auxins)**	Sphericalmicroparticles with average size of 20 and 100 μm for IAA and NAA, respectively. Sustained release of the PGRs.	***No evaluation***		Fan et al. 2012
	Cs nanoparticles	**NAA (Auxin)**	Authors demonstrated the chemical interaction between O-naphthylacetylhormone with Cs. Sustained release of the PGR.	***No evaluation***		Tao et al. 2012
	Cs microspheres	**D-31 analogue (Brassinosteroids)**	Microspheres with average size of 790-1490 μm. Sustained release of the PGR.	***No evaluation***		Quiñones et al. 2010
	Mesoporous silica nanoparticles	**ABA**	Smart system with average size of 20 nm. The nanoparticles containing	***Arabidopsis thaliana***	Reduction of drought stress. Reduction of	Sun et al. 2014

			gatekeepers though gluthathione. Sustained release of the PGR.		leaf stomatal aperture and reduction of water loss	
	Cs nanoparticles	***S*-nitroso-MSA(NO donor)**	Average size of 39 nm, zeta potential of -18 mV. Sustained NO release.	***Zea mays***	Protection against salt stress	Oliveira et al. 2016
	Csmicroparticles	**SA**	Spherical particles with average size of 2μm. Sustained release of the PGR.	***Lactuca sativa***	Enhancement of root growth and expression of defense proteins	Martinez-Saldaña et al. 2018
	Mesoporous silica/Gold core nanoparticles	**2,4-D (Auxin)**	Mesoporous nanostructures rangingfrom 40 to 60 nm, Au core between 10-15 nm.	***Linumusitatis simum***	Biotechnological application in plant cell culture. Increase of ploidy numbers, embryogenesis.	Kokina et al. 2017
nanoparticles systems with plant growth effects	Cs-cooper	**No hormone**	Nanoparticles with average size 326 nm and zeta potential of 22.1 mV. Release profile of cooper from Cs.	***Zea mays***	Growth effects as increase of height, steam diameter, root length, root number, chlorophyll content and increase of production. Additional effect, defense responses against *Curvularia leaf spot*	Choudhary et al. 2017
	Cs-cooper nanoparticles	**No hormone**	Nanoparticles with average size of 374 nm and zeta potential of + 22.6 mV	***Zea mays***	In seeds, treatments increase the α-amylase and protease enzymes and total pro protein content in seeds with	Saharan et al. 2016

					the decrease of starch and protein.	
	Cs-cooper nanoparticles	**No hormone**	Nanoparticles with average size of 88.21 nm and zeta potential of -29 mV.	***Eleusinecoracana***	Increase plant development and production. Increase of defense enzymes. Suppression of Blast disease after seed and foliar treatment.	Sathiyabama and Manikandan 2018
	Zinc nanoparticles coated with phycomolecules	**No hormone**	Spherical nanoparticles with average size 0f 2 - 54 nm.	***Gossypiumhirsutum***	Growth promotion effects with increase of biomass, levels of chlorophyll, carotenoids and soluble proteins.	Venkatachalam et al. 2017
	Silver-Cs nanoparticles	**No hormone**	Nanoparticles with average size of 59 nm and zeta potential of + 24 mV.	***Cicerarietinum***	Seeds treatments increase the seed germination, seedlings length fresh and dry weight. Increase of α and β-amylase, ascorbate peroxidase, peroxidase, catalase activity and chlorophyll content	Anusuya and Banu 2016
	Cs	**No hormone**	Cs nanoparticles with differentaverage sizes (420, 750 and 970 nm).	***Coffeacanephora***	Increase of the chlorophyll content, nutrient uptake and plantgrowth,	Nguyen Van et al. 2013

					regardless the particle size.	
	Cs	**No hormone**	Nanoparticles with average size of 100 nm.	***Hordeumvulgare***	Increase of leaf area and grain production. Protection against drought stress	Behboudi et al. 2018
	Cs	**No hormone**	Spherical nanoparticles with average size of 80-180 nm.	***Cammeliasinensis***	Improvement of plant innate immune response (induction of defense-related genes,antioxidant enzymes phenolic production).	Chandra et al. 2015
	Cs	**No hormone**	Nanoparticles with average size of 143 nm and zeta potential of 55.7 mV	***Triticumaestivum***	Increase of leaf gas exchange parameters and grain protein, iron and zinc contents.	(Xue et al. 2018)
	Cs	**Nitrogen, phosphorus and potassium**	Nanoparticles with average size o 330 – 580 nm)	***Triticumaestivum***	Improve plant development and increase of harvest, crop and mobilization index.	(Abdel-Aziz et al. 2016)

IAA constitutes the widespread natural auxin in plants, however, there are different synthetic auxins such as 2,4-D or NAA, which are used as phytohormones to promote auxin-mediated processes but also as herbicides at higher doses in which auxins inhibit growth and trigger plant death (Enders and Strader, 2015). The development of Cs-based particlesusing glutaraldehyde as a crosslinkerfor the controlled IAA and NAAdelivery has been performed by Fan et al.(2012). These particles efficiently encapsulated around 60% of auxins and released the bioactive by a super Case-II transport diffusion mechanism.The NAArelease from NAA-Cs derivative synthetized by protecting amino groups of Cs with phthalic anhydride and then mixed with 1-naphthylacetyl chloride has been studied(Tao et al. 2012). NAA release depended on pH and temperature. AtpH 12.0 and 60 °C a sustained release of the hormone for 55 days*in vitro*could be achieved. However, their biological actions in plants have not yetbeen assayed. Alternatively, non-polymeric silica nanoparticles for the control delivery of NAA with proved biology action in the modulation of root development in wheat plants where described (Ao et al 2013).

The phytohormone SA triggers local and systemic defense responses against pathogen attack. The synthesis of SA-Cs particles with different doses of immobilized SA has been recently described (Martin-Saldaña et al 2018). SA1%-Cs particles showed very low cytotoxicity and enhanced root growth in *Lactuca sativa* seedlings. In accordance with the activation of SA signaling *in planta,* SA-Cs particles promoted the induction of NPR1 and PR2 protein levels required for plant defense responses. However, the action of SA-Cs nanosystem in the protection of plants against environmental stress has not been assayed yet.

The NO donor *S*-nitroso-mercaptosuccinic acid (*S*-nitroso-MSA) was also encapsulated in Cs for the generation of nanoparticles (Oliveira et al. 2016). The sustained release of

S-nitroso-MSAfrom Cs nanoparticles enhanced the efficiency of NO donor compared with non-encapsulated compound. *S*-nitroso-MSA-Cs nanoparticles developed a better performance in the protection of *Zea mays* plants against salt stress, evidenced by higher levels of chlorophyll and reduced inhibition of root and shoot growth. Hence, the nanoparticles of Cs for the controlled delivery of GA, SA and S-nitroso-MSA as bioestimulants/growth promoter and stress protection agentswith proved action in plants constitutepromising biomaterials for agricultural applications (Pereira et al 2017, Oliveira et al 2016, Martin-Saldaña et al 2018).

5.4. Potential of polymeric nanoparticles to be used as PGRs

Unlike nanocarrier systems whose activity is related to the active ingredient, some nanoparticles have direct effects on plants, being able to alter their metabolism.Little is known about the phytotoxic or stimulate effects of polymeric nanoparticles systems without an ingredient active on plants, however, some studies have shown that these nanomaterials are capable of being uptake by vegetables and transported, as well uptake by vegetal cells (Valletta et al. 2014; Nguyen et al. 2016; Prasad et al. 2017a).

The evaluations of these nanoparticles are of extreme importance mainly for agricultural application, in which these systems cannot cause phytotoxic effects. Studies conducted by Nakasato et al. (2017) demonstrated the effects of solid lipid and Cs nanoparticles on the germination of *Zea mays*, *Brassica rapa* and *Pisumsativum* species. An inhibition of germination was observed depending on the concentration of the Cs nanoparticles while the lipid nanoparticles did not cause phytotoxic effects.

Novelty, Chandra et al. (2015) demonstrated thatCs nanoparticles function as an immune modulator. The foliar treatment with these nanoparticles increased the activity of the immune system inducing the production of defense enzymes and increasing the upregulation of genes linked to the vegetal immune system in *Cammelia sinensis*. In *Triticuma estivum*, the treatment with Cs nanoparticles favored the leaf gas exchange and the grains showed increase of protein and micronutrient levels (Xue et al. 2018). Cs nanoparticles have shown fungicidal properties, mainly when bound to copper as metal ion (Saharan et al. 2016).For example, *Zea mays* seeds treated with copper-containing Cs nanoparticles resulted in physiological and biochemical changes including, high germination rates and increase of dry mass and activation of amylases and proteases enzymes (Saharan et al. 2016).

Choudhary et al. (2017) demonstrated that seeds treated with copper-containing Cs nanoparticles increased antioxidant enzyme activities such as superoxide dismutase, peroxidase and polyphenol oxidase and phenylalanine ammonia-lyase showed protection against the fungus *Curvularia* leaf spot. In addition to these effects, a promoter stimulus was observed in the development of the *Zea mays* plants treated with the Cs nanoparticles.This is an important point of view for products that aim at a more sustainable agriculture, since systems that promote plant development resulting in seed vigor, plant development and increased production can also improve the immunological activity of the plant and resistance against pathogens(Anusuya and Banu 2016; Venkatachalam et al. 2017; Choudhary et al. 2017; Sathiyabama and Manikandan 2018).

Also, as example of hybrid systems, many metal nanoparticle systems have potential as a plant growth promoter. Silver nanoparticles may have bactericidal or fungicidal action but they have phytotoxic effects. However, in order to maintain their biological activity and reduce phytotoxic effects one of the alternatives is the coating of these nanomaterials with polymers. These systems have great applications, many of which are capable of increasing the uptake of plant nutrients, the immune system, alleviating adverse effects under stress conditions, as well as increasing production in the field (there is a lack in the development of nanocarrier systems for PGRs, and these systems may have many applications such as flowering, fruiting and fruit ripening). However, for the use of these systems to be safe, it is important to have a broad spectrum of evaluation in different plants, as well as in other living organisms.In summary, the use of polymeric nanocarrier systems for PGRs such as the coating of metal nanoparticles by polymers has a great potential for use in field applications and the stimulation of plant growth. These systems can be used for different stages, such as in the treatment of seeds or during plant development resulting in greater plant development, increase of production and quality of agricultural products.

5.5. Uptake, transport and distribution of nanoparticles

PGR-loaded system can be extracellularly sensed or incorporated from the extracellular matrix to be metabolized or secreted. Nanoparticles are highly effective as carrier systems for phytohormone; they can confer high stability and enhanced and prolonged delivery to the target cell (Revell 2006). Thus, currently, controlled release systems are improving stability, efficiency and minimizing the applied doses of traditional PGR in plants. Some PGR are unstable and have quick metabolism limiting their application *in planta*. This is the case of two unstable synthetic analogues of brassinosteroids D121 and S7 that have been recently reported to be loaded in polyethylene glycol micelles to extend their stability (Pérez Quiñones et al. 2018). However, the underlying mechanisms of adhesion and transportation onto plant tissues have not yetbeen explored.

On the other hand, bioengineered polymeric nanoparticlesexert positive or negative effects on growth and development by regulating endogenous PGR homeostasis and metabolism in the plant (Vankova et al. 2017).The exposition of rice shootstomesoporous carbon nanoparticlesshowed negative effects on growth and increased the concentrations of the phytohormones brassinosteroids, indolepropionic acid, and dihydrozeatinriboside(Hao et al. 2018).

In general, physico-chemical properties of PGR-loaded nanoparticles can affect its behavior including adherence, penetration and circulation nalong the plant. Once applied on plant, PGRs-loaded polymeric nanoparticles could also have different adherence depending on target plant cells. Apparently, size and shapeare key parameters for penetration into plant tissues (Pérez-de-Luque 2017). Adhesion to the plant cell mainly takes place in the epidermic tissues of different organs such as leaves, shoots or roots (Khutoryanskiy 2011). Nanoparticles might enter into the plant by apoplastic or symplastic routes. Nanocapsules containing herbicides penetrate through cuticles and tissues, allowing the slow and constant release of the active substances (Pérez-de-Luque and Rubiales 2009).

Once internalized onto the plant, the PGR-loaded nanoparticles can modulate growth, development and morphogenesis depending on the level, distribution and sensing. Thus, in addition to get knowledge on the action of PGR-loaded nanoparticles on physiology processes it is important to investigate how theycan be sensed, taken up by cell and then, transported to other plant tissues or organs(Wang et al. 2016). Recently, a hormone-like activity has been assigned to Cs/TPP nanoparticles(Asgari-Targhi et al. 2018; Fu et al. 2018). This work highlights the positive effect of Cs nanoparticles for growth and *in vitro* micropropagation of *Capsicum annuum* plants. However, the authors do not describe by which mechanism nanoparticles are absorbed in these *in vitr* *o*plants. In Arabidopsis, the lysin motif (LysM)-containing chitin elicitor receptor kinase 1 (CERK1) has been shown to sense chitin and Cs(Petutschnig et al. 2010). CERK1 has an extracellular LysM motif–containing a transmembrane and intracellular kinase domains that is critical in chitin perception (Wan et al. 2008).Recently, a new model involving LysM-containing receptor complexes has been proposed (Gubaeva et al. 2018). Chitooligomers could also be generated from Cs nanoparticles in the apoplastic space by extracellular chitinases(Grover 2012). In this sense, the wall-associated protein W5G2U8 has found to be a chitooligomer receptor in wheat plants(Liu et al. 2018).

The plant cell wall is composed primarily of polysaccharides of which cellulose is the major component (Stavolone and Lionetti 2017). Being the pore diameter ofthe cell wallfrom 5 to 50 nm it can exclude the entry of any larger polymeric nanoparticle into cells. Cellulosemicrofibrils separation may be affected by a number of factors including cross-linking polysaccharides, spacing by interpenetrating polysaccharides and even by the water content in the cell wall.The water has a substantial effect on separations of cellulose microfibrils(Thompson 2007). Thus, application of nanoparticles might modify microfibril depositions by modifying water availability in the cell wall, consequently modifying its entry onto plant cells. Hence, Cs-loaded nanoparticles might physically affect cell wall architecture facilitating their incorporation into the cell.The size of Cs nanoparticle has been found to affect its viscosity, adding other level of regulation to the incorporation of nanoparticles into plant cells(Chattopadhyay and Inamdar 2010).

In the case of leaves, stomata are other possible point for nanoparticle penetration (Corredor et al. 2009).It could be investigated whether the passage of the particle through it does not imply its functional deregulation. Cytological observation and complementary approaches measuring stomatal conductance and infrared thermographic can be used to investigate stomatal opening/closure in response to nanoparticles application (Allègre et al. 2007). Since interactions between the plant cell wall and membrane trafficking have been reported(Kim and Brandizzi 2014; Ebine and Ueda 2015),endocytic pathways involved in the cellular uptake of nanoparticles might represent other level of specific regulation in plant cell. Although most of current studies have revealed that PGR-loaded nanoparticles are highly promising for agriculture use, there is still much to learn about how nanoparticles are incorporated, translocated and distributed in vascular plants.Studies on the mechanism of interactions between plant cells and polymeric nanoparticles must be performed.

5.6. Gap, obstacles and challenges

There are many challenges for the use of PGR in nanocarrier systems. First isto increase the interest of the scientific community in the development of controlled release systems for PGRs or even nanoparticles with potential plant growth promotion effects. Second is the evaluation and the comprehension of these systems, to understand how different polymers, methodologies of preparation and the characteristics of the nanomaterials couldaffect the biological effect of the PGR, and how these different systems interact with specific targetsof the plant. Finally, evaluation using different biological models and their responses, whether in relation to their activity or even possible toxic in order tounderstand the applicability of these systems. The understanding of how these systems act in different plant tissues and at the cellular level related to the physico-chemical characteristics of these nanomaterials will help in the development of more efficient and intelligent systems for the immobilization/control delivery of the different types of PGRs.

5.7. Conclusions and remarks

PGRs have great potential for agricultural application. The use of nanocarrier systems associated with PGRs and nanoparticles that have a promoter effect or even relieve vegetable stress are of great interest for field application. These systems can be applied in different stages of plant development in order to increase field performance. However, it is still necessary to develop and exploit the applications of these PGRs associated with polymer nanoparticles which can not only potentiate the production, but also increase the plant immune system and alleviate adverse environmental conditions. In short, the association of PGRs with polymer systems constitutes a promising strategy in order to increase productivity without causing major damage to the environment.

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