Energ. Ecol. Environ. (2018) 3(3):137–148
https://doi.org/10.1007/s40974-018-0090-2

ORIGINAL ARTICLE

State of the art of polymeric nanoparticles as carrier systems with agricultural applications: a minireview

Mônica Pascoli[1] · Patrícia Juliana Lopes-Oliveira[2] · Leonardo Fernandes Fraceto[1] · Amedea Barozzi Seabra[3] · Halley Caixeta Oliveira[2]

[1] Laboratory of Environmental Nanotechnology, Institute of Science and Technology of Sorocaba (ICTS), São Paulo State University (UNESP), Avenida Três de Março, 511, Sorocaba, SP CEP 18087-180, Brazil
[2] Department of Animal and Plant Biology, Universidade Estadual de Londrina (UEL), Rodovia Celso Garcia Cid, km 380, Londrina, PR CEP 86057-970, Brazil
[3] Center for Natural and Human Sciences, Universidade Federal do ABC (UFABC), Av. dos Estados 5001, Santo André, SP CEP 09210-580, Brazil

Received: 24 November 2017 / Revised: 19 March 2018 / Accepted: 28 March 2018 / Published online: 9 April 2018

Abstract Polymeric nanoparticles have been developed as carrier systems for agrochemicals aimed at pest control and increased crop yields. This minireview summarizes the recent progress and challenges in the design and application of polymeric nanoparticles loaded with herbicides, fungicides, insecticides and plant growth regulators. The many advantages of these nanoagrochemicals are discussed including: (1) the availability, biocompatibility and biodegradability of many polymers, (2) the decreased impact on non-target organisms, (3) the protection of the active compounds against degradation, (4) their increased solubility, (5) modified release, and (6) an improved efficacy of the active ingredients. We also discuss the major gaps and obstacles in this area, such as the large-scale production of these systems and the need for investigations of the toxicity to non-target organisms.

Keywords Agrochemicals · Nanotechnology · Pesticide · Plant growth regulator · Polymers

Abbreviations

γ-PGA	Poly(γ-glutamic acid)
GA_3	Gibberellic acid
LC_{50}	Lethal concentration 50%
NO	Nitric oxide
PCA	Poly(citric acid)
PCL	Poly(epsilon-caprolactone)
PEG	Polyethylene glycol
PGA	Polyglutamic acid or polyglycolides
PGR	Plant growth regulators
PLGA	Poly(lactide-*co*-glycolides)
PVA	Poly(vinyl alcohol)
S-Nitroso-MSA	*S*-Nitroso-mercaptosuccinic acid

✉ Halley Caixeta Oliveira
halley@uel.br

1 Introduction

Agriculture has a vital worldwide importance as one of the greatest providers of food resources as well as one of the main drivers of the economy of many countries. Agribusiness is estimated to be a US$ 2.9 trillion industry in global investment by 2030 (World Bank 2013). The use of agrochemicals, such as fertilizers, pesticides and plant growth regulators, plays a pivotal role for the maximization of agricultural production facing innumerable challenges including, weeds, phytopathogenic fungi, herbivorous insects and other pests, and abiotic stresses driven by climate changes (Sekhon 2014; Mishra et al. 2017). The worldwide consumption of agrochemicals is huge with approximately 2.5 million tons of pesticides consumed per year (FAO 2012). However, the indiscriminate use of agrochemicals can contribute to environmental contamination, leading to hazards to non-target organisms (humans, soil microbiota, native fauna and flora) and to pest resistance (Tilman et al. 2002; Oliveira et al. 2014).

Nanotechnology is the control and restructuring of matter at the dimension of roughly 1–100 nm, where new phenomena enable new applications (Lindquist et al. 2010). According to the European Union law, the acceptable definition of "nanomaterial" is: "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm" (European Commission 2011). Nanoparticles are particles that are unique in their size, with large surface area which enables unique features that are absent in bulk materials or larger particles (Lee et al. 2015). In this sense, some authors consider that the nanoparticle definition is not necessarily limited on the exact particle size, but rather on whether nanoparticles have different properties compared with non-nanoparticles of the same material (Lee et al. 2015).

Nanotechnology has an enormous potential to benefit agriculture, making the agro industry more eco-friendly with its current annual growth rate of 25% (US$ 1.08 billion) (Sabourin 2015). In addition to nanoparticles, nanomaterials that can be used in agriculture include nanoclays, nanogels, and carbon nanotubes (Choudhary et al. 2017; Sadeghi et al. 2017). Nanoclays are layered mineral silicates nanomaterials that provide well-dispersed and interactive surfaces upon exfoliation (Hetzer and Kee 2008). Nanogels are highly crosslinked polymers at nanosize scale able to retain a significant amount of water and biological fluids, proving a reservoir to hold biomolecules and active drugs (Sonzogni et al. 2018). Carbon nanotubes are materials composed of carbon atoms linked in hexagonal shapes, with each carbon atom covalently bonded to three other carbon atom (a cylinder fabricated of rolled up grapheme sheet) (Eatemadi et al. 2014).

In general, nanoparticles are developed with the goal of providing a controlled release system for agrochemicals, improving the solubility of products or protecting the bioactive compounds against premature degradation (Shang et al. 2013; Perez and Francois 2016). Nanoparticles may, therefore, increase the efficacy of the agrochemicals, offering better results with lower doses and number of applications, as well as they may decrease the risk of environmental contamination and the toxicity to humans and other non-target organisms (Saharan et al. 2015; Chhipa 2017; Choudhary et al. 2017).

1.1 Polymeric nanoparticles

Different types of nanoparticles can be used in agricultural systems, such as silica, metallic, metal oxide, lipid and polymeric nanoparticles (Sabir et al. 2014), for carrying many classes of agrochemicals, including herbicides, insecticides, fungicides, acaricides, fertilizers and plant growth regulators (Grillo et al. 2016; Mishra et al. 2017).

Polymeric nanoparticles are considered the simplest form of soft-materials for drug delivery applications owing to their facile synthesis and wide applicability across all aspects of the field (Bobo et al. 2016). Polymeric nanoparticles, which are the subject of this minireview, have been one of the most important nanostructured systems used for the controlled release of pharmaceuticals with satisfactory results (Mallakpour and Behranvand 2016; Pelegrino and Seabra 2017; Seabra and Durán 2017). These nanoproducts are particularly suitable as carriers for agrochemicals due to their biocompatibility, biodegradability and low toxicity (Grillo et al. 2012). Polymeric nanoparticles have the ability to efficiently encapsulate agrochemicals, which protects them from the surrounding environment and controls their release (Kashyap et al. 2015; Perez and Francois 2016).

Considering environmental aspects, green nanotechnology can contribute desalination treatment, wastewater remediation, generation of alternative clean energy, combat of drug-resistant pathogens, sustainable chemical synthetic routes, and sustainable agriculture and food production (Villasenor and Ríos 2018). Nanotechnology might permit the precise control of manufacturing and novel nanotechnological materials have been available for improving farming sustainable practices (Villasenor and Ríos 2018). In agricultural applications, the sustained release of active chemicals from the nanomaterial might avoid temporal overdose, decreasing the levels of chemicals and reducing the input and waste, in an economical feasible manner. Furthermore, the synthesis of nanomaterials under environmental-friendly conditions can reduce the environmental impact of the products and toxicity (Sanchez-Mendieta and Vilchis-Nestor 2012). To this end, "green" approaches to synthesize nanomaterials are desirable, such as the absence of organic solvents and hazardous chemicals and avoid the uses of high energy input. Green approaches include the use of non-toxic chemicals, biodegradable, biocompatible and natural materials, among other environmental-friendly tools (Seabra and Durán 2015).

Polymeric nanoparticles can be synthesized using different types of biodegradable synthetic or natural polymers. As green reagent, it should be highlighted polymeric polysaccharides, which have been extensively employed in bio-applications due to their low cost, biocompatibility, and biodegradability (Kollarigowda 2017). In agriculture, chitosan and pectin are natural polymers that are widely used for the development of nanoparticles (Kheiri et al. 2016; Sun et al. 2014; Chauhan et al. 2017; Gabriel Paulraj et al. 2017; Sandhya et al. 2017).

Chitosan is obtained by the *N*-deacetylation of chitin, a natural and ubiquitous polysaccharide, obtained from the exoskeleton of crustaceans, insects, and fungi (Elieh-Ali-Komi and Hamblin, 2016). Chitosan is the most popular biopolymer used in drug delivery due to its low cost, biodegradability, biocompatibility, antimicrobial and insecticidal activities, high permeability, high drug-loading ability, and muco-adhesive properties (Kashyap et al. 2015; Khan et al. 2017; Pelegrino et al. 2017c). In agricultural applications, chitosan has emerged as one of the promising natural polymers for successful delivery of agrochemicals, enhancing the stability of the loaded active drug (Kashyap et al. 2015). In addition, chitosan has the ability to chelate inorganic compounds for controlled delivery in plants (Saharan et al. 2015). Encapsulation of agrochemicals in chitosan-based nanoparticles has the following advantages: (1) the ability of chitosan to absorb to plant surfaces prolongs the contact time between the agrochemical and the plant absorptive surface (e.g., epidermis of stems or leaves), (2) chitosan itself plays an important role in plant defense against pathogens, (3) chitosan might stimulate plant development, inducing biotic and abiotic stress responses making plants more tolerant to pathogens (Kashyap et al. 2015; Malerba and Cerana 2016; Khan et al. 2017). Similar to chitosan, the polysaccharide pectin is biocompatible and biodegradable and extensively employed in the food industry, biomedical applications and agriculture (Kollarigowda 2017). Pectin is suitable for agricultural applications because it is a constituent of plant cell walls. It is rich in 1,4-linked 2-D-galactosyluronic acid residues (Luo and Wang 2014; Santos and Grenha 2015) (Fig. 1).

Among the synthetic polymers used for nanoagroparticle formulations, we can cite poly (lactide-*co*-glycolides) (PLGA), poly(epsilon-caprolactone) (PCL), polyglutamic acid or polyglycolides (PGA), poly (vinyl alcohol) (PVA), poly(citric acid) (PCA), and polyethylene glycol (PEG) (Yang et al. 2009; Forim et al. 2013; Pradhan et al. 2013; Memarizadeh et al. 2014; Pereira et al. 2014; Oliveira et al. 2015a; González et al. 2016; Mondal et al. 2017; Pasquoto-Stigliani et al. 2017; Tong et al. 2017). Figure 2 represents the structure of the most important polymers used for the preparation of polymeric nanoparticles.

Polymeric nanoparticles can be synthesized from preexisting polymers or by the direct polymerization of monomers (Rao and Geckeler 2011). They are classified as nanocapsules or nanospheres according to their physical composition (Fig. 2). While nanocapsules have a polymeric vesicular structure and internal oil phase, nanospheres present a solid matricial organization with the polymeric chains (Soppimath et al. 2001).

When designing a nanostructured delivery system, the control of the particle size, charge, chemical surface, and other physico-chemical properties is necessary to allow the desirable penetration, solubility and release pattern of the bioactive from the polymeric nanoparticle, in order to target the selected action to a specific site at a particular time (Bennett and Littlejohn 2014). The properties of many polymers, such as great availability, bioactive compound protection, biocompatibility and easy biodegradability in

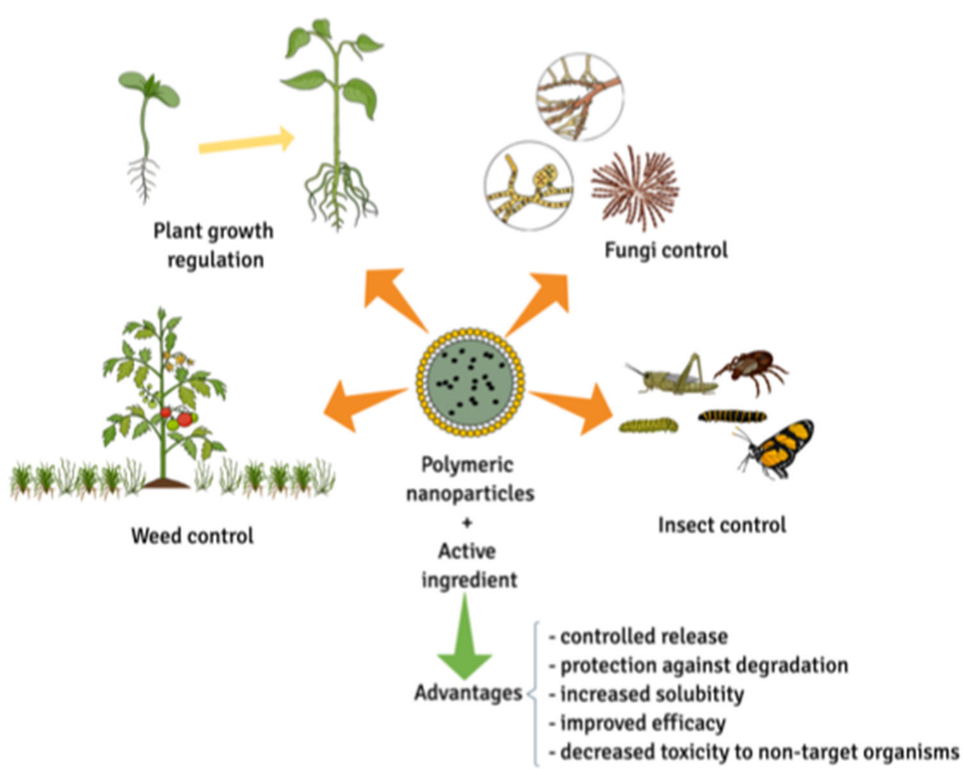

Fig. 1 Major agriculture applications of polymeric nanoparticles

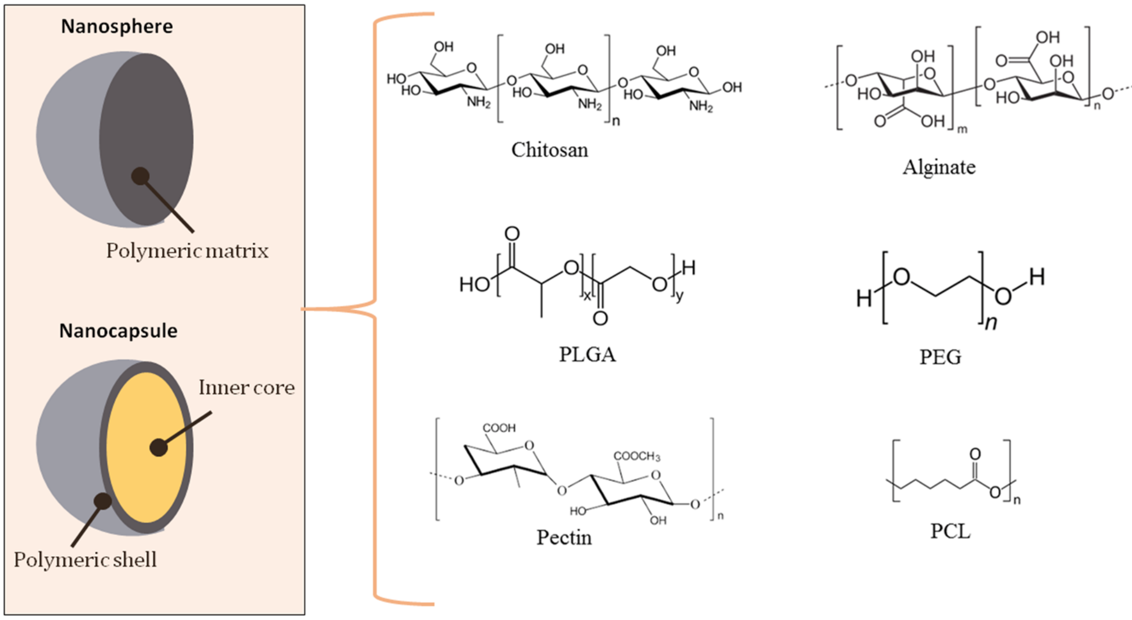

Fig. 2 Schematic representations of typical polymeric nanoparticles used in agriculture applications. The figure showed the nanospheres (matrix system) and nanocapsules (reservoir systems), as well as the chemical structure of some important polymers used to prepare carriers systems to agri-applications

non-toxic metabolites, allow them to be used in the development of nanocarriers for different types of agrochemicals. Here, we will discuss the recent progress and challenges in the design and uses of polymeric nanoparticles as carrier systems for herbicides, fungicides, insecticides and plant growth regulators (Table 1).

2 Methodology

This article is a minireview of polymeric nanoparticles as carrier systems in agricultural applications. Papers on polymeric nanoparticles in agriculture, active compound protection, efficacy against weeds, insects and fungi, plant growth regulation, phytotoxicity, genotoxicity, and cytotoxicity were identified through a comprehensive survey in the electronic databases PubMed, ISI and Science Direct. The search was performed in the period from 2001 to 2017. The following terms were used to identify the documents that composed this review: polymeric nanoparticles, nanocapsules, agriculture, herbicides, insecticides, fungicides, plant growth regulators, natural insecticides, neem oil, biological effects and toxicity study. Also, all terms were used in English and as Booleans descriptors it has been used AND or OR.

3 Polymeric nanoherbicides

Herbicides are applied in agricultural fields for the control of weeds, which compete with crops for water, light and nutrients. Despite the importance of herbicides in maximizing crop yield, the indiscriminate use of these compounds has been associated with the contamination of water resources and intoxication of non-target organisms, with deleterious effects to the environment and human health (Albuquerque et al. 2016). With the aim of reducing the environmental impacts of herbicides, polymeric nanoparticles have been successfully developed as efficient carrier systems for some of these agrochemicals. This section highlights the recent progress in the use of polymeric nanoparticles containing herbicides.

Reports have shown that nanoherbicides have many advantages over conventional formulations. For example, the nanoencapsulation of diuron, imazapic + imazapyr, paraquat and triazines resulted in a slower release profile of the herbicides, which could significantly help to minimize herbicide losses and environmental contamination (Grillo et al. 2012, 2014; Pereira et al. 2014; Yu et al. 2015; Maruyama et al. 2016). Moreover, atrazine-loaded PCL nanoparticles, metsulfuron methyl-loaded pectin nanoparticles, and chitosan nanoparticles co-loaded with imazapic and imazapyr were less toxic to non-target organisms than the respective non-nanoherbicides, as demonstrated through in vitro toxicity assays using *Allium cepa* and/or

Table 1 Summary of the studies describing the development of nanoparticles loaded with agrochemicals and their major biological effects

Class	Active ingredient(s)	Nanomaterials	Major biological effects[a]	Active compound doses	Reference
Herbicide	Ametryn, atrazine or simazine	PCL nanocapsules	Reduced genotoxicity in *Allium cepa* chromosome aberration and human blood Comet assays	*A. cepa* assay: 100 mg mL^{-1}; Comet assay: 100 mg mL^{-1}	Grillo et al. (2012)
Herbicide	Atrazine	PCL nanocapsules and nanospheres	Reduced genotoxicity in *Allium cepa* assays. Effective pre-emergent control of *Brassica* sp. (seedling emergence). No effects on the growth of non-target *Zea mays*	*A. cepa* assay: 0.7–56.7 μg mL^{-1}; Phytotoxicity: 2.5 kg ha^{-1}	Pereira et al. (2014)
Herbicide	Paraquat	Chitosan/ tripolyphosphate nanoparticles	Reduced genotoxicity in *Allium cepa* assays. Effective post-emergent control of *Brassica* sp. and *Zea mays* (visual symptoms). Reduced cytotoxicity in mammalian cell viability assays	*A. cepa* assay: 0.38 mg mg mL^{-1}; Cytotoxicity: 0.0048 and 0.12 mg mL^{-1}; Phytotoxicity: 2 kg ha^{-1}	Grillo et al. (2014)
Herbicide	Atrazine	PCL nanocapsules	Increased post-emergent herbicidal activity against *Brassica juncea* (visual symptoms, induction of oxidative stress, inhibition of growth and photosynthesis). No persistent deleterious effects on non-target *Zea mays*	Phytotoxicity: 2 kg ha^{-1}	Oliveira et al. (2015a, b)
Herbicide	Diuron	Carboxymethyl chitosan nanoparticles	Increased pre-emergent herbicidal activity against *Echinochloa crusgalli* (growth analysis). No effect on the growth of non-target *Zea mays*	Phytotoxicity: 3 kg ha^{-1}	Yu et al. (2015)
Herbicide	Imazapic and imazapyr (co-loaded)	Alginate/chitosan and chitosan/ tripolyphosphate nanoparticles	Reduced genotoxicity in *Allium cepa* assays. Reduced toxicity to mammalian cells. Herbicidal activity against *Bidens pilosa* was sustained	*A. cepa* assay: 0.5 mg mL^{-1}; Cytotoxicity assay: 0.1 mg mL^{-1}; Phytotoxicity: 400 g ha^{-1}	Maruyama et al. (2016)
Herbicide	Metsulfuron methyl	Pectin nanocapsules	Increased post-emergent herbicidal activity against *Chenopodium album* (visual symptoms). Reduced toxicity to mammalian cells	Phytotoxicity: 0.05 g L^{-1}; Cytotoxicity: 2 and 4 μg mL^{-1}	Kumar et al. (2017a, b)
Herbicide	Metolachlor	PCL and PLGA nanoparticles	The nanoparticles internalized the roots of rice, decreased seed and roots size of *Oryza sativa* and *Digitaria sanguinalis*	Cytotoxicity: 10–400 mg L^{-1}	Tong et al. (2017)
Fungicide	Chitosan	Chitosan nanoparticles	Increased chitosan antifungal activity against *Fusarium graminearum*	Antifungal activity: 100–5000 ppm	Kheiri et al. (2016)
Fungicide	Carbendazim and Tebuconazole	Polycaprolactone nanocapsules	Decreased phytotoxicity in *Phaseolus vulgaris* and cytotoxicity in animal cells	Phytotoxicity: 0.05–0.7 g kg^{-1}; Cytotoxicity: 31.25–250 μg mL^{-1}	Campos et al. (2015)
Fungicide	Azomethine	PCL nanoparticles	Increased antifungal activity and yields of plants in the treatment against *Sclerotium rolfsii*, *Rhizoctonia bataticola* and *Rhizoctonia solani*	Antifungal activity: 3.9–250 μg mL^{-1}	Mondal et al. (2017)
Fungicide	Carbendazim	Chitosan/pectin nanoparticles	Increased antifungal activity against *Fusarium oxysporum* and *Aspergillus parasiticus*. Increased germination and root length of the maize, cucumber and tomato seeds	Antifungal activity: 0.5 and 1 ppm; Phytotoxicity: 0.5–1 mg L^{-1}	Sandhya et al. (2017)
Fungicide	Hexaconazole	Chitosan nanoparticles	Increased effectiveness against *Rhizoctonia solani*. Lower toxicity to non-target cell lines.	Antifungal activity: 0.1–1 ppm; Cytotoxicity: 10 and 20 ppm	Chauhan et al. (2017)
Insecticide	Garlic essential oil	PEG nanoparticles	Increased insecticidal activity against *Tribolium castaneum*	Insecticidal activity: 2000–8000 mg kg^{-1}	Yang et al. (2009)

Table 1 continued

Class	Active ingredient(s)	Nanomaterials	Major biological effects[a]	Active compound doses	Reference
Insecticide	Neem essential oil	PCL nanocapsules	Increased toxicity against *Plutella xylostella*	Insecticidal activity: 4000 and 5000 mg kg^{-1}	Forim et al. (2013)
Insecticide	Acephate	PEG nanoparticles	Increased insecticidal activity against *Sitophilus oryzae*. Decreased oral toxicity in mice and human fibroblast cell lines	Insecticidal activity: 180–300 ppm; Toxicity in mice: 0.5–2 g kg^{-1}; Cytotoxicity: 25–200 ppm	Pradhan et al. (2013)
Insecticide	Imidacloprid	PCA and PEG nanoparticles	Increased mortality of *Glyphodes pyloalis* larvae and decreased LC_{50} in non-target organisms	Insecticidal activity: 25–300 ppm	Memarizadeh et al. (2014)
Insecticide	Methomyl	Chitosan nanocapsules	Increased efficacy against armyworms	Insecticidal activity: 50 and 100 ppm	Sun et al. (2014)
Insecticide	Geranium and bergamot essential oils	PEG and chitosan nanoparticles	Increased acute and residual larvicidal activity on *Culex pipiens*	Insecticidal activity: 1–20 mg cm^{-2}	González et al. (2016)
Insecticide	Neem essential oil	Chitosan nanoparticles	Decreased *Helicoverpa armigera* feeding, larval activity, and pupal weight	Insecticidal activity: 0.1–0.3%	Gabriel Paulraj et al. (2017)
PGR	*S*-Nitroso-mercaptosuccinic acid	Chitosan/tripolyphosphate nanoparticles	Improved protection of *Zea mays* plants against salt stress	Plant protection: 50 and 100 μM	Oliveira et al. (2016)
PGR	Gibberellic acid	Alginate/chitosan and chitosan/tripolyphosphate nanoparticles	Increased leaf area and photosynthetic pigment content of *Phaseolus vulgaris*	Plant growth: 0.012–0.05%	Pereira et al. (2017a)
PGR	Gibberellic acid	γ-Polyglutamic acid/chitosan nanoparticles	Enhancement of germination rate, root development and leaf area in *Phaseolus vulgaris*	Plant growth: 0.07–2.1 μg/g of seeds	Pereira et al. (2017b)

[a]In comparison with the non-nano bioactive compound

mammalian cell lines (Grillo et al. 2014; Pereira et al. 2014; Maruyama et al. 2016; Kumar et al. 2017a, b).

At the same time, the nanoencapsulation of herbicides maintained or even increased the herbicidal activity against target plants, whereas deleterious effects on the growth of non-target plants were not observed. A notable example is the atrazine-loaded PCL nanocapsule. The analysis of parameters related to growth, photosynthesis and oxidative stress of mustard (*Brassica juncea*) plants showed an increased post-emergent herbicidal activity of this nanoherbicide compared to the conventional atrazine (Oliveira et al. 2015a). Thus, the atrazine-loaded PCL nanocapsule allowed for a ten-fold reduction of the atrazine application dose without compromising the biological activity of the herbicide, which would reduce the amount of highly contaminating atrazine in the environment (Oliveira et al. 2015a). In addition, atrazine-loaded PCL nanocapsules did not persistently affect the physiological parameters of maize (*Zea mays*) plants, thereby having no effects on the growth of this non-target crop (Oliveira et al. 2015b). An efficient pre-emergent herbicidal activity of atrazine-containing PCL nanocapsules was also reported, which was associated with the reduced soil sorption and greater bioavailability of the nanoherbicide compared with the conventional atrazine (Pereira et al. 2014).

Recently, PEG and PLGA nanoparticles were synthesized as a carrier system for metolachlor, which improved the water solubility of this hydrophobic herbicide (Tong et al. 2017). The metolachlor-loaded nanoparticles were internalized into root cells. Thus, this nanoformulation increased the metolachlor utilization by rice (*Oryza sativa*) and hairy crabgrass (*Digitaria sanguinalis*) plants, resulting in a higher herbicidal activity than the conventional herbicide and a lower toxicity to non-target human cells (Tong et al. 2017).

4 Polymeric nanofungicides

Fungal diseases are recognized as a general threat to plants, the environment and food health and are responsible for extensive losses in agriculture affecting levels as high as 90% of the crop production (Chen and Yada 2011). Fungicides are natural or synthetic compounds often used in agriculture to prevent the penetration or development of pathogenic fungi in plants and also to control fungal diseases. Nanotechnology can increase the efficiency of fungicides by lowering the amounts of the chemicals required as well as by reducing their environmental impact (Campos et al. 2014). This section describes important papers based on the use of polymeric nanoparticles (particularly chitosan-based nanomaterials, due to chitosan intrinsic antimicrobial activity) containing fungicides.

Polymers have unique properties that make them particularly promising for the development of nanofungicides. In addition to their suitability for the design of nanocarriers for fungicides, some polymers per se have fungicidal activity, such as chitosan (Kashyap et al. 2015). Interestingly, chitosan nanoparticles have higher antifungal activity against *Fusarium graminearum* than non-nano chitosan, as demonstrated in tests of inhibition of radial mycelial growth (Kheiri et al. 2016). Chitosan was also used to synthesize hexaconazole-loaded nanoparticles. In comparison with the free bioactive compound, the nanoformulation was much more effective in controlling *Rhizoctonia solani*, whereas the toxicity toward non-target cell lines was reduced (Chauhan et al. 2017). In addition to a reduced cytotoxicity, the nanoencapsulation of carbendazim and tebuconazole into PCL nanocapsules was associated with a lower phytotoxicity against common bean (*Phaseolus vulgaris*) compared to the conventional fungicides (Campos et al. 2015).

In a recent study, chitosan-pectin nanoparticles containing carbendazim showed higher antifungal activity against *Fusarium oxysporum* and *Aspergillus parasiticus* than the pure fungicide (Sandhya et al. 2017). Moreover, these carbendazim-loaded nanoparticles interfered less in seed germination and root growth in assays with maize, cucumber (*Cucumis sativus*), and tomato (*Lycopersicum esculentum*) (Sandhya et al. 2017). In another recent study, azomethine was encapsulated into PEG nanoparticles (Mondal et al. 2017). The in vitro inhibitory activities against *Sclerotium rolfsii*, *Rhizoctonia bataticola* and *Rhizoctonia solani* were significantly increased by azomethine nanoencapsulation. Moreover, in vivo tests using mung bean (*Vigna radiata*) plants contaminated with the fungi demonstrated that the application of the nanofungicide resulted in lower plant mortality and higher plant growth compared to conventional azomethine (Mondal et al. 2017).

5 Polymeric nanoinsecticides

Insects are one of the main contributors to crop damage, reducing productivity due to losses in the field and during food storage. Thus, insecticides are widely applied to control unwanted insects and to guarantee crop quality (Spencer et al. 2014). However, insecticides are often highly toxic to non-target organisms, which emphasizes the importance of developing modified release systems to improve their effectiveness toward target insects (Gogos et al. 2012). This section describes the recent progress in the design and uses of polymeric nanoparticles containing insecticides. According to the literature, PEG and PCL are the most employed polymers for this goal.

Poly(citric acid) (PCA) and PEG were used to load imidacloprid into nanoparticles. Imidacloprid nanoencapsulation was associated with increased mortality of *Glyphodes pyloalis* larvae and a reduced LC_{50} compared to the same parameters of the free insecticide (Memarizadeh et al. 2014). Similarly, Sun et al. (2014) showed that the efficacy of methomyl-loaded chitosan nanocapsules against armyworm larvae was higher than that of the conventional insecticide.

Pradhan et al. (2013) also used PEG to nanoencapsulate acephate and found excellent insecticidal activity against *Sitophilus oryzae*, as indicated by the high mortality of the larvae, pupae malformation and inhibition of acetylcolinesterase activity. In addition, acephate nanoencapsulation decreased acute oral toxicity in a mouse model and in vitro cytotoxicity in a human fibroblast cell line (Pradhan et al. 2013).

Given the adverse impacts of synthetic insecticides, there are intense efforts to replace them with natural products. Botanical insecticides (i.e., insecticidal biomolecules derived from plants) have advantages such as low toxicity to non-target species, low residual activity and low development of resistance by target organisms. However, the rapid degradation by sunlight and low persistence in the environment can hamper crop protection. Nanotechnology can, thus, provide a solution to allow for more intensive use of botanical insecticides (Oliveira et al. 2014).

For example, PEG nanoparticles have been developed as carrier systems for the essential oil of garlic (*Allium sativum*) (Yang et al. 2009). These authors have reported increased insecticidal activity of this nanoformulation against the red flour beetle (*Tribolium castaneum*) over the non-nano garlic essential oil. PEG and chitosan were also used to synthesize polymeric nanoparticles loaded with geranium (*Geranium maculatum*) and bergamot (*Citrus bergamia*) essential oils, which showed high acute and residual larvicidal activity on mosquitoes (*Culex pipiens*) (González et al. 2016).

Neem essential oil is one of the most applied botanical insecticides due to its wide range of effectiveness against insects and low toxicity to humans and non-target organisms. It is extracted from *Azadirachta indica* and is used in agriculture to control insects by acting as an insecticide and repellent (Campos et al. 2016). Chitosan nanoparticles containing PONNEEM® were associated with decreased *Helicoverpa armigera* feeding and larval activity and pupal weight (Gabriel Paulraj et al. 2017). Similarly, neem oil-loaded PCL nanocapsules were more effective against *Plutella xylostella* in comparison with the conventional essential oil (Forim et al. 2013).

Despite these promising results for the use of these nanomaterials, there is still a need for extensive evaluation of potential toxicity to non-target organisms, including plants. Pasquoto-Stigliani et al. (2017) have reported that exposure of maize plants to PCL nanocapsules containing oleic acid and neem oil resulted in a decrease in CO_2 assimilation and stomatal conductance. These nanoformulations also showed increased toxicity against *Allium cepa* and mammalian cell lines. On the other hand, these increased adverse effects were not induced by PCL nanocapsules containing only neem oil.

The macrocyclic lactone, emamectin benzoate, is employed for the control of insect pests on a variety of crops worldwide (Ishaaya et al. 2002). In order to increase the photostability of emamectin benzoate, the active ingredient was conjugated with polyacrylate nanoparticles by emulsion polymerization. The resultant nanoparticles protected the decomposition of the pesticide (Shang et al. 2013).

6 Polymeric nanoparticles containing plant growth regulators

Plant growth regulators (PGR) are a class of natural or synthetic compounds that behave as plant hormones or affect the plant hormonal balance. PGRs usually act at low concentrations and are applied in agriculture to modulate plant growth and development, to increase crop yield, to ameliorate the quality of agricultural products, and to induce the plant response to stresses (Rademacher 2015). Auxins, cytokinins, gibberellins, ethylene, abscisic acid, brassinosteroids and nitric oxide (NO) are examples of PGRs (Nambara 2013).

One of the main pitfalls of PGR application in agriculture is the rapid degradation of these compounds under conditions of light and temperature found in the field, resulting in the loss of biological activity (Kah and Hofmann 2014). Moreover, most PGRs may be phytotoxic when applied at high concentrations, which makes the development of controlled release systems for PGRs highly desirable (Campos et al. 2014). Nevertheless, only a few studies have reported the development of modified release systems for PGRs, which include brassinosteroid-loaded chitosan microspheres (Quiñones et al. 2010), *O*-naphthylacetyl chitosan (Tao et al. 2012) and gibberellin-chitosan conjugates (Liu et al. 2013). The conjugation of gibberellic acid (GA_3) with chitosan also led to an increase in the bioactive solubility and to a protection against photo and thermal degradation (Liu et al. 2013).

There is a recent pioneering study regarding the use of polymeric nanoparticles as carrier systems for PGRs (Oliveira et al. 2016). In this study, chitosan/tripolyphosphate nanoparticles containing the NO donor *S*-nitroso-mercaptosuccinic acid (*S*-nitroso-MSA) were more efficient than the non-encapsulated NO donor in the protection of maize plants against salt stress (Oliveira et al. 2016). The improved bioactivity of NO was associated with the sustained release of this molecule by the polymeric nanoparticles (Oliveira et al. 2016). NO donors have been successfully encapsulated into chitosan/tripolyphosphate nanoparticles for anti-cancer (Pelegrino et al. 2017a), antibacterial (Cardozo et al. 2014) and anti-parasitic activities (Seabra et al. 2015), to enhance NO delivery to human skin (Pelegrino et al. 2017b), and more recently to protect plants from abiotic stress (Oliveira et al. 2016). The NO donor molecule has strong electrostatic interactions with the chitosan backbone leading to a high encapsulation efficiency of this molecule (Pelegrino et al. 2017c), allowing for the versatile application of NO-containing chitosan nanoparticles in several biomedical and agricultural applications.

In a recent study, Pereira et al. (2017a) described the development of alginate/chitosan and chitosan/tripolyphosphate nanoparticles as controlled release systems for GA_3. In assays of biological activity using common bean plants, GA_3-loaded alginate/chitosan nanoparticles were more effective in increasing leaf area and the levels of photosynthetic pigments than the free hormone or the chitosan/tripolyphosphate nanoparticles (Pereira et al. 2017a). In another approach, GA_3-loaded γ-PGA/chitosan nanoparticles also presented a sustained release of the plant hormone (Pereira et al. 2017b). In addition, the nanoencapsulation of GA_3 into γ-PGA/chitosan nanoparticles resulted in an enhancement of the biological activity of GA_3 toward common bean plants, inducing higher germination rates, root development and leaf area than the free hormone. As described in this section, chitosan is the most employed polymer for preparation of PGR-containing nanoparticles.

7 Conclusions, challenges and perspectives

There are an increasing number of scientific publications based on the synthesis, characterization and application of nanoparticles (particularly polymeric nanocarriers) in agriculture. Overall, the encapsulation of agrochemicals promoted a sustained and site-specific release of the bioactive compound and enhanced the desired effect.

Polymeric nanocarriers are able to control the delivery of active ingredients to plants and reduce excess run-off (Chhipa 2017). In fact, encapsulation of agrochemicals into polymeric nanoparticles might reduce undesirable toxic effects on non-target organisms and enhance the thermal and photochemical stability of the encapsulated active ingredient (Cicek and Nadaroglu 2015). In this sense, the use of agrochemical-containing nanoparticles is expected to decrease the required dosage for efficacy and to ensure a sustained drug delivery (Nair et al. 2010; Kashyap et al. 2015; Oliveira et al. 2016). The use of nanotechnology in agriculture aims to maximize agriculture output (crop yields) and simultaneous minimizing input (such as herbicides, pesticides, and fertilizers).

What are the main challenges to propose the realistic use of nanomaterials in agriculture? Although significant progress has been made at laboratory settings in the investigation of potential uses of polymeric nanoparticles carrying agrochemicals, compared to biomedical and pharmaceutical applications, the use of nanoparticles in agriculture is still in its infancy. To enhance the research employed in the field the following important issues must be addressed:

1. The nanotoxicity of the agrochemical-containing polymeric nanoparticles requires further investigation to determine the environmentally relevant concentrations of the nanoparticles, their toxicity in acute and long-term exposure to plants, the environment, animals and humans (Sadeghi et al. 2017). In this regard, there are investigations attempting to determine the possible toxicity of nanoparticles in agriculture, their environmental behavior, phytotoxicity in plants and soil biota in order to establish the safe use of these promising materials (Iavicoli et al. 2017; Kah 2015; Tripathi et al. 2017).
2. The characterization of the potential risks resulting from the interactions of nanoparticles with biological systems must be reviewed in detail. Although there has been important progress on the knowledge about the uptake, distribution and bioavailability of polymeric nanoparticles in plants, there are still some important gaps to be overcome (Pérez-de-Luque 2017).
3. Although polymeric nanoparticles are mainly composed of biodegradable and biocompatible materials (such as chitosan and pectin), the nanoparticle internalization in plant cells and their accumulation require further investigation. Nanoparticles can be easily internalized, translocated, and accumulated in different plant cell compartments, leading to diverse and/or unexpected responses. Nanoparticles that accumulate in plant organs may act as sinks, or they may be translocated to other (undesirable) parts of the plant, in a similar fashion reported for animals.
4. Importantly, physical and chemical properties of engineered polymeric nanoparticles are dependent on a range of variables, including: size distribution, surface chemistry, surface charge, morphology, reactivity, concentration, hydrophobicity, target organism, composition of test media, and aggregation state. The behavior of the polymeric nanoparticle depends on the medium in which the nanoparticle is applied. Chemical and physical soil and/or water parameters (such as pH, temperature, and ionic strength) might interfere to the behavior of polymeric nanoparticles containing agrochemicals.
5. Another important issue is the cost and industrial production of nanoparticles. In this regard, chitosan-based polymeric nanoparticles are an ideal material for this task, owing to their low cost, biocompatibility and biodegradability.
6. For the appropriate transfer from laboratory setting to realistic agricultural applications, important studies on the production scheduling of the nanoparticles, their long-term stability and effects need to be addressed.
7. Finally, consumers are still unfamiliar with nanotechnology and they can distrust agrochemical-containing nanoparticles similar to the situation with transgenic crops. Hence, these gaps in knowledge need to be filled so that polymer nanoparticle technology can jump from the laboratory bench to field applications (Pérez-de-Luque 2017).

As reported in this minireview, the use of polymer nanoparticles in agriculture is recent but is steadily increasing, which demands the need for the evaluation of the toxicity and phytotoxicity of these materials. It is important to note that insecticide nanoformulations in particular are evaluated only on target organisms and rarely on non-target organisms, mainly in plants. We hope that this minireview inspires new avenues in this exciting field.

Acknowledgements The authors would like to thank Coordination for the Improvement of Higher Education Personnel (PJLO) and São Paulo State Science Foundation (ABS, 2016/10347-6; LFF, 2015/15617-9; MO, 2015/17120-4). The authors also thank Proof-Reading-Service for the English revision of the text.

Compliance with ethical standards

Conflict of interest On behalf of all author, the corresponding authors states that there is no conflict of interest.

References

Albuquerque AF, Ribeiro JS, Kummrow F, Nogueira AJ, Montagner CC, Umbuzeiro GA (2016) Pesticides in Brazilian freshwaters: a critical review. Environ Sci Process Impacts 18:779–787. https://doi.org/10.1039/c6em00268d

Bennett BL, Littlejohn L (2014) Review of new topical hemostatic dressings for combat casualty care. Mil Med 179:497–514. https://doi.org/10.7205/MILMED-D-13-00199

Bobo D, Robinson KJ, Islam J, Thurecht KJ, Corrie SR (2016) Nanoparticle-based medicines: a review of FDA-approved materials and clinical trials to date. Pharm Res 33:2373–2387. https://doi.org/10.1007/s11095-016-1958-5

Campos EVR, de Oliveira JL, Fraceto LF (2014) Applications of controlled release systems for fungicides, herbicides, acaricides, nutrients, and plant growth hormones: a review. Adv Sci Eng Med 6:373–387. https://doi.org/10.1166/asem.2014.1538

Campos EVR, de Oliveira JL, da Silva CMG, Pascoli M, Pasquoto T, Lima R et al (2015) Polymeric and solid lipid nanoparticles for sustained release of carbendazim and tebuconazole in agricultural applications. Sci Rep. https://doi.org/10.1038/srep13809

Campos EVR, de Oliveira JL, Pascoli M, de Lima R, Fraceto LF (2016) Neem oil and crop protection: from now to the future. Front Plant Sci. https://doi.org/10.3389/fpls.2016.01494

Cardozo VF, Lancheros CA, Narciso AM, Valereto EC, Kobayashi RK, Seabra AB, Nakazato G (2014) Evaluation of antibacterial activity of nitric oxide-releasing polymeric particles against *Staphylococcus aureus* and *Escherichia coli* from bovine mastitis. Int J Pharm 473:20–29. https://doi.org/10.1016/j.ijpharm.2014.06.051

Chauhan N, Dilbaghi N, Gopal M, Kumar R, Kim KH, Kumar S (2017) Development of chitosan nanocapsules for the controlled release of hexaconazole. Int J Biol Macromol 97:616–624. https://doi.org/10.1016/j.ijbiomac.2016.12.059

Chen H, Yada R (2011) Nanotechnologies in agriculture: new tools for sustainable development. Trends Food Sci Technol 22:585–594. https://doi.org/10.1016/j.tifs.2011.09.004

Chhipa H (2017) Nanofertilizers and nanopesticides for agriculture. Environ Chem Lett 15:15–22. https://doi.org/10.1007/s10311-016-0600-4

Choudhary RC, Kumaraswamy RV, Kumari S, Sharma SS, Pal A, Raliya R, Biswas P, Saharan V (2017) Cu-chitosan nanoparticle boost defense responses and plant growth in maize (*Zea mays* L.). Sci Rep. https://doi.org/10.1038/s41598-017-08571-0

Cicek S, Nadaroglu H (2015) The use of nanotechnology in the agriculture. Adv Nano Res 3:207–223. https://doi.org/10.12989/anr.2015.3.4.207

Eatemadi A, Daraee H, Karimkhanloo H, Kouhi M, Zarghami N, Akbarzadeh A, Abasi M, Hanifehpour Y, Joo SW (2014) Carbon nanotubes: properties, synthesis, purification, and medical applications. Nanoscale Res Lett 9:393. https://doi.org/10.1186/1556-276X-9-393

EC-European Commission (2011) Commission Recommendation of 18 October 2011 on the definition of nanomaterial. Off J Eur Union 275:38

Elieh-Ali-Komi D, Hamblin MR (2016) Chitin and chitosan: production and application of versatile biomedical nanomaterials. Int J Adv Res 4:411

FAO (2012) Food and Agriculture Organization of the United Nations. FAOSTAT. www.faostat.fao.org. Accessed 6 Oct 2017

Forim MR, Costa ES, da Silva MF, Das GF, Fernandes JB, Mondego JM, BoiçaJunior AL (2013) Development of a new method to prepare nano-/microparticles loaded with extracts of *Azadirachta indica*, their characterization and use in controlling *Plutella xylostella*. J Agric Food Chem 61:9131–9139. https://doi.org/10.1021/jf403187y

Gabriel Paulraj M, Ignacimuthu S, Gandhi MR, Shajahan A, Ganesan P, Packiam SM et al (2017) Comparative studies of tripolyphosphate and glutaraldehyde cross-linked chitosan-botanical pesticide nanoparticles and their agricultural applications. Int J Biol Macromol 104:1813–1819. https://doi.org/10.1016/j.ijbiomac.2017.06.043

Gogos A, Knauer K, Bucheli TD (2012) Nanomaterials in plant protection and fertilization: current state, foreseen applications, and research priorities. J Agric Food Chem 60:9781–9792. https://doi.org/10.1021/jf302154y

González JW, Yeguerman C, Marcovecchio D, Delrieux C, Ferrero A, Band BF (2016) Evaluation of sublethal effects of polymer-based essential oils nanoformulation on the german cockroach. Ecotoxicol Environ Saf 130:11–18. https://doi.org/10.1016/j.ecoenv.2016.03.045

Grillo R, dos Santos NZP, Maruyama CR, Rosa AH, de Lima R, Fraceto LF (2012) Poly(epsilon-caprolactone) nanocapsules as carrier systems for herbicides: physico-chemical characterization and genotoxicity evaluation. J Hazard Mater 231:1–9. https://doi.org/10.1016/j.jhazmat.2012.06.019

Grillo R, Pereira AES, Nishisaka CS, de Lima R, Oehlke K, Greiner R, Fraceto LF (2014) Chitosan/tripolyphosphate nanoparticles loaded with paraquat herbicide: an environmentally safer alternative for weed control. J Hazard Mater 278:163–171. https://doi.org/10.1016/j.jhazmat.2014.05.079

Grillo R, Abhilash PC, Fraceto LF (2016) Nanotechnology applied to bio-encapsulation of pesticides. J Nanosci Nanotechnol 16:1231–1234. https://doi.org/10.1166/jnn.2016.12332

Hetzer M, Kee DD (2008) Wood/polymer/nanoclay composites, environmentally friendly sustainable technology: a review. Chem Eng Res Des 86:1083–1093. https://doi.org/10.1016/j.cherd.2008.05.003

Iavicoli I, Leso V, Beezhold DH, Shvedova AA (2017) Nanotechnology in agriculture: opportunities, toxicological implications, and occupational risks. Toxicol Appl Pharmacol 329:96–111. https://doi.org/10.1016/j.taap.2017.05.025

Ishaaya I, Kontsedalov S, Horowitz AR (2002) Emamectin, a novel insecticide for controlling field crop pests. Pest Manag Sci 58:1091–1095. https://doi.org/10.1002/ps.535

Kah M (2015) Nanopesticides and nanofertilizers: emerging contaminants or opportunities for risk mitigation? Front Chem 3:64. https://doi.org/10.3389/fchem.2015.00064

Kah M, Hofmann T (2014) Nanopesticide research: current trends and future priorities. Environ Int 63:224–235. https://doi.org/10.1016/j.envint.2013.11.015

Kashyap PL, Xiang X, Heiden P (2015) Chitosan nanoparticle based delivery systems for sustainable agriculture. Int J Biol Macromol 77:36–51. https://doi.org/10.1016/j.ijbiomac.2015.02.039

Khan FI, Rahman S, Queen A, Ahamad S, Ali S, Kim J et al (2017) Implications of molecular diversity of chitin and its derivatives. Appl Microbiol Biotechnol 101:3513–3536. https://doi.org/10.1007/s00253-017-8229-1

Kheiri A, Moosawi Jorf SA, Malihipour A, Saremi H, Nikkhah M (2016) Application of chitosan and chitosan nanoparticles for the control of Fusarium head blight of wheat (*Fusarium graminearum*) in vitro and greenhouse. Int J Biol Macromol 93:1261–1272. https://doi.org/10.1016/j.ijbiomac.2016.09.072

Kollarigowda RH (2017) Recent view on pectin-based polysaccharide nanoscience and their biological applications. Nano LIFE. https://doi.org/10.1142/S1793984417300023

Kumar S, Bhanjana G, Sharma A, Dilbaghi N, Sidhu MC, Kim KH (2017a) Development of nanoformulation approaches for the control of weeds. Sci Total Environ 586:1272–1278

Kumar S, Kumar D, Dilbaghi N (2017b) Preparation, characterization, and bio-efficacy evaluation of controlled release carbendazim-loaded polymeric nanoparticles. Environ Sci Pollut Res 24:926–937. https://doi.org/10.1007/s11356-016-7774-y

Lee BK, Yun YH, Park K (2015) Smart Nanoparticles for drug delivery: boundaries and opportunities. Chem Eng Sci 125:158–164. https://doi.org/10.1016/j.ces.2014.06.042

Lindquist EL, Mosher-Howe KN, Liu X (2010) Nanotechnology. What is it good for? (Absolutely everything): a problem definition approach. Rev Policy Res 27:255–271. https://doi.org/10.1111/j.1541-1338.2010.00441.x

Liu Y, Sun Y, He S, Zhu Y, Ao M, Li J, Cao Y (2013) Synthesis and characterization of gibberellin–chitosan conjugate for controlled-release applications. Int J Biol Macromol 57:213–217. https://doi.org/10.1016/j.ijbiomac.2013.03.024

Luo Y, Wang Q (2014) Recent development of chitosan-based polyelectrolyte complexes with natural polysaccharides for drug delivery. Int J Biol Macromol 64:353–367. https://doi.org/10.1016/j.ijbiomac.2013.12.017

Malerba M, Cerana R (2016) Chitosan effects on plant systems. Int J Mol Sci 17:996. https://doi.org/10.3390/ijms17070996

Mallakpour S, Behranvand V (2016) Polymeric nanoparticles: recent development in synthesis and application. Express Polym Lett 10:895–913. https://doi.org/10.3144/expresspolymlett.2016.84

Maruyama CR, Guilger M, Pascoli M, Bileshy-José N, Abhilash PC, Fraceto LF, de Lima R (2016) Nanoparticles based on chitosan as carriers for the combined herbicides imazapic and imazapyr. Sci Rep 6:19768. https://doi.org/10.1038/srep19768

Memarizadeh N, Ghadamyari M, Adeli M, Talebi K (2014) Preparation, characterization and efficiency of nanoencapsulated imidacloprid under laboratory conditions. Ecotoxicol Environ Saf 107:77–83. https://doi.org/10.1016/j.ecoenv.2014.05.009

Mishra S, Keswani C, Abhilash PC, Fraceto LF, Singh HB (2017) Integrated approach of agri-nanotechnology: challenges and future trends. Front Plant Sci. https://doi.org/10.3389/fpls.2017.00471

Mondal P, Kumar R, Gogoi R (2017) Azomethine based nano-chemicals: development, in vitro and in vivo fungicidal evaluation against *Sclerotium rolfsii*, *Rhizoctonia bataticola* and *Rhizoctonia solani*. Bioorg Chem 70:153–162. https://doi.org/10.1016/j.bioorg.2016.12.006

Nair R, Varghese SN, Nair BG, Maekawa T, Yoshida Y, Kumar DS (2010) Nanoparticulate material delivery to plants. Plant Sci 179:154–163. https://doi.org/10.1016/j.plantsci.2010.04.012

Nambara E (2013) Plant hormones. In: Hughes SM (ed) Brenner's encyclopedia of genetics. Academic Press, San Diego, pp 346–348. https://doi.org/10.1016/B978-0-12-374984-0.01170-0

Oliveira JL, Campos EVR, Bakshi M, Abilash PC, Fraceto LF (2014) Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: prospects and promises. Biotechnol Adv 32:1550–1561. https://doi.org/10.1016/j.biotechadv.2014.10.010

Oliveira HC, Stolf-Moreira R, Martinez CBR, Grillo R, de Jesus MB, Fraceto LF (2015a) Nanoencapsulation enhances the post-emergence herbicidal activity of atrazine against mustard plants. PLoS ONE 10(7):e0132971. https://doi.org/10.1371/journal.pone.0132971

Oliveira HC, Stolf-Moreira R, Martinez CBR, Sousa GFM, Grillo R, de Jesus MB, Fraceto LF (2015b) Evaluation of the side effects of poly(epsilon-caprolactone) nanocapsules containing atrazine toward maize plants. Front Chem 3:61. https://doi.org/10.3389/fchem.2015.00061

Oliveira HC, Gomes BCR, Pelegrino MT, Seabra AB (2016) Nitric oxide-releasing chitosan nanoparticles alleviate the effects of salt stress in maize plants. Nitric Oxide 61:10–19. https://doi.org/10.1016/j.niox.2016.09.010

Pasquoto-Stigliani T, Campos EVR, Oliveira JL, Silva CMG, Bilesky-José N, Guilger M et al (2017) Nanocapsules containing neem (*Azadirachta indica*) oil: development, characterization and toxicity evaluation. Sci Rep. https://doi.org/10.1038/s41598-017-06092-4

Pelegrino TM, Seabra AB (2017) Chitosan-based nanomaterials for skin regeneration. AIMS Med Sci 4:352–381. https://doi.org/10.3934/medsci.2017.3.352

Pelegrino MT, Silva LC, Watashi CM, Haddad PS, Rodrigues T, Seabra AB (2017a) Nitric oxide-releasing nanoparticles: synthesis, characterization and cytotoxicity to tumorigenic cells. J Nanopart Res 19:57. https://doi.org/10.1007/s11051-017-3747-4

Pelegrino MT, Weller RB, Bernardes JS, Seabra AB (2017b) Chitosan nanoparticles for nitric oxide delivery in human skin. Med Chem Commun 8:713–719. https://doi.org/10.1039/C6MD00502K

Pelegrino MT, Araújo DR, Seabra AB (2017c) *S*-Nitrosoglutathione-containing chitosan nanoparticles dispersed in Pluronic F-127 hydrogel: potential uses in topical applications. J Drug Deliv Sci Technol. https://doi.org/10.1016/j.jddst.2017.10.016

Pereira AE, Grillo R, Mello NF, Rosa AH, Fraceto LF (2014) Application of poly(epsilon-caprolactone) nanoparticles containing atrazine herbicide as an alternative technique to control weeds and reduce damage to the environment. J Hazard Mater 268:207–215. https://doi.org/10.1016/j.jhazmat.2014.01.025

Pereira AES, Silva PM, Oliveira JL, Oliveira HC, Fraceto LF (2017a) Chitosan nanoparticles as carrier systems for the plant growth hormone gibberellic acid. Colloids Surf B Biointerfaces 150:141–152. https://doi.org/10.1016/j.colsurfb.2016.11.027

Pereira AES, Sandoval-Herrera IE, Zavala-Betancourt SA, Oliveira HC, Ledezma-Pérez AS, Romero J, Fraceto LF (2017b) γ-Polyglutamic acid/chitosan nanoparticles for the plant growth regulator gibberellic acid: characterization and evaluation of biological activity. Carbohydr Polym 157:1862–1873. https://doi.org/10.1016/j.carbpol.2016.11.073

Perez JJ, Francois NJ (2016) Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers. Carbohydr Polym 148:134–142. https://doi.org/10.1016/j.carbpol.2016.04.054

Pérez-de-Luque A (2017) Interaction of nanomaterials with plants: What do we need for real applications in agriculture? Front Environ Sci 5:12. https://doi.org/10.3389/fenvs.2017.00012

Pradhan S, Roy I, Lodh G, Patra P, Choudhury SR, Samanta A et al (2013) Entomotoxicity and biosafety assessment of PEGylated acephate nanoparticles: a biologically safe alternative to neurotoxic pesticides. J Environ Sci Health Part B 48:559–569. https://doi.org/10.1080/03601234.2013.774891

Quiñones JP, García YC, Curiel H, Covas CP (2010) Microspheres of chitosan for controlled delivery of brassinosteroids with biological activity as agrochemicals. Carbohydr Polym 80:915–921. https://doi.org/10.1016/j.carbpol.2010.01.006

Rademacher W (2015) Plant growth regulators: backgrounds and uses in plant production. J Plant Growth Regul 34:845–872. https://doi.org/10.1007/s00344-015-9541-6

Rao JP, Geckeler KE (2011) Polymer nanoparticles: preparation techniques and size-control parameters. Prog Polym Sci 36:887–913. https://doi.org/10.1016/j.progpolymsci.2011.01.001

Sabir S, Arshad M, Chaudhari SK (2014) Zinc oxide nanoparticles for revolutionizing agriculture: synthesis and applications. Sci World J. https://doi.org/10.1155/2014/925494

Sabourin V (2015) Commercial opportunities and market demand for nanotechnologies in agribusiness sector. J Technol Manag Innov 10:40–51. https://doi.org/10.4067/S0718-27242015000100004

Sadeghi R, Rodriguez RJ, Yao Y, Kokini JL (2017) Advances in nanotechnology as they pertain to food and agriculture: benefits and risks. Annu Rev Food Sci Technol 8:467–492. https://doi.org/10.1146/annurev-food-041715-033338

Saharan V, Sharma G, Yadav M, Choudhary MK, Sharma SS, Pal A et al (2015) Synthesis and in vitro antifungal efficacy of Cu-chitosan nanoparticles against pathogenic fungi of tomato. Int J Biol Macromol 75:346–353. https://doi.org/10.1016/j.ijbiomac.2015.01.027

Sanchez-Mendieta V, Vilchis-Nestor A (2012) Green synthesis of noble metal (Au, Ag, Pt) nanoparticles, assisted by plantextracts.

In: Yen-Hsun S (ed) Noble metals. INTECH, Rijeka, pp 391–408. https://doi.org/10.5772/34335

Sandhya Kumar S, Kumar D, Dilbaghi N (2017) Preparation, characterization, and bio-efficacy evaluation of controlled release carbendazim-loaded polymeric nanoparticles. Environ Sci Pollut Res Int 24:926–937. https://doi.org/10.1007/s11356-016-7774-y

Santos MA, Grenha A (2015) Polysaccharide nanoparticles for protein and peptide delivery: exploring less-known materials. Adv Protein Chem Struct Biol 98:223–261. https://doi.org/10.1016/bs.apcsb.2014.11.003

Seabra AB, Durán N (2015) Nanotoxicology of metal oxide nanoparticles. Metals 5:934–975. https://doi.org/10.3390/met5020934

Seabra BA, Durán N (2017) Nanoparticulated nitric oxide donors and their biomedical applications. Mini Rev Med Chem 17:216–223. https://doi.org/10.2174/1389557516666160808124624

Seabra AB, Kitice NA, Pelegrino MT, Lancheros CAC, Yamauchi LM, Pinge-Filho P, Yamada-Ogatta SF (2015) Nitric oxide-releasing polymeric nanoparticles against *Trypanosoma cruzi*. J Phys Conf Ser 617:012020. https://doi.org/10.1088/1742-6596/617/1/012020

Sekhon B (2014) Nanotechnology in agri-food production: an overview. Nanotechnol Sci Appl. https://doi.org/10.2147/NSA.S39406

Shang Q, Shi Y, Zhang Y, Zheng T, Shi H (2013) Pesticide-conjugated polyacrylate nanoparticles: novel opportunities for improving the photostability of emamectin benzoate: pesticide-conjugated polyacrylate nanoparticles. Polym Adv Technol 24:137–143. https://doi.org/10.1002/pat.3060

Sonzogni AS, Passeggi MCG, Wedepohl S, Calderon M, Gugliotta LM, Gonzalez VDG, Minari RJ (2018) Thermoresponsive nanogels with film-forming ability. Polym Chem 9:1004–1011. https://doi.org/10.1039/c7py01798g

Soppimath KS, Aminabhavi TM, Kulkarni AR, Rudzinski WE (2001) Biodegradable polymeric nanoparticles as drug delivery devices. J Control Release 70:1–20. https://doi.org/10.1016/S0168-3659(00)00339-4

Spencer JL, Hughson SA, Levine E (2014) Insect resistance to crop rotation. In: Onstad DW (ed) Insect resistance management, 2nd edn. Academic Press, San Diego, pp 233–278. https://doi.org/10.1016/B978-0-12-396955-2.00007-2

Sun C, Shu K, Wang W, Ye Z, Liu T, Gao Y et al (2014) Encapsulation and controlled release of hydrophilic pesticide in shell cross-linked nanocapsules containing aqueous core. Int J Pharm 463:108–114. https://doi.org/10.1016/j.ijpharm.2013.12.050

Tao S, Pang R, Chen C, Ren X, Hu S (2012) Synthesis, characterization and slow release properties of *O*-naphthylacetyl chitosan. Carbohydr Polym 88:1189–1194. https://doi.org/10.1016/j.carbpol.2012.01.076

Tilman D, Cassman KG, Matson PA, Naylor R, Polasky S (2002) Agricultural sustainability and intensive production practices. Nature 418:671–677. https://doi.org/10.1038/nature01014

Tong Y, Wu Y, Zhao C, Xu Y, Lu J, Xiang S et al (2017) Polymeric nanoparticles as a metolachlor carrier: water-based formulation for hydrophobic pesticides and absorption by plants. J Agric Food Chem 65:7371–7378. https://doi.org/10.1021/acs.jafc.7b02197

Tripathi DK, Shweta Singh S, Singh S, Pandey R, Singh VP, Sharma NC, Prasad SM, Dubey NK, Chauhan DK (2017) An overview on manufactured nanoparticles in plants: uptake, translocation, accumulation and phytotoxicity. Plant Physiol Biochem 110:2–12. https://doi.org/10.1016/j.plaphy.2016.07.030

Villasenor MJ, Ríos A (2018) Nanomaterials for water cleaning and desalination, energy production, disinfection, agriculture and green chemistry. Environ Chem Lett 16:11–34. https://doi.org/10.1007/s10311-017-0656-9

World Bank (2013) Growing Africa: unlocking the potential of agribusiness. AFTFP/AFTAI. World Bank, Washington, DC

Yang FL, Li XG, Zhu F, Lei CL (2009) Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). J Agric Food Chem 57:10156–10162. https://doi.org/10.1021/jf9023118

Yu Z, Sun X, Song H, Wang W, Ye Z, Shi L, Ding K (2015) Glutathione-responsive carboxymethyl chitosan nanoparticles for controlled release of herbicides. Mater Sci Appl 6:591–604. https://doi.org/10.4236/msa.2015.66062