1. Introduction

Agriculture and deforestation are major factors in the acceleration of climate change, increasing environmental pollution, ongoing loss of biodiversity, and the rising consumption of resources [1]. Projections by the UN Food and Agriculture Organization (FAO) suggest that the world population will reach 10.0 billion people by 2050, which will further exacerbate these trends [2]. With the global food system alone generating 21-37% of global greenhouse gases, the use of agrochemicals in agriculture is contributing to the eco-toxicological impacts and it might reduce the amount and increase the effectiveness of agrochemicals administration in the field. This review article focuses on carriers with diameters below 1 μm, such as capsules, spheres, tubes and micelles that promote the sustained release of actives. Biopolymer nanocarriers represent a potentially environmentally friendly alternative due to their renewable origin and biodegradability, which prevents the formation of microplastics. The social aspects, economic potential, and success of commercialization of biopolymer based nanocarriers are influenced by the controversial nature of nanotechnology and depend on the use case. Nanotechnology’s enormous innovative power is only able to unfold its potential to limit the effects of climate change and to counteract current environmental developments if the perceived risks are understood and mitigated.
fertilizers [5,10].

Nanoparticle and microcarriers applied to agricultural purposes have been studied for the encapsulation of agrochemicals to develop more sustainable formulations that provide the sustained release of actives. Furthermore, there are many prospects in which nanotechnology can be applied to agriculture such as nanofertilizers [11], nanoherbicides [12], nanopesticides [13], and in plant nanobionics [14]. Nannencapsulation reduces the rate of dissolution of the agrochemical and allows slow, sustained release of actives, which are more efficiently taken up by the plant, and thus, reducing the biotic stress and the total amount necessary in comparison to bulk formulations. In addition, drugs, fertilizers, and actives in general are protected against oxidation, light, and other deteriorating conditions by (nano)encapsulation [13,15,16].

The “Third Agricultural Revolution”, also called “Green Revolution” [17,18], took place in the 1960s and generated an undeniable agricultural productivity growth through the change in traditional farming to a production model encompassing the use of high-yielding grain seed genotypes, chemical pesticides and fertilizers, novel farm management techniques and modern equipment and machinery. Increased food production has contributed to lower food prices globally [18], and has increased the crop yield-to-use ratio [17]. Nevertheless, the Green Revolution was accomplished in detriment of the environmental sustainability and generating several consequences such as soil degradation, chemical pollution, aquifer depletion, and soil salinity; in addition, profound socioeconomic impacts have also emerged from the accentuation, chemical pollution, aquifer depletion, and soil salinity; in addition, profound socioeconomic impacts have also emerged from the accentuation.

In this review, we highlight the application and economic potential of bio-based polymers to produce sustained release formulations (with diameters < 1 μm) of agrochemicals; in contrast, previous reviews [19–21] have focused on the sustained release itself rather than on the constituent materials of nanocarriers. Bio-based polymeric nanocarriers is an underexplored alternative for drug release in agriculture and offers promising solutions to the impacts to soil, the environment and human health by the unwary use of agrochemicals. In contrast to previous review articles about sustained release of active in agriculture we focus on biopolymer nanocarriers because even though encapsulation provides many advantages such as improved eco-safety and efficient uptake of actives, the material in which agrochemical actives are encapsulated are just as important due to environmental issues that might be caused by recalcitrant materials. Thereby, biopolymers represent environmentally friendly alternatives comprising several advantages commonly related to green materials as worldwide availability, renewability, biodegradability and low toxicity to the environment which enables the integration of these materials into the biogeochemical cycles.

In addition, the potential of nanotechnology in agriculture will be analyzed from a social perspective as well as the challenges that still need to be overcome in order for the technology to unfold its potential will be discussed, with a special attention on how biobased materials might influence this market potential.

2. Agrochemicals administration and nanotechnology

The use of agrochemicals is necessary due to the voluminous agricultural production. Agrochemicals are needed to protect plants from diseases, pests, or to deliver fertilizers and other compounds; in the last decades, a plethora of agrochemicals has been developed with different modes of action (Tables 1,2).

Most of the nanomaterials employed for agricultural purposes, to date, are inorganic nanoparticles, which have been applied as nanofertilizers to provide the necessary amount of micronutrients [25]. Moreover, nanoparticles can exhibit antifungal, herbicide and insecticide properties. During the last decades the agricultural production and crop yields have increased immensely in detriment of the condition of the soil, which has been depleted of many nutrients causing the impoverishment of soils [26]. Fertilizers are used to supply the necessary macro- and micronutrients, and to recover the organic fertility.

| Herbicides | MoA Groups | Target site | Chemical family | Selected examples |
|------------|------------|-------------|-----------------|-------------------|
| Photosynthesis Inhibitors | Photosystem II Inhibitors A | Triazines | Atrazine, Metribuzin |
| Photosynthesis Inhibitors | Photosystem II Inhibitors B | Nitriles | Bromoxynil |
| Photosynthesis Inhibitors | Photosystem II Inhibitors C | Amides | Propanil |
| Microtubule Inhibitors | Nicotianamines | Phenylureas | Linuron |
| Seedling Root Growth Inhibitors | Long-Chain Fatty Acid Inhibitors | Chloracetamide | Alachlor |
| Seedling Root Growth Inhibitors | Lipid Synthesis Inhibitor | Thiocarbamates | Etc |
| Seedling Root Growth Inhibitors | TIR1 Auxin receptors | Benzoic Acids | Dicamba |
| Growth Regulators | Synthetic Auxins | Phenoxo acids | 2,4-D |
| Amino Acid Synthesis Inhibitors | ALS Inhibitors | Sulfonylureas | Chlorosulfuron |
| Nitrogen Synthesis Inhibitors | Epp Synthase Inhibitor | Organophosphorous | Glyphosate |
| Nitrogen Metabolism Inhibitor | Glutamine Inhibitor | Organophosphorous | Glufosinate |
| Cell Membrane Disrupters | Photosystem I Electron Diverter | Bipyridulium | Paragquat, Diquat |
| Pigment Inhibitors | Deep Synthase Inhibitor | Pyrazole | Pynasulfotole |

Scientists have demonstrated the enhancement in soil recovery through the application of nanofertilizers [27]. Crop protection against pests relying on inorganic nanoparticles has also been investigated [28,29].

2.1. Fertilizers

Fertilizers are industrially produced or naturally occurring compounds applied to increase soil fertility by supplying nutrients essential to crop growth. The nutrients necessary for plant growth are categorized in macronutrients and micronutrients. Macronutrients are the major elements required: nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), and sulphur (S); typically, the most important in terms of macronutrients supplementation are first three elements which are referred to as NPK (Table 4) [26,30]. Micronutrients are trace elements essential for higher plants: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn) [26,30]. Macronutrients shortage in the soil is generally overcome with the use of a group of agrochemicals called NPK fertilizers such as urea, diammonium phosphate (DAP) and single superphosphate (SSP). Unfortunately, it is well known that most of the NPK fertilizers are significantly lost by run-off causing the water contamination or volatilization of gases such as NH3 to the atmosphere [19,31]. It is estimated that about 40–70% of nitrogen, 80–90% of phosphorus, and 50–70% of potassium of the applied fertilizers are lost to the environment and cannot be absorbed by the plant causing financial and environmental damage [25]. For instance, the application of nitrogen fertilizers is responsible for 80% of the increase in atmospheric N2O, a greenhouse gas that contributes to global warming [32].

2.2. Herbicides, insecticides, fungicides

Pest is a general term used to denote any living organism detrimental to crops, for instance, insects, rodents, birds, fungi, virus, weeds, nematodes and microorganisms [13,34]. Thereby, pesticides are synthetic and natural chemicals, biotic agents and microorganisms that reduce the impact caused by pests and/or avoid crop contamination by them [34].
control of harmful pests by using other pests, plants, or any other or has been suggested as an effective substitute for chemicals. It is the nanocarriers for agriculture. Biological control of pests or biopesticides has been extensively studied for the eradication of insect pest [37].

The three types of pesticides that dominate the market[35]: herbicides, insecticides, and fungicides, are most frequently used as cargo in Nanocarriers. Herbicides inhibit photosynthesis and are applied to 92–97% of acreage – 97% of acreage

Unfortunately, due to indiscriminate of pesticide application, pest resistance to pesticides is a troublesome global phenomenon. Indeed, hundreds of species of insects, plant pathogens, rodents, and weeds have become resistant to chemical pesticides [38].

Herbicides are used to reduce the vigour, reproductive capacity, density, or impact of weeds in agricultural or natural ecosystems [39]. Herbicides can be either chemical agents, synthetic or natural, biotic agents or microorganisms, the so-called bioherbicides. About half of all herbicides inhibit photosynthesis and are applied to 92–97 % of acreage planted with corn, cotton, soybeans, and citrus; three quarters of vegetable acreage; and two thirds of the acreage planted with apples and other fruit [35].

Insect pest management in agriculture is an imperative issue especially in Asia, Africa and Latin America due to the tropical climate [35]. The protection of crops against insect pest is achieved through the

Table 2
Selected examples of fungicides classified according to the mode of action (MoA) groups, target site and chemical family [23].

| Fungicides                          | MoA Groups                        | Target site                        | Chemical family                          | Selected examples                      |
|-------------------------------------|-----------------------------------|------------------------------------|------------------------------------------|----------------------------------------|
| Nucleic acids metabolism            | RNA polymerase I                  | Acetylalaines (PA)                 | Benalaxyl, kiralaxyl, mefenoxam          |
| Cytoskeleton and motor protein      | β-tubulin assembly in mitosis     | Benzimidazole (MBC)                | Benomyl, Carbendazim                      |
|                                    | SDHI                              | Thiophanates (MBC)                 | Thiophanate, thiophanate-methyl          |
|                                    |                                   | Pyridine carboxamides              | Boscalid                                  |
|                                    |                                   | phenyl-benzenamides                | Benomyl, mepronil                         |
|                                    |                                   | methoxy-acrylates                  | Anaxystrobin, exuaxstrobin               |
|                                    |                                   | Methoxy-carbanates                 | Pyraclostrobin, triclopyrcarib            |
|                                    | Energy Metabolism                 | Oximino-acetates                   | kresoxin-methyl, trifloxstrobin          |
|                                    | QoI                               | cyano-imidazole                    | cyanofamid                                |
|                                    |                                   | Picolinamides                      | fenpicoxam                                |
|                                    | Amino acids and Protein Synthesis | methionine biosynthesis            | Cypromitin, mepanipyrim, pyrimethanil     |
|                                    | Signal Transduction               | MAP/Hisidine-kinase in osmotic signal | Chlormequat, fadifosol                   |
|                                    | Lipid Metabolism / Membrane       | phospholipid biosynthesis, methyltransferase cell peroxidation | Edifenphos, iprosbenfos (IBP) pyrazophos |
|                                    | Sterol biosynthesis               | C14-demethylase                    | Chlorpyrifos, dithiothreitol              |
|                                    |                                | Δ^14-reductase and Δ^8=Δ^7-isomerase | Aldimorph, dodecophen, fenpropimorph tridemorph |
|                                    | Cell wall biosynthesis            | cellulose synthase                 | dimethoxymer flumor pyrimorph            |
|                                    |                                | valinamide carboxatems (C4A)       | benhiavacil valifenate                    |
|                                    | Chemicals with multi-site activity: Multi-site contact activity | mandelic acid amides (C4A)          | mandipropamid                             |
|                                    |                                | Dithiocarbamate                    | Mancozeb                                  |
|                                    |                                | quinones                          | Dithianon                                 |
|                                    |                                | phthalonitrile                     | Captan                                    |
|                                    |                                |                                      | Chlorothalonil                            |

Table 3
Selected examples of insecticides classified according to the mode of action (MoA) groups, target site and chemical family [24].

| Insecticides                         | MoA Groups                        | Target site                        | Chemical family                          | Selected examples                      |
|--------------------------------------|-----------------------------------|------------------------------------|------------------------------------------|----------------------------------------|
| Nerve and/or muscle action           | Acetylcholinesterase (AChE) inhibitors | Carbamates                      | Aldicarb, Carbaryl, Carbobufan, Methomyl, |
|                                     | GABA-gated chloride channel blockers | Organophosphates                  | Parathion, malathion, chlorpyrifos, cichlorovos |
|                                     | Sodium channel modulators          | Cyclodiene Organochlorines        | Chlordane, Endosulfan                     |
|                                     | Nicotinic acetylcholine receptor (nAChR) competitive modulators | Phenylpyrazoles (Fiproles)        | Ethiprole, Fipronil                       |
|                                     | Ryonidine receptor modulators      | Pyrethroids and Pyrethrins         | Bifenthrin, Fenpropathrin, Imizoprin, Pyrethrins |
|                                     | Juvenile hormone mimics            | Organochlorines                   | DDT, Methoxychlor                         |
| Growth and development regulation   | Inhibitors of chitin biosynthesis  | Neonicotinoids                    | Acetamiprid, clothianidin, Imideloprid, Thiaclopriod, Thiamethoxam |
|                                     | Inhibitors of acetyl CoA carboxylase | Tetronic/Tetramic acid derivatives | Chlorantranilprole, Cyntranilprole, Flubendiamide, Fenoxycarb |
|                                     | Inhibitors of mitochondrial ATP synthase  | Thiourea                          | Pyropyroxyn                               |
|                                     | Uncouplers of oxidative phosphorylation | Organatin                        | Chlorfluazuron, Teflubenzuron            |
|                                     | Mitochondrial complex electron transport inhibitors | Dinitrophenols                  | Buprofezin                                |
|                                     |                                    | Pyrazole-carboxamides (METI)      | Spirodiclofen, Spirodipion,              |
|                                     |                                    | Beta-ketoniitrile derivatives      | Spirodiclofen, Spirodipion,              |

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application of insecticides, natural or synthetic compounds that eradicate insects and arthropods. These compounds may be applied to the soil to kill soil-borne pests or to the aerial part of the plant. A major part of the applied insecticides reaches the soil, either by direct applications to the soil or indirectly by run-off from leaves and stems [40].

The long-term insect pest management by means of synthetic agrochemicals has led to insect pest resistance. Although scientists recognized resistance of insects to chemical pesticides nearly 76 years ago, the problem became widespread in the 1940s during an era of extensive use of synthetic organic insecticides and acaricides [38]. Research on the phenomenon of resistance progressed slowly over the next three decades, despite a steadily growing list of documented cases. In the 1970s three unrelated factors converged, heightening concern around the world and lending momentum to scientific research focused on the genetic, biochemical, and ecological factors associated with resistance [38].

Fungicides of natural or synthetic origin have greatly contributed to control crop diseases in the last centuries protecting plants against contamination by fungi and eradicating established fungal infections. Diseases of crops are caused by a vast range of organisms that include the true fungi (e.g. Ascomycota and Basidiomycota), fungal-like but unrelated Oomycota (e.g. Phytophthora and Pythium), Plasmodiophora, bacteria, viruses and nematodes [41]. Fungi are by far the most important group of plant pathogens especially in terms of the number of species and their pathogenic lifestyles, but also in incidence and damage. Fungal diseases compromise not only crop yield, but also posing a threat to food security, animal and ecosystem health [42]. There are direct measurable economic and ecological consequences of the impacts of fungal diseases associated with die-off in forest and urban environments. Losses that are due to persistent and epidemic outbreaks of fungal diseases compromise not only crop yield, but also posing a threat to food security, animal and ecosystem health [42].

Fungicide resistance develops when a working mode of action loses its efficacy against target fungal pathogen. A fungicide or mode of action, when used for a several years or seasons, might have its efficacy noticeably reduced or even lost [38]. Therefore, for intensively managed growing regions, wine growers apply more than 10 applications of fungicide yearly but in other regions such as the Central part of Mexico, more than 20 fungicide applications can be done on strawberries in a single growing season [43,44]. Consequently, a wide variety of classes of fungicides such as methyl benzimidazole carbamates, succinate dehydrogenase inhibitors, anilino pyrimidines, morpholines, Qo inhibitors and azoles are used either concomitantly or alternately throughout seasons and many different synthetic and natural compounds are investigated regarding their potential as fungicides for crop protection [45].

The indiscriminate use of fungicides can lead to soil contamination, environment pollution, accumulation of hazardous chemicals in food chain and threat human health [46]. Optimization of fungicide field administration together with the development of green fungicides is fundamental to reduce the harmful effects to the environment and human health. In this context, nanostructured fungicides might be a promising solution to optimize fungicide administration through the sustained release of actives, which would prevent fung resistance, soil contamination, biotic stress, and risk to human health.

2.3. Current formulation technology of agrochemicals

Nowadays, several pesticides and fertilizers formulations are found on the market and the demand for high performance products has driven the companies to develop a range of technologies for agrochemical administration. The conventional formulation technologies, that include granules, wettable powders, emulsifiable concentrates and soluble concentrates, are becoming progressively more obsolete in favor of the water-based formulations due to their environmental advantages and easier application.

Commercial fungicides, for example, are generally soluble in lipophilic solvents and insoluble in water. Therefore, fungicide uptake and its translocation to the infected sites are restricted due to physicochemical properties. Thus, water-based dispersion formulations were created with the addition of surface-active agents, or emulsifiers, and other stabilizers, which enables the formation of emulsions comprising small droplets (<10 μm diameter) of organic solvent–fungicide in the spray [41]. The current water-based dispersion technologies mainly comprise suspension concentrates (SC), oil-in-water emulsions (EW), microemulsions (ME), and seed treatment formulations. There are also dry formulation counterparts, portraying a recent improvement over water-based dispersions, such as water dispersible granules and dispersion concentrates, which are resuspended or diluted in water, respectively, prior to use. Dry formulations have become commercially attractive alternatives to water-based dispersions due to their convenient packaging and handling.

In the past decades, controlled release formulations (CRF) have entered the market as microcapsules suspensions (CS) [47,48]. Microcapsules are comprised of polymer shells that provide a slow-release profile of the active ingredient and protect encapsulated compounds against degradation. Mostly, polymers used for CRFs are thermosets, including epoxy resin, alkyd resin, unsaturated polyester resin, phenol resin, urea resin, melamine resin, phenol resin and silicon resin and, the most used, urethane resin [49]. Except for polyolefin coating of fertilizer granules, thermoplastic resins are less often used due to their inferior physicochemical characteristics in comparison to thermosets [49]. As an alternative to the current commercially available polyolefin- and PU-based non-environmentally friendly CRF technologies, CRF shells could be prepared from biopolymers, which can be degraded and prevent the active spreading of microplastics. Depending on the biopolymer and the intended application, the degradation can occur hydrolytically or by the enzymatic action of microorganisms, such as bacteria, fungi, or algae [49].

Selected commercial controlled-release formulations of fertilizers and pesticides are shown in Tables 5 and 6. There are examples of commercially available polymer-coated sustained-release fertilizer formulations with particle sizes in the range of micrometres to millimetres. Polymers utilized for commercial CRF shells include alkyd resin (Osmocote), polyurethane and polyurea (Polyon, Multicote Plantacote, Trophy and Demand) and polyolefin (Polyzone). Several of the commercially available slow-release formulations consist of encapsulated fertilizers, herbicides, and insecticides; in contrast, few
Commercially available controlled release formulations of fertilizers [49].

| Trade name | Manufacturer | Coating materials | Selected commercial products |
|------------|--------------|-------------------|----------------------------|
| Agroco®     | Everris, Inc. | Coated with polymer/sulfur and resin coating | Agroco® 19-6-12, Agroco® 39-0-0 |
| Duration®   | Agrium, Inc. | Clay-coated polystyrene-coated urea (PCU) or micro-thin polymer membrane | Duration® CR, Duration® 44-0-0, Duration® 19-6-13 |
| ESN®        | Agrium, Inc. | Urea is coated with flexible micro-thin nitrogen polymer | ESN® 44-0-0 (Environmentally smart nitrogen) |
| Florikote   | J.R. Simplot  | Coated with dual layer technology | Florikote® 40-0-0, Florikote® 12-0-40, Florikote® 19-6-13 |
| Meister®    | Chisso-Asahi Fertilizer Co. | Coated with a polymer composition of natural products, resin and additives | Meister® 15-5-15, Meister® 19-5-14 |
| Multicote®  | Haifa Group  | Nutrients encapsulated in a polymeric shell | Multicote® Agri 6 22-8-13, Multicote® Agri 6 34-0-7, Multicote® Agri 8 34-0-7 |
| Nutricote®  | Chisso-Asahi Fertilizer Co | Polymer coating with a special chemical release agent | Nutricote® NPK 20-7-10 |
| Osmocote®  | Everris, Inc. | Granule contains NPK coated with organic resin | Osmocote® Exact, Osmocote® Exact Mini, Osmocote® Pro, Osmocote® Start |
| Polyon®     | Koch Agronomic Services, LLC. | Coated with patented ‘Reactive Layers Coating’ (ultra-thin ployurethane coating) | Polyon® 41-0-0, Polyon® NPK 20-6-13 |
| Poly-S®     | Everris, Inc. | Urea coated with sulfur followed by polymer | Poly-S® 37-0-0 |
| XCU®        | Koch Turf & Ornamental | Polymer-Coated Sulfur-Coated Urea | XCU® 43-0-0 |

Commercially available nanofertilizers [57].

| Product       | Content                                      | Company                                      |
|---------------|----------------------------------------------|----------------------------------------------|
| Nano-GroTM    | Plant growth regulator and immunity enhancer | Agro Nanotechnology Corp., FL, United States |
| Nano-green    | Extracts of corn, grain, soybeans, potatoes, coconut, and palm | Nano Green Sciences, Inc., India |
| Nano-Ag Answer| Microorganism (fungi, algae and bacteria), sea kelp, and mineral electrolyte | Urth Agriculture, CA, United States |
| Biozar nano-fertilizer | Combination of organic materials, micronutrients, microorganisims, and macromolecules | Fanavar Nano, Pachooseh Markazi Company, Iran |
| Nano max NPK fertilizer | Multiple organic acids (protein-lacto-glucolates) chelated with major nutrients, amino acids, organic carbon, organic micronutrients trace elements, vitamins, and probiotics. | JU Agri Sciences Pvt. Ltd, Janakpuri, New Delhi, India |
| Master Nano Chitosan Organic Fertilizer | Water soluble liquid chitosan, organic acid and salicylic acids, phenolic compounds | Pannaraj Intertrade, Thailand |
| TAG Nano fertilizers | Proteino-lacto-glucolate chelated with micronutrients, vitamins, probiotics, seaweed extracts, humic acid | Tropical Agro system India (P) Ltd, India |

2.4. Nanoformulations of agrochemicals

The application of nanotechnology in or on plants has the potential to change the conventional plant protection, e.g. for the controlled release of agrochemicals and target-specific delivery of biomolecules (e.g., nucleotides, proteins, and activators) [52]. The overall prominence and development of nanotechnology industry is estimated to reach up to $126.8 billion by 2027. Essentially, this innovation approach has sponsored the farming-based business segment with Compound Annual Growth Rate of 12.9% over the analysis period 2020–2027 [53].

In the past decade, an increasing number of studies concerning the encapsulation of fertilizers and pesticides in nanocarriers aiming for the sustained release of substances to tune uptake and efficiency, target specific plant organs, avoid pest resistance and overcome environmental issues [16,54]. Nanofertilizers and nanopesticides have been investigated to provide a sustained release of agrochemicals with efficient uptake by the plant, thereby decreasing harmful environmental consequences by avoiding pollution due to runoff or leaching into the groundwater, and reducing biotic stress and risk to human health [55].

Recently, several nanofertilizers have entered the market (Table 5) [56]. Nanofertilizers currently available in the market may contain nano zinc, silica, iron and titanium dioxide, as well as other metal oxides. Moreover, some formulations, such as Nano-green (Table 5), contain micelles formed by long-chain fatty acids, long-chain alcohols, and vegetable oils. These commercial products surely make way in the market for more nanoformulations. Their success could awake in big companies the interest for nanotechnological solutions involving sustained release and targeted delivery of actives using complex nanocarriers, which are not yet available in the market.

Besides the use of nanotechnology alone, the combined use with bio-based polymers will drive a further sustainability in agriculture by replacing petroleum-based polymers. Biopolymers are considered as microcarriers are constituted by petroleum-derived polymers, such as polyurea and polyolefins, which either accumulate in the environment or are degraded by microorganisms. Microparticle particles are intentionally added to formulations and thus actively release microplastics to the environment. Fertilizer- and pesticide-products are at the top of the list for intentionally added microplastic pollution [50,51].

The current slow-release microcarriers provide the slow-release of different actives. However, they are limited to soil and to plant surfaces, such as leaves, stem, and trunk surfaces; on the other hand, the appliance of nanotechnology to develop nanocarriers could push the sustained release further and control the uptake and the targeting of agrochemicals inside of the plants. Furthermore, the majority of encapsulated fungicide formulations are available yet, such as Mevalone™. (See Table 7.)

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environmentally friendly and can be assimilated into the biogeochemical cycle after their biodegradation. Several publications have explored the advantages of nanotechnology applied to agriculture [13,16,54]; however, this review aims at the sustained and targeted release promoted by biopolymer-based nanostructures loaded with active compounds.

Bulk nanocomposites [58–60], nanoparticles [29,61,62], and nanocarriers [63–67] have shown outstanding performance for the treatment of diseases caused by nutrients deficiency and pathogens. Currently, nanotechnology has been used to improve traditional strategies of the application of agrochemicals to reduce the biotic stress and the collateral damage in the fields such as the decline in soil fertility, or to increase the efficiency against crops diseases, pests, and nutrients depletion [25,68]. For instance, foliar delivery of nanoparticles may help to enhance nanoparticle uptake and reduce environmental impacts of chemical fertilizers conventionally applied through a soil route [69,70]. The reader is referred to the work by Grillo et al. [70] for a recent and comprehensive review in foliage adhesion and foliar nanoparticulate delivery systems.

Nonetheless, the application of nanostructures for sustained release of actives with high selectivity and effectiveness is among the main challenges in this research area. Nanostructures for agricultural application were mainly nanoemulsions [71] and nanoparticles including metal oxides [72–75], silica [59,76,77], magnetic materials [78,79], quantum dots [80,81], lipids [65,82], or polymers [83–86].

However, studies regarding the uptake, translocation, or accumulation of nanocarriers within plants are fairly discussed in the literature [69,72]. Observations suggested that nanocarriers could be taken up by the plant through direct penetration and transport through the stomatal opening. Observed translocation of nanoparticles from leaf to root shows evidence that nanoparticles travel by the phloem transport mechanism. Accumulation and transport of nanoparticles depend on nanocarrier shape, application method, and nature of plant tissues [65,69,87,88]. In addition, some studies have shown in vitro evidence of cell internalization and association of biomolecular signalling, biological kinetics, transport and toxicity to the composition, size, shape, surface chemistry and ζ-potential of nanomaterials [89,90]. A recent study by Beckers et al. studied the transport of polymer nanoparticles of cation were mainly nanoemulsions [71] and nanoparticles including metal oxides.

In agriculture the demand for biobased pesticides, herbicides, and fertilizers to replace rather environmentally harmful agrochemicals has increased [13]. The enclosure of fertilizers and pesticides in nanoparticles or nanocapsules is beneficial mainly due to the potential for sustained or controlled release of substances, their high surface area to volume ratio and the protection of the active ingredients from premature degradation and run-off. Furthermore, nanocapsulation technology enables innovative strategies of agrochemicals administration such as foliar application [65,70,87] or trunk injection [67], which circumvents problems associated with soil penetration and degradation of the actives by microorganisms contained in the soil [65]. Biobased polymer nanocarriers represent an environmentally friendly alternative due to their renewable origin and biodegradability, which enable the integration of these materials into the biogeochemical cycles, and also the use of waste materials, e.g., in biorefineries from pruning or compost waste might be proposed as additional feedstocks for biopolymers and to establish a circular economy [92,93,97,98].

Many biopolymers (Table 8) have been already extensively investigated for biomedicai applications, but only recently they have become agriculture, polymeric nanocarriers have been a much less researched. However, there has been some interest in polymeric nanocompounds for soil analyses and diagnostics in plants, especially to identify the presence of unsafe substances [25]. In contrast to synthetic polymers, biopolymers, especially wood-based materials, might be interesting materials for the development of modern nanotechnology for agriculture, due to their biocompatibility, biodegradability, and independence of food production [92,95,96].

The most used biopolymer for the synthesis of nanostructures and their applications. Table 8

| Biopolymer | Nanostructure | Non-agricultural applications | Agricultural applications |
|------------|---------------|--------------------------------|-------------------------|
| Alginate   | Spheres, fibres, polypoxes [99]. | Drug delivery [100], gene therapy [101], tissue engineering [102]. | Pesticide delivery [103,104], growth promoter [105], sustained irrigation [106]. |
| Cellulose  | Spheres, crystal, whiskers, fibres [107–109]. | Tissue engineering [110], drug delivery [111], biosensing [107]. | Pesticide delivery [112], fertilizer delivery [86]. |
| Chitosan   | Spheres, hydrogels, fibres, membranes, polypoxes [113,114]. | Tissue engineering [115], gene therapy [116], biosensing, drug delivery [117]. | Oil herding [130], wastewater treatment [129], drug delivery [134], supercapacitors [127], tissue engineering [128], antioxidant and antimicrobial [132]. |
| Lignin     | Particles[126], nanofibers [127–129]. | Drug delivery [134], supercapacitors [127], tissue engineering [128], antioxidant and antimicrobial [132]. | Pesticide delivery [133,134]. |
| PLA        | Spheres, fibres [135], Polymersomes [139]. | Drug delivery [136], tissue engineering [140]. | Pesticide delivery [141]. |
| Polypeptides | Polymersomes [139,140], fibers [141], polypoxes [142], spheres [146]. | Tissue engineering [141], gene therapy [142,143], biosensors [144], drug delivery [140]. | Pesticide/nutrient delivery [145,146], gene delivery [147]. |

3. Biopolymer-based Nanocarriers

Polymer nanocarriers have been an intense field of research in the biomedical field to develop drug delivery systems for sustained and targeted release or as nanodevices for diagnostics in medicine [94]. In
trending materials for sustained release systems in agriculture. In this section, the most relevant biobased polymers for the development of environmentally friendly nanocarriers for sustained release in agriculture are discussed.

3.1. Chitosan

Chitosan, a naturally occurring polysaccharide consisting of β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units, is the foremost biopolymer used to produce nanocarriers for agricultural purposes [39,84,114,148,149]. The main source of commercial chitosan is the processing stream of sea crustaceans, specifically, chitosan is derived from chitin present in seashells. The global market for chitin and chitosan derivatives is expected to reach around 400 tonnes in 2024 according to a report from Global Industry Analysts [150]. Philibert, 2017 stated that there are over 2000 concrete applications of chitin, chitosan and their derivates [151]. Chitosan is approved for use as a food additive or dietary supplement in countries such as Japan, England, the USA, Italy, Portugal, and Finland and was accepted as a functional food ingredient by Japan’s health department in 1992. The main producing countries are Japan and the USA with smaller operations in India, Italy and Poland [152].

Chitosan has been long utilized for agricultural and horticultural applications, typically as biopesticide to positively modulate the innate plant immune system [124], as plant growth enhancer and seed coating [66,153]. Thereby, it is one of the most commonly utilized polymers [114] for agricultural purposes nowadays. Chitosan nanoparticles in comparison to chitosan in bulk have resulted in an improvement in the effects aforementioned [114,154–156]. Therefore, chitosan has been the most investigated polymer to produce nanocarriers to enclose agrochemicals and provide a sustained release of active compounds in agriculture. Chitosan nanocarriers [157] have been reported to promote the delivery of fertilizers, [87,123] pesticides [158,159], and genetic material [149]. They have also been loaded with the herbicide paraquat as an environmentally safer alternative for weed control [119,158].

Saharan et al. have reported the application of Cu-chitosan hybrid nanoparticles (Fig. 1) to boost plant defence and plant growth [160,161]. The authors studied the Cu release from the chitosan matrix and its effects on the plant’s health.

In 2015, they further investigated the antifungal and growth promotory effects in tomato plants by ionic gelation of chitosan with tripolyphosphate (TPP) anions. Before the completion of cross-linking reaction, a solution of CuSO₄ (0.01%) was added into the formulation. Nanocarriers with average particle sizes of ca. 400 nm, measured by DLS, were obtained. Cu-loaded chitosan nanocarriers were tested towards their effect in growth of tomato seedlings (Fig. 2) and in vitro antifungal activities by inhibition in mycelial growth and spore germination. Moreover, the scientists assessed the treatment of early blight and Fusarium wilt of tomato in pot conditions using Cu-chitosan nanocarriers (Fig. 3).

Later, in 2017, Saharan’s group reported[160] the in vitro release study of Cu from the chitosan matrix in the pH range of 1 to 7; the protonation of the amino groups of chitosan influenced the release profile: with decrease in pH from 3 to 1, release of Cu increased rapidly from 21.5 to 44.11 %. At pH > 6, release of Cu drastically decreased (4.94 %) due to deprotonation of amino group of chitosan. The authors studied the release profile over time in pH 4.5 and reported ca. 85% Cu release after 96 h. Cu-loaded chitosan nanocarriers presented effects over the activity of antioxidant and defence enzymes, namely SOD, POD, PAL and PPO. The enhancement enzyme activity was significant in comparison to control (water), bulk chitosan and CuSO₄ treatments; POD, SOD and PAL presented the higher activity enhancement up to 2 – 3-fold, while PPO had its activity enhanced in 0.12 – 0.16 %.

![Fig. 1. Hypothetical model of ionic cross-linking reaction of chitosan, tripolyphosphate (TPP) and Cu²⁺.](image-url)
Cu-chitosan nanoparticles applied to improve plant growth; a significant enhancement in plant height, stem diameter, root length, root number, chlorophyll-a and chlorophyll-b content was reported. The effect in plant growth with Cu-chitosan NPs compared to CuSO$_4$ in solution showed that even though the Cu content in the nanocarrier was lower, they were multiple times more effective. Furthermore, Cu-chitosan nanoparticles were used to treat Curvularia leaf spot (CLS) disease caused by Curvularia lunata in corn. Nanocarrier dispersions showed an improved health of the infected plants evaluated by several growth parameters after 80 and 95 days in comparison control (water), bulk chitosan (0.01 %) dissolved in 0.1 % acetic acid, CuSO$_4$ (0.01 %), and fungicide (0.01 % of Bavistin). A similar study [87] carried out by Saharan’s group on chitosan nanocarriers containing zinc (Fig. 4), which were applied to the leaves against CLS disease proved to be very effective(Fig. 5). Seed treatment and foliar application of NPs (0.01–0.16 %) significantly controlled Curvularia leaf spot (CLS) disease, increased grain yield from 20.5 to 39.8 % and enriched the grain with zinc micronutrient from 41.27 to 62.21 μg/g.

Sharma et al. [118] have loaded chitosan nanocarriers with agrochemicals against insect pest, spinosad and permethrin, subsequently the nanocarriers were tested against Drosophila melanogaster, a model organism, in several concentrations (10, 50, 100 μg/mL) [118]. Spinosad and permethrin were encapsulated with > 95 % and > 99 % efficiencies respectively; in addition, nanocarriers were submitted to release studies where about 80 % of spinosad and 30 % of permethrin were released after 5 h in tris-HCl buffer solution (pH 7.4) at 37 °C. The authors performed survivability, climbing, and the larval crawling assays to study the efficiency of the nanoformulation. Survivability assays were performed by measuring, up to 14 days, the number of eggs deposited into different food vials containing 15–20 flies along with the nanopesticide dispersion and the control. The climbing assays were performed by adding the same number of flies inside different measuring cylinders with a threshold mark of 10 cm containing nanopesticides dispersion and the controls (untreated flies, and flies treated with chitosan solution, or free spinosad, or free permethrin), and then the upward movement of flies was recorded for 1 min.

Fig. 3. Symptoms of early blight on tomato plants in pot experiments: (a) concentric lesions expending in control and (b) micro lesions on nanoformulation treated plants. Symptoms of Fusarium wilt in potted tomato plants: (c) uprooted plants showing effect of various treatments on Fusarium wilt (d) disintegration of vascular tissues at right and healthy vascular tissues at left side [161].

Fig. 4. Corn plant growth in (a) control and (b) Zn-chitosan NPs in field conditions [87].
Nanocarriers consisting of chitosan-complexed single-walled carbon nanotubes have been developed for chloroplast-selective gene delivery and expression in plants [149]. The potential use of chitosan as a polycationic gene carrier has been evaluated for biomedical applications due to its capability to complex with negatively charged DNA via electrostatic interactions, protecting DNA from nuclease degradation [116]. Kwak et al. applied this same reasoning. In addition, chitosan is a biodegradable polysaccharide, abundant in nature and beneficial to plant systems [83,124,153].

Carbon nanotubes, as chitosan, had already been studied for agricultural applications such as plant growth enhancement [162,163]. Some works demonstrated that SWNTs were internalized by plant cells, being able to pass through the rigid cell walls, membranes and the double lipid bilayers of cell organelles, such as chloroplasts. Some authors even suggested the ability of controlling subcellular localization of SWNTs-based nanocarriers as a targeting strategy [164–166]. This nanoparticle subcellular uptake mechanism can be described by the lipid exchange envelope penetration (LEEP) model, whereby the ability of nanoparticles to penetrate the cell membrane and the chloroplast envelope is governed primarily by the nanoparticle size and surface charge [167]. Nonetheless, existing applications of SWNTs in plants were limited to studies of the transport of SWNTs in plant cells [163,164], and none of the work explored the possibility of utilizing SWNTs as nanocarriers for gene delivery into specific plant organelles. Therefore, Kwak et al. developed chitosan-wrapped SWNTs with sufficiently high surface charge to passively traffic past the plasma membrane and localize in the chloroplasts for successful gene delivery [125,168].

The pDNA was condensed by chitosan-functionalized SWNTs and safely transported to the chloroplasts after crossing plant membranes, intracellularly detached and transiently expressed within the chloroplast stroma [125].

The chitosan-SWNTs nanocarriers uptake mechanism was described by the lipid exchange envelope penetration model, whereby the ability of nanocarriers to penetrate the cell membrane and the chloroplast double lipid bilayer is governed mainly by the nanocarrier size and surface charge. Plasmid DNA was conjugated to the nanocarriers due to electrostatic interaction between the positively charged amine groups in chitosan and the negatively charged pDNA. Particle size was analyzed by nanoparticle tracking analysis, which captures the Brownian trajectories of individual nanoparticles in solution. Chitosan-wrapped SWNTs presented hydrodynamic radii around 95–120 nm depending on the formulation; once complexed with pDNA, the average hydrodynamic radii increased to 127–275 nm [125].

Nanocarriers loaded with pDNA were applied foliarly and by using a pDNA encoding an YFP reporter gene. Kwak et al. [149] demonstrated chloroplast-targeted gene delivery and transgene expression in mature arugula, watercress, spinach and tobacco plants as well as in isolated A. thaliana mesophyll protoplasts. pDNA-SWNT complexes enter the leaf mesophyll through stomata pores, traverse plant cell walls, plasma membranes and eventually chloroplast bilayers (Fig. 5a). The morphology of nanocarriers with and without pDNA were 3.9 ± 0.9 nm and 11.3 ± 1.6 nm, respectively, evaluated by atomic force microscopy (AFM).

The scientists were able to observe CS-SWNTs in chloroplasts (Fig. 6a) within the isolated protoplasts via near-infrared fluorescence. Furthermore, fluorescence confocal micrographs (Fig. 7b) showed YFP expression from pDNA conjugated to CS-SWNTs (1:6 pDNA:SWNT w/w ratio) in isolated protoplasts after 24 h. These results show reliable evidence that engineered nanocarriers can be distributed in a subcellular level within plant cells. Moreover, the authors argue that the developed platform could also be optimized further to enable stable chloroplast transformation in crop species to benefit crop improvement and agricultural applications. In addition, few works with carbohydrates blends, films and nanomaterials from starch, alginate and pectin have been also developed for agricultural applications [169,170].

3.2. Cellulose and hemicellulose

Cellulose is the most abundant biopolymer. It is the main structural
Fig. 6. a) Colocalization of CS-SWNTs in chloroplasts within the isolated protoplasts. Near-infrared fluorescence of SWNTs was observed in chloroplasts after removal of chloroplast autofluorescence. b) Fluorescence confocal micrographs showing yellow fluorescent protein (YFP) expression from pDNA conjugated to CS\textsuperscript{COV}-SWNTs (1:6 pDNA:SWNT w/w ratio) in chloroplasts (red) within the isolated protoplasts after 24 h.

Fig. 7. Scheme protocol (top) for the generation of hollow lignin nanocontainers by inverse miniemulsion. Obtained. SEM (bottom) images of several hollow lignin nanocontainers with varying amount of cross-linker TDI [198].
component of the primary cell wall in green plants; in addition, it is produced by some strains of bacteria. The worldwide availability, mechanical, optical and thermal properties and excellent biocompatibility have contributed to place cellulose as a biomaterial of increasingly importance, especially for tissue engineering. Cellulose nanomaterials have been extensively studied as nanofibers and nanocrystals in diverse morphologies. In despite of the difficulty to work with cellulose in solution due to the harsh conditions required, some strategies have arisen recently and enable the production of nanostuctures derived therefrom; in addition, recently cellulose-based nanoparticles have been developed. Cellulose derivatives have been reported as microcarriers of microorganisms for the controlled release of pesticides. Silica–epichlorohydrin–carboxymethylcellulose microcapsules exhibited a sustained release of insecticides against Myzus persicae in the presence of cellulases. Allium cepa chromosome aberration assays demonstrated that the microcapsules had less genotoxicity than the pure emamectin benzoate.

Hydroxypropyl cellulose (HPC) nanocapsules were utilized for curcumin encapsulation, which is an active component of turmeric (Curcuma longa Zingiberaceae) and can be used as an insecticide. Therefore, even though the authors did not consider the application in agriculture, curcumin loaded HPC nanocapsules might be interesting for pest control management in crops. Bielska et al. synthesized anionic and cationic HPC derivatives and encapsulated curcumin by nanoencapsulation into a polyelectrolyte complex. Nanocarriers with diameters between 150 and 250 nm were obtained with encapsulation efficiencies of curcumin of ca. 70 %. A sustained release of curcumin in vitro up to 80 % at room temperature after 5h was reported. Kumar et al., 2015, investigated the delivery of clodinafop-propargyl herbicide to plants via carboxymethyl cellulose nanocarriers.

Machado et al. chemically modified cellulose with undec-10-enolic acid to encapsulate hydrophobic fungicides in situ via thiol-ene cross-linking in a miniemulsion. Fungicides captan and pyraclostrobin were encapsulated with encapsulation efficiencies of 80–100 %. Further, cellulose nanocarriers were tested in antifungal assays in vitro against Neonectria ditissima, Phaeoacremonium minimum and Phaeomoniella chlamydospora using the plain growth medium as positive control and the drug Hygromycin as positive control. Neonectria ditissima is a fungus strain related to the apple canker disease in Europe, while Phaeoacremonium minimum and Phaeomoniella chlamydospora are Esca-related fungi strains. Drug-loaded cellulose nanocarriers have efficiently inhibited pathogenic fungi growth for cellulase-producing strains up to 75 %.

Not much has been reported for the use of hemicellulose for the preparation of nanocarriers for application in agri- or horticulture. Xylan is a polysaccharide that is present in high concentrations in hemicellulose. A recent work by Beckers et al. used xylan from corn cobs to prepare pyraclostrobin-loaded xylan-based nanocarriers and were able to prove their antifungal activity against fungal pathogens, such as Pyricularia oryzae (respnsible for the rice blast disease) and Botrytis cinerea – a fungus occurring in viticulture and horticulture, which produces high amounts of xylanases and could degrade the nanocarriers.

3.3. Lignin (Polyphenols)

Lignin is generated in million tons every year by the paper industry alone, as byproduct from the Kraft wood pulping. During this process, lignin is separated from cellulosic fibres under alkaline conditions in combination with sodium sulphide. The bulk of the so-generated Kraft lignin is burned as fuel or is discarded as waste. It is regarded as a promising biopolymer and is expected to play a pivotal role in biorefinery design. Currently Lignin is an underutilized bio-based compound, which has the potential to contribute to sustainability. Although the saying that you can make anything out of lignin except money continues to be used, a lot of research is being done to identify higher-value use cases of lignin. However, lignin is a complex and interesting polyfunctional macromolecule that can undergo chemical modification and thus giving rise to a vast variety of derivatives and fine chemicals. Soluble lignin is an abundant renewable feedstock, it has been scarcely used to synthesize nanostructures and only recently has been the focus of studies synthesize lignin-based nanomaterials for biomedicine, cosmetics, oil recovery, coatings, and agriculture.

Lignin nanocarriers have been produced from different sources such as Kraft and sulphite wood pulp wastes and spent mushroom substrate. Additionally, studies have shown the biodegradability of the nanocarriers towards laccase producing fungi; therefore, lignin nanocarriers have been used to encapsulate antifungal agrochemicals in the anticipation that the re201 lease would be triggered by degradation towards the presence of fungal laccases. Also, other waste streams can be utilized to produce nanomaterials, e.g. polyphenols from green tea or coffee extracts have been utilized as reducing agents.

Fischer et al. have produced pyraclostrobin-loaded lignin nanocarriers with diameters from 200 to 700 nm via azamicroemulsion. Pyraclostrobin-loaded nanocarriers selectively inhibited the growth in vitro of Esca-related fungi, Phaeomoniella chlamydospora and Phaeoacremonium minimum. In follow-up investigations, Wurm’s group has demonstrated the versatility of the encapsulation method to produce submicron carriers loaded with a variety of agrochemicals, e.g. boscalid, tebuconazole, prothioconazole and azoxystrobin, to treat plants against fungal diseases. The versatile drug load is important to overcome fungicide resistance that might be developed after excessive use of agrochemicals; therefore, the application of sustained release of drugs with different drugs combination is an effective approach to treat fungal diseases over long times.

Fischer et al. have demonstrated the efficacy of the lignin particles in a 3-year field trial in planta in Vitis vinifera L. cv. ‘Portugueser’ plants. Forty-three plants were treated with the pyraclostrobin-loaded lignin particles, 19 plants were treated with ‘empty’ lignin NCs, 8 plants were treated by the injection of an F500 formulation (commercialized product of BASF, Germany), and the remaining 2877 plants were not treated. All 2958 plants of the vineyard were monitored over a period of 5 years (2014–2018).

The treated plants showed a significant improvement in their conditions after 3 months and up to 4 years. In addition, nanoformulations delivered a superior performance by reducing the amount of fungicide over 4 years in 360 % in comparison to the commercial F500 formulation.

More recently, lignin-based nanocarriers have been used for the delivery of antagonistic fungi as an alternative to the conventional fungicides used in agriculture. The encapsulation inhibited premature germination and enabled the application as an aqueous dispersion via trunk injection for an enzymatic release of the spores, which was shown in vitro.

3.4. Polypeptides

Polypeptides, polymers derived from amino acids, have also found their importance as nanocarriers within precision agriculture; though, polypeptides nanocarriers are not as widespread as carbohydrate/polyphenol-based nanocarriers. Polypeptide nanocarriers have been utilized in some studies due to their capability, unlike many other biomolecules, of crossing the plasma membrane of living cells, which are selectively permeable to exogenous molecules.

Peptide-based crosslinked nanoparticles from L-aspartic acid have been applied for the sustained release of fertilizer in soil. The sustained release of the fertilizer was achieved in soil and the release of nitrogen and phosphorus was 79.8 % and 64.4 % after 30 days, respectively. Furthermore, the crosslinked polypeptide nanoparticles...
acted as superabsorbent that improved the water-holding and water-retention capacities of soil. For 200 g of soil with 1.5 g of superabsorbent, authors reported a water-holding capacity of 81.8 %, and the water-retention capacity remained 22.6 % after 23 days.

The capability of polypeptides pass through plasma membranes is an important feature for drug targeting and has been depicted in some studies. A study concerning the production of polysuccinimide nanoparticles (PSI-NPs) loaded with Coumarin-6 by nanoprecipitation from pre-formed PSI (Mn = 8190 g mol⁻¹, Mw/Mn = 1.24) demonstrated that the PSI-NPs (<30 nm) were able to pass through plant (grapefruit) cell wall pores. In addition, the controlled release of the loaded model compound (Coumarin-6) was observed under alkaline condition (as in phloem) and found to be pH-dependent [146]. The dye-loaded NPs were internalized into grapefruit cell lines ca. 10 min, with most of the absorbed PSI-NPs distributed in the cytoplasm and nucleus after 2 h (Fig. 10). Therefore, the polypeptides nanocarriers revealed a great potential for delivering agrochemicals to phloem in plants with minimal effects on soil microbial growth and activity.

Polypeptide nanocarriers have been also studied for growth-promotory effects. Polyglutamic acid nanoparticles were prepared via ionic pre-gelation for encapsulating the pro-growth regulator gibberellic acid (GA3) which is used in the field for improving germination, plant development, productivity, and the quality of food. The GA3-loaded nanocarriers presented encapsulation efficiency of 63 % and a cumulative sustained release of 58 % after 48 h. In tests using Phaseolus vulgaris seeds, nano-γPGA/CS-GA3 showed high biological activity, enhancing the rate of germination in the first day (50–70%) when compared with free GA3 (10–16 %). Encapsulated GA3 was more efficient than the free hormone in the increase of leaf area and the induction of root development (including the formation of lateral roots). These effects were not

Fig. 8. In vitro investigations of lignin NCs. Pch and Pmi were used as ligninolytic enzyme-segregating fungi, whereas Eul was applied as control fungus without laccase segregation. A) Optical density (at 600 nm) of fungal cultures in 96-well microtiter plates after 48 h for samples empty and pyraclostrobin-loaded lignin NCs (see Table S1 for details, Supporting Information). B) HPLC-MS analysis of NC supernatant after the incubation with culture filtrate of Pch after 24 and 72 h. Release compared to a pyraclostrobin standard curve and the amount of applied fungicide.

Fig. 9. Treated grapevine plants (with pyraclostrobin-loaded nanocarriers, top) and a non-treated plant (bottom) over a period of 4 years (dates are noted below the photos) [137].
Fig. 10. Delivery of Trichoderma spores encapsulated by layer-by-layer deposition of lignosulfonate and cationic lignin to form nanocarriers as a biological control agent [200].

observed when seeds were treated with nano-γ-PGA/CS without GA3. The results demonstrated the considerable potential of nano-γ-PGA/CS-GA3 for use in agriculture [203].

Recently, polysuccinimide (PSI) nanoparticles conjugated with glycine methyl ester were investigated to deliver fludioxonil, a fungicide, in the phloem tissue of banana trees [204]. Authors’ main goal was to treat Fusarium wilt disease, a serious vascular disease that threatens the global banana production. The strategy of using PSI NPs relies on the responsiveness of this polymer to change in pH, and because of their remaining succinimidyl groups, in vitro studies showed that PSI nanoparticles could be hydrolysed at pH ~ 8 of the plant phloem, thereby releasing the encapsulated fludioxonil. The conjugation of the glycine ester was determined based on authors’ previous investigations [205], where the conjugation of the amino acid glycine to polysuccinimide (PGA) improved the bioactivity and absorption of avermectin in rice.

PGA nanocarriers loaded with fludioxonil (~29 %) were submitted to drug release assays in vitro, in which the pH-responsiveness was evidenced. NPs at pH 8 (physiological pH in the phloem) release twice more fludioxonil than NPs at pH 5. In vivo experiments in potted bananas demonstrated the downward delivery of NCs to banana rhizomes and roots after foliar application, reducing disease severity by 50 %. Furthermore, phloem transport and uptake studies revealed that the phloem loading of nanocarriers was involved in an active transport mechanism at the organ level in castor bean seedlings, that nanocarriers could be absorbed by mesophyll cells and loaded into vascular tissues through the symplastic pathway, and that nanocarriers possessed an enhanced enhanced transmembrane uptake at cellular level.

Polypeptide-based nanocarriers are promising in agriculture as they can be degraded into metabolizable degradation units and possess the ability of changing secondary conformation in response to outer stimuli. Unlike the synthetic copolymers, which generally present a coil or globular structure, polypeptides can adopt ordered conformations, such as α-helices or β-strands [139].

3.5. Alginate

The anionic polysaccharide alginate has been used in nanocarriers for various drugs because of its biocompatibility and non-toxicity. Alginate has been used to produce nanocarriers loaded with pesticides such as imidacloprid [169], cypermethrin [104], and phloxine B [103], all of them for insect pest management. They have been prepared by self-assembly of polymeric micelles or emulsion crosslinking [104,169] or conjugated with the polymer to form a polymeric prodrug [103]. In the case of phloxine B, the formation of a prodrug nanocarrier prevented the early photoactivation of the pesticide before it reached its target [103]. In crosslinked alginate delivery systems, the main mechanism governing active compound release in physiologic fluids is the sodium–calcium exchange. When calcium alginate is introduced in an environment rich in monovalent salts, insoluble calcium alginate is converted into soluble alginate, resulting in solubilization of the nanof ormulation and subsequent release of the cargo [169]. While for prodrug systems the release should be triggered by an stimulus, e.g. enzymatic degradation or by metabolic compounds such as glutathione (GHS), required for oxidative stress regulation in cells [103]. The authors demonstrated that in the absence of esterase and GSH, the phenolic ester bonds are stable at pH 7.4 because they were mostly embedded in the hydrophobic core. However, once the esterase or GSH was added, PB was released up to a complete release in vitro after 70 h. Yin et al. verified the cytophototoxicity of the nanopesticide in vitro using S9 insect cells, where a group of cells received nanocarriers subjected to light pre-treatment and another group of cells received nanocarriers without light pretreatment. These results were compared to plain PB with and without light pre-treatment. The light pre-treatment of plain PB reduced the cytophototoxicity to 40 % for the highest concentration tested, whereas the light pre-treatment only resulted in a cytophototoxicity of 3 %, which evidenced the effectiveness of nanoformulation in providing the necessary photostability.

Kumar et al. produced calcium alginate nanocarriers loaded imidacloprid with sizes between 50 and 350 nm depending on the amounts of surfactant, diocyl sodium sulfo-succinate. The in situ encapsulation of imidacloprid was achieved via emulsion crosslinking with loading efficienciesup to 99 %. The authors performed in planta studies, in which they perceived the efficacy of the nanof ormulation in pest control. They tested four different formulations, i.e., control (no treatment), dummy (empty alginate nanoparticles), plain pesticide (0.145 mg⋅L−1 of imidacloprid) and nanencapsulated pesticide (0.145 mg⋅L−1 of imidacloprid), in bhindi plants subjected to sucking pests (leafhoppers). The authors observed a long-lasting effect of the biopolymer-based pesticide nanoformulation up to the 15th treatment, where the effect of nanencapsulated insecticidal reduced leafhopper population with time. For the other treatments, the leafhopper population increased with time at the point where the recorded population on the 15th day was above the threshold level which has harmful effect in crop. Therefore, the normal insecticidal treatment has shown an immediate effect, enabling the re-growth of insect population, whereas the alginate-based nanocarriers loaded with imidacloprid provided a sustained release of imidacloprid and lasting insecticidal effect that combats insect pest.

In summary, alginate-based nanocarriers are prepared readily. Alginate-based pesticide nanoformulations have been tested in vitro and in planta regarding their effectiveness, displaying promising results and potential as biopolymer platform for the sustained release nanoformulations; however, more in-depth, and longer in planta experiments and field trials are essential for on-farm applications and commercial prospects.
3.6. Poly(lactic acid) and copolymers

Poly(lactic acid) (PLA) and poly(lactic acid-co-glycolic acid) (PLGA) belong to the family of aliphatic polyesters commonly made from α-hydroxy acids and are considered biodegradable and compostable. For many years, PLA has been utilized as a biodegradable polymer for many applications, but especially for biomedical applications. In the past few years, there has been a growing interest in using PLA for agricultural applications, including the development of nanoformulations [138, 206–208].

PLGA has been used in combination with PEG to synthesize polymeric nanocarriers (90–125 nm) by a dialysis method to encapsulate metolachlor, a hydrophobic herbicide, with high encapsulation efficiency (> 85%). Scientists investigated their uptake by rice seedlings and the effect of the nanoparticle in the control of Gramineae weeds [208]. Scientists aimed to enhance the water-solubility of metolachlor and thus eliminate the requirement for organic solvents and surfactants, which represent two of the most important sources of pesticide pollution. The absorption study of Cy5-labeled nanoparticles into rice roots (Fig. 11) suggested a possible transmitting pathway of this metolachlor formulation and increased utilization of metolachlor. Furthermore, the bioassay test demonstrated a higher effect than bulk formulations on the formulation and increased utilization of metolachlor. Furthermore, the bioassay test demonstrated a higher effect than bulk formulations on the Gramineae weeds Oryza sativa, Digitaria sanguinalis, and Arabidopsis thaliana seedlings.

The use of PLA-based nanocarriers was also investigated for foliar application. Functionalized abamectin poly(lactic acid) (Abam-PLA) nanoparticles were synthesized [138] to increase both the foliar adhesion and effective utilization rate of pesticides; three types of Abam-PLA (CH₂CO-PLA-NS, HOOC-PLA-NS, and H₂N-PLA-NS) nanoparticles with different adhesion abilities to cucumber leaves were prepared. PLA-based nanoparticles were prepared by miniemulsion/solvent evaporation, exhibiting diameters of ca. 450 nm and a abamectin loading efficiency up to 50%. The nanoformulation granted continuous release of abamectin and higher photostability when compared with plain abamectin. Authors observed a slightly favorable deposition of Abam-PLA nanocarriers on cucumber leaves, which was controlled by tuning the interaction mode between the nanoparticles and leaf-surface (Fig. 12). More polar groups provided a better adhesion to the leaf surface, even though the leaf surface is considered mostly hydrophobic. This observation was rationalized by the presence of carbohydrates, fatty acids, fatty alcohols, and fatty aldehydes. The possible interaction of these polar groups on the cucumber leaves with the functional groups on the Abam-PLA nanoparticle surface could result in the adhesion. (See Figs. 13–1.)

4. Social science perspective of nanotechnology in agriculture

Nanotechnology is clearly seen as one of the major breakthrough technologies of the 21st century as its fields for application are extremely versatile due to its purpose technology-related characteristics [209, 210]. Some researchers even see it as the driving force of the next Schumpeterian or Kondratieff wave [211, 212]. The European Commission has recognized nanotechnology as one of its six “Key Enabling Technologies” [213]. Furthermore, nano has been included as an emerging policy issue under the Strategic Approach to International Chemicals Management (SAICM) [213].

Having already generated various inventions and patents, nanotechnology has the opportunity to provide solutions to meet both basic and self-actualization needs being embedded in many industries such as food, medicine, cleaner water, fuel cells, solar cells, cleaning products, energy, environment, and health [209, 214, 215]. At the moment there are 8,878 nanoproducts manufactured worldwide of which 222 nanoproducts can be classified as nano-based products in agriculture [216]. Nanofertilizers account for 46% of these products in the agricultural sector [216]. Most nanotechnology-based products are currently manufactured in India, Germany, UK, USA and Vietnam [216]. In 2008 the market for nanotechnology was $7.6 billion [214]. According to Campos, 2021 the compound annual growth rate (CAGR) of the global nanotechnology market is expected to be 18% in the next decades, reaching $173.95 billion by 2025 [216]. The nanotechnology market in the agricultural sector is even expected to grow at a much higher CAGR of around 28% [216].

Since nanotechnology is a controversial technology and the number of nanotech-products in agriculture reaching market maturity is increasing, it is pivotal to analyze the risks, benefits, and drawbacks of the approach [217].

We first derive that there is an urgent need for action in agriculture to implement novel solutions for coping with current trends. Some of the UN 2030 sustainable development goals (SDGs) could be achieved through changes in agriculture practices. Nevertheless, missing the targets such as zero hunger, responsible consumption and production, and no poverty seems realistic in the face of 800 million people suffering daily from hunger in the world. Furthermore, forecasts assume that 8% of the world’s population will still be affected by hunger in 2030 [218, 219]. According to projections the world population will increase to 10 billion people by 2050 and could even reach 16.5 billion by the end of the century [218]. This makes achieving the SDGs in the field of agriculture currently seem improbable [218]. Thus, such a rapidly growing world population would lead to a 70% increase in food demand by the middle of the current century being reinforced by megatrends such as urbanization, which also increase the demand for processed food and meat, in particular [218]. There is no doubt that agriculture contributes considerably to climate change, with the global food system alone generating 21–37% of global greenhouse gases, with agriculture using approximately 37% of the land surface worldwide and with a contribution of 80% to the global deforestation activities [3, 218, 220].

It can be deducted that that all these negative effects on the global climate also in turn increasingly affect agriculture itself, such as decreasing yields, due to approximately 25% of farmland being highly degraded [218]. Such a vicious circle could be escaped by investing $160 billion in soil conservation and food control. However, given the aforementioned trends, it is clear that investments alone are not sufficient to solve the problems. Thus, innovations such as 3D printing of food, cultured meat, genetic modification and targeted drug delivery are

![Fig. 11. Time-dependent uptake of Coumarin 6-loaded PSI-NPs by grapefruit cells in suspensions. c represents cytoplasm; and n represents nucleus. Scale bar represents 20 μm [146].](image-url)
needed as disruptive catalysts for the industry [218]. After decades of underrepresentation of sustainable agriculture, the topic has also recently appeared on the agenda of international politics [220].

Under the right circumstances nanotechnology has the potential to create numerous new business models, change consumer behavior, and shift our agricultural system towards a greener economy [213, 221]. Even though the research and development status of the industry is partially limited by confidentiality, as early as 16 years ago by Lau-terwasser, already in 2005, major companies such as BASF, Monsanto and Syngenta were associated with nanotechnology research [222]. So far, some biotech startups and a few larger companies are exploring nanotechnology and encapsulation and developing fully biological, biodegradable and microplastic-free products in the fields of agriculture, pharmaceuticals, and cosmetics as a priority. That means that the usage of nanotechnology and biopolymer based nanocarriers in agriculture can lead to preservation of environmental health and biosafety, and improvement of farmer’s welfare due to increased crop yields [223]. However, few nanotechnology-labeled products are currently available on the market and found on the websites of major agrochemical companies [216, 222]. Most of the patents belong to large agricultural companies, but only a few products have already reached market maturity, as the companies seem to be waiting for future opportunities to commercialize their products [216]. It also seems that due to regulatory restrictions, they have distanced themselves from using the prefix "nano" [222]. In addition, numerous nanopesticides are described in the literature as nanotechnologies whose particle size significantly exceeds the ECHA’s official definition of 1 to 100 nanometers. Kah, 2015 suggests a definition which is not only based on size to avoid excluding many recent so-called nanoformulations and to not include harmless products such as microemulsions which have already been on the market for decades. She brings up the idea of calling those products nano-enabled or formulation technology [222].

With respect to the agricultural sector, nanotechnology is able to minimize the aforementioned dilemmas with relation to human health.

Fig. 12. a) Schematic Illustration of the PGA Nanoparticles as Targeted Nanocarriers of the Fungicide FLU and the Proposed Carrier-Mediated Transport to Plant Phloem. b) Uptake and phloem transport of the PGA nanoparticles in castor beans. A) Concentration of FLU in phloem sap. The data are presented as the mean ± SE with 8 plants for each treatment (n = 8). B) Concentration of FLU in cotyledon tissues at the end of the experiment represented as mean ± SE (n = 8). The Kruskal–Wallis test was used to assess significant differences at the P = 0.05 level, and different letters indicated significant differences. ND, not detected. C and D) Cross sections of midveins were taken from cotyledons that were incubated without (control) 100 mg/L FITC-cad-labeled PGA nanoparticles. E and F: Cotyledons that were incubated with 100 mg/L of FITC-cad-labeled PGA nanoparticles. The arrowheads indicate the presence of FITC-cad-labeled PGA nanoparticles. EC: epidermal cells; MC: mesophyll cells; P: phloem; X: xylem. Scale bar =100 μm [204].

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The two: (A) untreated rice seedlings, (B) rice seedlings incubated with free Cy5, mizing nutrient losses in fertilization, and increasing yield through pest This is achieved by reducing the amount of spread chemicals, mini-

- environment while facilitating social and economic equity [224].  

- PLGA (Mw, 95 kDa) [208].  

- PLGA (Mw, 5 kDa) particles prepared by mPEG (Mw, 5 kDa)  

- bright field mode using white light, and the right rank was the superposition of  

- Plant root cross section imaging using confocal laser scanning mi-

- and environment while facilitating social and economic equity [224].  

- is achieved by reducing the amount of spread chemicals, mini-

- formulations [228].  

- and nutrient management [225]. Nanocarriers can be used to perfectly  

- achieve the delivery and slow release of nanoparticles which can be called “precision farming”. Hereby crop yields are improved without  

- damaging soil and water due to lower water solubility, and the dosage of  

- pesticides and fertilizers can be lowered without any loss of efficiency [226,227]. Sabourin and Ayande state that nanotechnology even has the  

- opportunity to transform the whole agri-food sector as it increases productivity, food security and economic growth by at least 30 % [214].  

- The multidisciplinary applications of nanotechnology in agriculture have shown relevant use cases and innovative products with new or  

- improved functional attributes in multifield areas of food science such as sensing, crop protection and reduction of pest-disease incidence, crop  

- management, food processing, food safety through improved packaging, and enhancement of food nutrition [223,227,228]. Additionally, agric-  

- and viticultural machinery [223]. The research of nanotechnology comprises multiple disciplines such as materials science, physics, chemistry, biology, mathematics and eningeering [229]. But its  

- multidisciplinary character is also caused by the fact that single scholars are just not able to handle innovation on their own which implies that complementary skills of individuals, companies and other stakeholders such as universities, and public policy agents are needed [211,230].  

- Looking at nanopesticides, the market is segmented into product type, application, end-user, and region whereas the different product  

- types comprise of insecticides herbicides, fungicides and nematicides [221]. The global nanopesticide market is expected to grow at a signif-

- icant compound annual growth rate (CAGR) of 14.6 % from 2020–2027 [221]. Bratovic states that nanoagrochemicals can improve the toxicity of  

- pesticides to their target pest up to 20 % compared to their conventional analogues, whereas nanofertilizers increase crop production by 20–30 % compared to conventional fertilizers, which are considered to be rather inefficient [221,232,233]. Nanofertilizers are also more effective than conventional fertilizers because their small  

- dimensions ensure that they are able to penetrate through the pores to get the nutrients to the interior places of the plant where they are needed such as the leaves, stems or roots [227,228] Moreover, nanofertilizer surfaces can be designed in a way that adhesion to the plant surface is  

- amplified, resulting in less leakage and pollution. It is further possible to combine types of fertilizers and / or pesticides into one nanobased formulation [228].  

- This advantage could be used to reduce environmental contamination as well as costs while improving the quality and quantity of the yields. However, the efficacy of nanofertilizers depend on the doses and varies from plant to plant [232]. Using foliar spray of zinc in pomegranate increased the fruit yield by 17–44 % which leads to the conclusion that nanofertilizers can improve the socioeconomic status of the farmers [232]. A study mentioned by Dimpka & Bindraban, 2017 investigated the generated profit when using nanofertilizer to treat
eggplants compared to a conventional analog [234]. They showed that eggplants being foliar fertilized with an equal dose of bulk CuO, which costs $18.5 per bottle and nano CuO ($44 per bottle), the yield increased over two years by 17 and 31 % and by 45 and 58 %. They calculated this using 3,500 plants per acre and concluded that in this case nano Cu fertilizer could generate a profit of $4,637 compared to conventional Cu fertilizer [234,235]. McClemens, 2020 also stated that the higher investment pays off offset as in an example an additional spending of $26 per acre for a nanofertilizer resulted in increased watermelon yields by ca. $4,600 per acre [228]. This clearly shows that nanotechnology in agriculture has a great role in creating income for farmers; however, nanofertilizers have not yet gained momentum to unfold their full potential compared to conventional fertilizers and the scientific community and government will only legalize the use of them under strict permissible and safety measures [232].

Nevertheless, there are a couple of environmental, economic, and social drawbacks of nanotechnology such as toxicological risks to human health and environment, unclear regulation, legislation, market adoption, and acceptance which could complicate or even prevent successful commercialization of biopolymer-based nanoformulations [213,226]. Some metal nanoparticles are known for their toxicity, yet are used for their antimicrobial activities. These include TiO$_2$, AgO, CuO, Fe$_3$O$_4$ and ZnO. On the other hand, biopolymer-based nanoparticles represent a less harmful alternative [236]. Those nanocomposites from natural polymers have a large surface area and an enhanced porosity essential for cellular adhesion and can be functionalized with bioactive molecules to enhance tissue regeneration [236]. This makes case-by-case approaches inevitable regarding the risk assessment, while also creating a major barrier to nanotechnology: for customers without background knowledge, the subject is opaque, which can reinforce a critical attitude. Regarding this aspect, Gauthier mentioned that resistance to nanotechnology could be managed by the industry making sustainability an official goal on the agenda, and by communicating differently by focusing on the efforts to develop sustainable products which can solve environmental problems [212].

| Environmental | Potential Risk / Drawback |
|---------------|--------------------------|
| Reduction of greenhouse gases and spraying | Toxicological risk for environment [213,226]. |

(continued on next column)
There are several environmental drawbacks and risks of nanotechnology in agriculture. As already mentioned, poor knowledge exists about toxicity and risks of novel nanotechnology in agriculture. This is particularly true for in vivo toxicity, as data is particularly sparse [226]. He et al., 2019 identified toxicity to mammal cells, migration of nanomaterials to food, degradation and bioaccumulation of nanomaterials as major gaps to be filled [226]. Multiple studies concluded that free radical formation can be triggered by certain nanoparticles [227]. As for instance metal based nanofertilizers are taken up by plants in large quantities, the formation of reactive oxygen species (ROS) may be initiated. Their accumulation in plant cells can lead to inflammatory reactions, tissue changes, neuron and DNA damages, etc. [226,227]. Damage from metal ion release and allergic reactions are also possible implications while their intensity depends on the concentration and frequency of interaction [226] Pandey et al., 2018 report that scientific studies have established toxicity of some nanoparticles (e.g., for human health) and therefore recommend strict regulations to ensure manufacturers correctly represent the composition of their developed nano-formulation [239].

Moreover, there are several economic obstacles for the industry to overcome to unleash the technology’s enormous potential. In 2015, Kah stated that agriculture was a low profit industry, which intensifed not only the regulatory but also the social acceptance of nanotechnology based products [222]. First, the interdisciplinary nature of the field has several implications for the importance and complexity of collaborations between science and business [237]. With even more stakeholders being involved, closer collaborations among government, academic and industry players are needed to lower the high costs and, therefore, increase the scalability of nanomaterials in the agricultural sector [213].

New market entrants either have the option to position themselves in the existing market and thus pursue a red ocean strategy or to seek a new market pursuing a blue ocean strategy [238,240]. Both cases will lead to significant structural changes in the agribusiness sector. It will be necessary for managers to be increasingly vigilant and alert to recognize the new competition and respond with appropriate measures such as strategic approaches and appropriate leadership [214]. The potential uses of e.g. nanofertilizers are expected to create resistance in the fertilizer industry because of the disruptive character of the technology [232]. Challenges, especially regarding the commercialization of nanotech products, are the time lag between research, completion, and commercialization, which can be three to five years, as well as bureaucratic delays with respect to patent policies, leading to funding problems. As the costs for commercialization are rather high, funding is crucial, but it also prevents many scientists from commercializing their inventions individually [238]. High costs for research and development also lead to high costs of nanobased products such as fertilizers compared to their conventional equivalents which is another barrier [227]. In addition, a lack of infrastructure and qualified professionals, unified voice and organized framework, and little public support for start-ups, further complicate commercialization [219,238]. Since many papers report on nanotech products on a laboratory scale, there is no doubt that upsampling is a major barrier to overcome [219]. This is also caused by the absence of standardization of formulation processes [227]. Regulation and safety concerns as well as consumer acceptance are crucial for the technique, and will decide the success or failure of nanotechnology in agriculture [238]. For example the wine industry, as a sub-sector of agriculture, is extremely vulnerable to the variability of climate and its consequences such as economic losses because the wine quality is highly dependant on the climatic conditions [241]. Currently, the industry only commands a few adequate adaptation strategies to avoid losses in product quantity, quality and sales, such as specialization and adoption of drought-resistant grape varieties [6]. Further research will be needed to show how biodegradable nanocarriers introduced by Fischer et al., 2019 can be commercialized and solve the problems such as esca disease and how winemaker’s willingness to buy will be [134].

This leads us to social drawbacks of nanotechnology in agriculture. According to Walz et al., trust is extremely important in consumer acceptance [242]. A lack of transparency would lead to less consumer acceptance, which in general will vary by area of application and will decrease the closer nanotechnology products are related to the human body [219,226].

Transparency would benefit from a comprehensive life cycle assessment (LCA) of nanotech-based agrochemicals as nanotechnology is currently researched along the whole spectrum of food technology and is used for is various practices in agriculture such as production, processing, storage, and distribution [243]. To be more precise, engineered nanomaterials are used as fertilizers, pesticides, and growth regulators which are products related to human consumption that have already been considered by the community. This fact reinforces the necessity of a proper LCA, which is a systems-level tool to evaluate the benefits and risks of products looking at different stages of their lifecycle, before using such direct applications on a large scale [244]. However, Pourzabedi et al., 2018 identified several challenges that arise when assessing the life cycle of engineered nanomaterials such as defining functional units, limited available data on industrial scales to develop LCA-inventory, necessity of data about human and environmental exposure, and spatial and temporal component’s effects on LCA. They consider the area of raw material extraction as well studied, whereas the data gaps are widening when focusing nano-enabled agrochemical production and crop protection [244].

In terms of public perception, the plant protection industry is concerned that a scenario similar to that of genetically modified organisms could repeat itself with nanotechnology-based products [222]. He et al., 2019 stated that public awareness and acceptance were often ignored by food manufacturers even though they are crucial factors [228,246]. They mentioned an example of silver nanoparticles, which were added into packaging materials due to their antimicrobial characteristics without informing the customers which has worsened their perception [226]. As a result of those ethical and regulatory implications, a mandatory labeling was introduced. The ignorance of manufacturers was further supported by a hyperlink analyst, showing parts of the scientific community have treated the social aspects of nanotechnology whereas commercial developers tend to be more reluctant to do so [243,245]. In addition, there is likelihood of confusion between genetically modified food and nanotechnology-based food due to inadequate access to information [228,247]. In general, there are large research gaps in the social field, and case- or product-specific individual research of perception and market adoption is recommended [228,125].

5. Conclusions and Outlook

This review highlights the importance of biobased polymer nano-carriers as platforms for sustained release of agrochemicals. The use of biopolymers provides targeted delivery of various actives necessary to ensure management of plant pathogens, enhanced plant growth, and efficient nutrition. Nanoformulations are associated to many advantages such as safer handling, efficient uptake of fertilizers, increased eco-protection, reduced biotic stress, reduced run-off and soil contamination, pest resistance circumvention. Nonetheless, the material inside of which agrochemical actives are encapsulated are just as important to achieve sustainable agriculture. Many polymers used in the current microcapsule technology are either recalcitrant materials that might accumulate within the plants and in the soil, or petrol-derived materials that contribute negatively to the carbon cycle.

Biopolymers represent environmentally friendly and economically promising alternatives comprising several advantages commonly related
to green materials as worldwide availability, renewability, inexpensive, biodegradability, and low toxicity to the environment which enables the integration of these materials into the biogeochemical cycles. Although biobased polymers being a promising alternative for sustained release systems in agriculture, works in the literatures has been focused mainly on chitosan. However, lignin and cellulose possess a high potential of application in agriculture; in addition, few works with carbohydrates nanocarriers such as starch, alginlate and pectin and other biodegradable polymers such as PCL and PLA have been also developed. Biobased polymer nanocarriers loaded with pesticides are able to treat plant diseases caused by various pathogens such as fungi, insects and weeds, while fertilizer release systems increased the uptake of nutrients by the plants and efficiently treated nutrient deficiency. Moreover, there are numerous administration strategies such as foliar spray, trunk injection and addition to the soil, some formulations presented increased adhesion to crop foliage providing resistance to run-off by precipitation. Nanocarriers comprised of biomimetic materials such as lignin and cellulose enable the stimuli-responsive release of actives towards enzymatic degradation of the biopolymeric shell and thus treat crop infections for years with reduced amount of fungicides.

Several studies have been reported the transport of nanoparticles with the plants and the alterations in phytophysioglogy cause by nanoparticles, which as important aspects that must be investigated systematically. Furthermore, regardless of the consideration by many scientists of nanocarriers for sustained release of agrochemicals as an environmentally safer alternative to bulk formulations, nanomaterials biosafety, adverse effects, fate in the environment, and food safety must be investigated in view of the limited knowledge gathered regarding these concerns. Some scientific efforts to assess possible nano-agricultural risks have been applied to comprehensively study the eco-toxicology of nanotechnology in agriculture and identify physico-chemical features affecting nanomaterial toxicity hazards for workers, the environment, and the final costumer of agricultural products.

Agricultural applications of nanocarriers, and nanotechnology in general, are often neglected in favour of biomedical applications, which also is also enormously benefited by the advantages achieved with nanotechnological solutions and, in addition, ensures higher impact to publications. Despite of the lack of exploration of biobased polymer nanocarriers even and nanocarriers in general for agricultural purposes, there is some solid research being conducted in the field. The economic potential and success of commercialization of biopolymer based nanocarriers and even nanocarriers in general for agricultural purposes, also is also enormously benefited by the advantages achieved with potential and success of commercialization of biopolymer based nano-materials in the environment and evaluate their impact on human health which enables the integration of these materials into the biogeochemical cycles. Although biobased polymers being a promising alternative for sustained release systems in agriculture, works in the literatures has been focused mainly on chitosan. However, lignin and cellulose possess a high potential of application in agriculture; in addition, few works with carbohydrates nanocarriers such as starch, alginolate and pectin and other biodegradable polymers such as PCL and PLA have been also developed. Biobased polymer nanocarriers loaded with pesticides are able to treat plant diseases caused by various pathogens such as fungi, insects and weeds, while fertilizer release systems increased the uptake of nutrients by the plants and efficiently treated nutrient deficiency. Moreover, there are numerous administration strategies such as foliar spray, trunk injection and addition to the soil, some formulations presented increased adhesion to crop foliage providing resistance to run-off by precipitation. Nanocarriers comprised of biomimetic materials such as lignin and cellulose enable the stimuli-responsive release of actives towards enzymatic degradation of the biopolymeric shell and thus treat crop infections for years with reduced amount of fungicides.

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Since the concept of nanotechnology was coined in the 60s, it has been developed at a hasty pace and one can anticipate the utilization of nanocarriers in agriculture at a large scale within the next couple of decades, and thereby promoting sustainable agriculture with minimum use of agrochemicals as to protect the environment and human health. In principle, international legislation, a standardized definition of nanotechnology and nanomaterials, and a method to track nanomaterials in the environment and evaluate their impact on human health should be developed to overcome the aforementioned challenges of nanotech-based product adoption [216].

Declaration of Competing Interest

None.

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