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Recent Advances on Lignocellulosic-Based Nanopesticides for Agricultural Applications

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Controlled release systems of agrochemicals have been developed in recent years. However, the design of intelligent nanocarriers that can be manufactured with renewable and low-cost materials is still a challenge for agricultural applications. Lignocellulosic building blocks (cellulose, lignin, and hemicellulose) are ideal candidates to manufacture ecofriendly nanocarriers given their low-cost, abundancy and sustainability. Complexity and heterogeneity of biopolymers have posed challenges in the development of nanocarriers; however, the current engineering toolbox for biopolymer modification has increased remarkably, which enables better control over their properties and tuned interactions with cargoes and plant tissues. In this mini-review, we explore recent advances on lignocellulosic-based nanocarriers for the controlled release of agrochemicals. We also offer a critical discussion regarding the future challenges of potential bio-based nanocarrier for sustainable agricultural development.

Keywords: nanopesticides, biopolymers, lignocellulosic materials, nanotechnology, nano-enabled agriculture, sustainable agriculture, circular bioeconomy

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INTRODUCTION

The development of environmentally friendly tools that can produce crops or livestock without negative impact on humans and the environment is central to the Sustainable Development Goals. Nowadays, with the development of nanotechnology, researchers are obtaining good outocomes using nanomaterials (NMs) (Mattos et al., 2017; Guo et al., 2021; Sikder et al., 2021). For instance, engineered nanoparticles (ENPs) are capable of improving the efficiency of pesticides and fertilizers through the controlled release of agrochemicals, as well as by providing enhanced plant performance or by enabling plants to act as real-time sensors, actuators, or electronic devices (Baker et al., 2017; Saleem and Zaidi, 2020; Agathokleous et al., 2020; Acharya and Pal, 2020; Usman et al., 2020; Singh et al., 2021; Grillo et al., 2021a). The increased surface area to volume ratio of the ENPs enables a greater control of interfacial interactions with a given cargo to act on demand or specific stimuli as well as many other features. Besides, several factors such as surface charge, particle size, composition, solubility, and manufacturing methods can be exploited to control the interaction of ENPs with specific plants and organisms (Jogaiah et al., 2021), with the goal of developing targeted systems. Although most of the current nanopesticides or nanocarriers

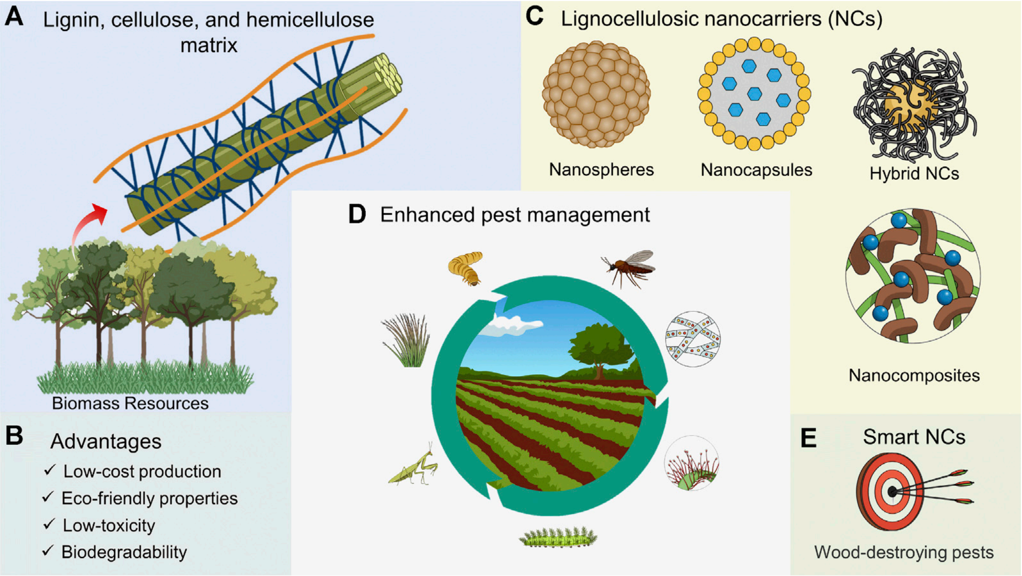

FIGURE 1 | Schematic representation of a **(A)** lignocellulosic building blocks matrix, **(B)** advantages to produce, and **(C)** different types of nanopesticides that can **(D)** enhance pest management (e.g., weeds, viruses, bacteria, fungi, and insects) as well as display unique properties such as **(E)** targeting wood-destroying pests.

are developed from synthetic (e.g., polymers) building blocks, several systems have been developed using biopolymers as tools for the controlled release system of agrochemicals (Mattos et al., 2017). Lignocellulosic-based nanopesticides are biodegradable and offer an interesting platform to produce safe-by-design nanopesticides as they can be non-toxic (Chamundeeswari et al., 2019; Zhang et al., 2019; Bhattacharyya et al., 2020; Shrestha et al., 2021; Ur Rahim et al., 2021) (**Figure 1**). Moreover, lignocellulosic material can be obtained from agriculture side streams, which is ideal to reduce costs during the production of nanopesticides, which are intended to be applied in large scale agricultural operations. This strategy also indicates a *from plant-to-plant* effort, ideal for a circular bioeconomy landscape.

There are mainly three non-edible lignocellulosic biopolymers that have been used in the development of materials: cellulose, lignin, and hemicellulose, along with pectin, tannins, acids, and proteins (Okolie et al., 2021). Even though the manipulation of its feedstock is challenging to engineer, lignocellulosic materials have low-cost production and eco-friendly properties (Li et al., 2021a). Although lignocellulosic-based nanocarriers are still under development for the agricultural sector, several advances have been achieved thus making this technology useful for nano-enabled agriculture. The increased use of lignocellulosics in nano-enabled agriculture is expected to take place because there are new technologies that can 1) increase the extraction efficiency of lignocellulosic materials; 2) modify lignocellulosic structures for desired properties; and 3) design hybrid nanostructures with controllable shape and size. Nonetheless, the application of lignocellulosics in nano-enabled agriculture is currently related to the controlled delivery and release of pesticides and nutrients (Worrall et al., 2018; Papadopoulos et al., 2019; Chen et al., 2020a; Teo and Wahab., 2020). However, lignocellulosic nanomaterials could potentially stabilize emulsions (such as those used in oil borne pesticides) instead conventional surfactants in multiphase systems (Tardy et al., 2021). In this review we summarize and discuss the recent advances in lignocellulosic nanocarriers for agricultural applications; in addition, we offer a critical discussion regarding the future challenges of lignocellulosic nano-enabled materials for sustainable agricultural development.

TYPES OF LIGNOCELLULOSIC-BASED NANOPESTICIDES FOR AGRICULTURE

Cellulose-Based Nanopesticides

Cellulose is a linear polymer composed of several hundreds of glucose units linked by β-1,4-glycosidic bonds (**Figure 2A**). Cellulose is highly abundant, being sourced from agro-industrial biomass (from 1st generation to wastes and residues), marine biomasses, and microorganisms. (Kaya and Tabak., 2020; Siqueira et al., 2020; Teo and Wahab., 2020; Bahloul et al., 2021). Cellulose nanomaterials have been marketed in several sectors of the economy, including agriculture. However, cellulose intra- and intermolecular hydrogen bonding interactions hinder its dissolution in water although being highly hydrophilic (Credou and Berthelot, 2014; Shatkin and Kim, 2015). Therefore, several studies have focused on the chemical modification of cellulose using a variety of routes to modify its physicochemical properties, enable dissolution, and therefore to facilitate the conception of nanocarriers that can be applied for improving agrochemical efficacy (Rop et al., 2020; Machado et al., 2021). For instance, dialdehyde carboxymethyl cellulose (DCMC) and carboxymethyl cellulose (CMC) were conjugated with zein (a protein from corn) to develop nanocarriers for avermectin (Chen et al., 2020b; Hao et al., 2020). In both cases, the resulting nanopesticides showed high

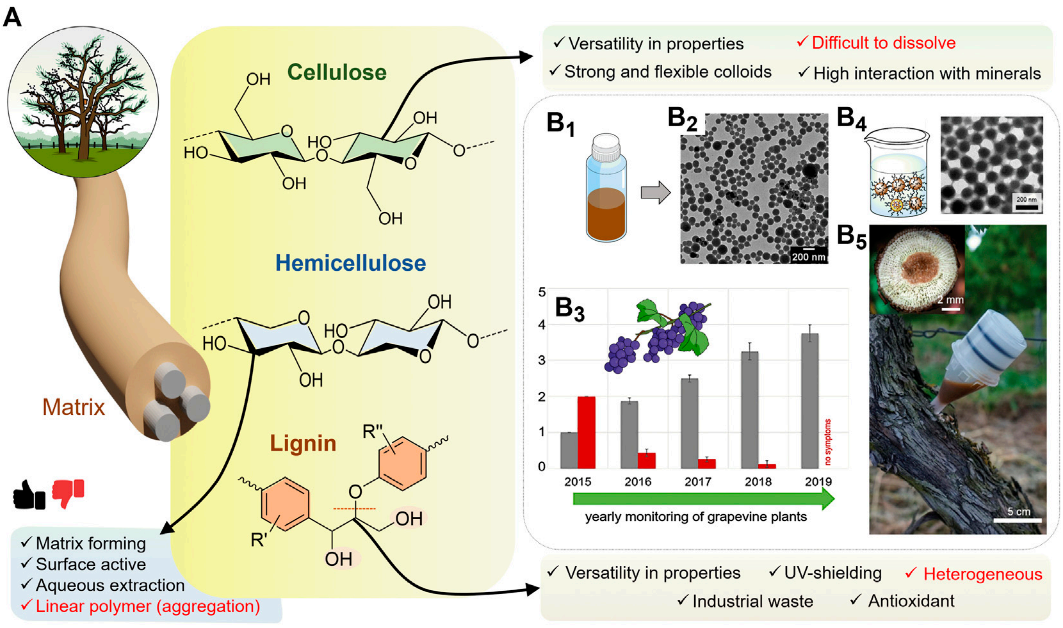

FIGURE 2 | (A) Types of lignocellulosic materials (cellulose, hemicellulose (e.g., xylan) and lignin) pointing out their main advantages (black) and disadvantages (red). **(B1)** Representation of a formulation containing lignin nanoparticles. **(B2)** Transmission electron microscopy image of pyraclostrobin-loaded lignin nanoparticles in the range of 100—300 nm. **(B3)** Effect of empty lignin (gray bars) and fungicide-loaded lignin (red bars) NPs on Esca leaf symptoms in four Portugieser grapevine plants monitored yearly from 2015 to 2019. **(B4)** Transmission electron microscopy image of fungicide-loaded lignin NPs. **(B5)** Lignin-based fungicide-loaded NPs being applied in a grapevine plant to target Esca. **(B2,B3)** were reproduced with permission from Machado, 2020, Copyright (2020) American Chemical Society, and **(B4,B5)** were reproduced with permission from Machado, 2020, Copyright (2019) John Wiley and Sons. Further permissions related to the material excerpted should be directed to the ACS and John Wiley and Sons.

leaf adhesion as well as efficient protection of the active ingredient against ultraviolet light (UV) when compared to its conventional form. Avermectin has been also encapsulated in CMC-grafted polyethyleneglycol (PEG) nanoparticles (Zhu et al., 2020) and in CMC grafted poly 2,2,3,4,4,4-hexafluorobutyl methacrylate (PHFBA) (Su et al., 2021a); both showed enhanced insecticidal activity against fall webworm (*Hyphantria cunea*) and an improved of the release profile of the active ingredient for 95 h, respectively. Additionally, glycine methyl ester (GLY) and glycidyl methacrylate (GMA) were used as intermediate and organic nitrogen sources, respectively, to modify CMC during the synthesis of a nanopesticide containing emamectin benzoate. Such nanopesticide and nanofertilizer increased the insecticidal activity against the diamondback moth insect (*Plutella xylostella*) and showed a potential system to be used as organic nitrogen fertilizer without toxic effect on seed germination (Zhao et al., 2021a).

On the other hand, nanoparticles crosslinked by cellulose have received an increased attention in the agricultural sector due to their good stability under environmental conditions (Sun et al., 2020). For instance, stimuli-responsive nanocapsules based on cellulose modified with fatty acid (undec-10-enoic) loaded captan and pyraclostrobin were developed against apple canker (*Neonectria ditissima*), and the results showed that the active ingredients were released when triggered by the presence of cellulolytic fungi (Machado et al., 2021). Another study showed the fabrication of carboxymethylcellulose sodium salt and hydroxyethyl cellulose-based biodegradable hydrogels using citric acid (CA) as a crosslinker; good water uptake and a sustainable release profile were observed (Das et al., 2021).

A mixture of (nano)cellulose with inorganic (nano)materials (for example clays) opens up strategies for the design of nanopesticides with a widened pallet of biological, thermal, and structural properties. For instance, carboxymethyl cellulose hydrogels filled with nanocellulose and nanoclays (Bauli et al., 2021) or cellulose-g-poly (ammonium acrylate-co-acrylic acid)/nano-hydroxyapatite (Rop et al., 2020) showed good efficiency on hydrogel nutrient release and improved the moisture retention around the plant in the soil. Furthermore, a hybrid nanopesticide composed of hollow mesoporous silica/hydroxypropyl cellulose was reported to control rice blast fungus (*Magnaporthe oryzae*), and a dual-responsive release profile of the active ingredient was observed when in presence of cellulase (enzyme) or under acid conditions (Gao et al., 2021a). Moreover, layered double hydroxides (LDH) were mixed with CMC to fabricate polymeric nanocomposite able to mitigate the downside effect of herbicides in paddy cultivation (Sharif et al., 2021). In addition, they observed high adhesion of nanocellulose towards hydrophilic surfaces has led to the development of biogenic nanohybrids containing biogenic silica and cellulose nanofibers for the encapsulation of various molecules including a biopesticide (thymol) (Mattos and Magalhães, 2016; Mattos et al., 2018).

TABLE 1 | Examples of lignocellulosic-based nanopesticides.

Lignocellulosic-based materials	Composition	Size (nm)	Agrochemical	Findings	References
Cellulose	Sodium carboxymethyl cellulose grafted by styrene/methyl methacrylate and butyl acrylate	180–280	Avermectin	Anti-ultraviolet photolysis ability of the active ingredient was improved and the release time was prolonged	Chen et al. (2018)
Cellulose	Myrtenal-based nanocellulose/diacylhydrazine	—	Boscalid and chlorothalonil	Complexes exhibited comparable or better antifungal activity than the commercial one against several fungi	Li et al. (2021c)
Lignin	Sodium lignosulfonate/poly (vinyl alcohol)-valine	~10	Emamectin benzoate	Higher bioactivity of nanogels compared to non-nanoformulations	Zhang et al. (2021b)
Lignin	Sodium lignosulfonate	162	Pyraclostrobin cyclohexanone	Nanocapsules improved control efficacy on tomato crown and root rot compared to micro- and other nanoformulations	Luo et al. (2020)
Lignin	Sodium lignosulfonate/epoxy resin	150	Abamectin	Higher efficiency to control root-knot nematodes (*Meloidogyne incognita*) compared to conventional agrochemicals	Zhang et al. (2020b)
Lignin	Sodium lignosulfonate	150–250	Emamectin benzoate	Nanopesticide improved the photostability of the active ingredient, as well enhanced the insecticidal activity against *Prodenia. Litura* (leafworm) when compared to the commercial formulation. Nanopesticide also exhibited pH-mediated release property	Cui et al. (2019)
Xylan	Lignin/xylan	166–210	Avermectin	Lignin–xylan hybrid nanospheres showed well-defined core-shell structures with encapsulation efficiency above 57%. Nanopesticide also showed enzyme-mediated release property	Jiang et al. (2020)
Tannic Acid	Fe^{3+}/tannic acid	141–160	Tebuconazole	Nanocapsules showed high fungicidal activities against rice sheath blight (*Rhizoctonia solani*) and wheat head blight (*Fusarium graminearum*) pathogenic fungi	Dong et al. (2021)
Tannic Acid	Mesoporous silica nanoparticles/copper/tannic acid	137	Pyraclostrobin	The complexes coating could improve the photostability of the active ingredient, as well enhanced deposition efficiency on rice leaves with good antifungal activity against Rhizoctonia solani	Liang et al. (2021)
Abietic acid	Carboxymethyl celulose/glycidyl methacrylate/rosin	167	Avermectin	Nanopesticide displays enhanced dispersibility and stability of the active ingredient, and improves the affinity and light stability on cucumber leaf, maintaining good insecticidal activity against *Plutella xylostella*	Zhao et al. (2021b)
Salicylic acid	p-amino salicylic acid-modified polysuccinimide	155–290	Avermectin	Aqueous nanopesticides showed a cumulative release rate of 70% with a pH-responsive profile. It was also reported to have good insecticide activity against *Plutella xylostella*	Su et al. (2021c)

The difficulty of promoting dissolution of cellulose, in parallel with the current regulation on bioplastics that defines cellulose derivatives as plastics, will accelerate the development of nanocarriers from cellulose colloids, such as cellulose nanofibers, which have unique physicochemical properties such as higher surface area, nanodimension, high-temperature resistance, and biocompatibility (Shahi et al., 2021; Tardy et al., 2021). Cellulose nanofibers (CNFs) have been reported as potential high performers in nanoformulations of fertilization (do Nascimento et al., 2021), as well as cellulose nanocrystals (CNC) with chitosan to control tomato bacterial speck disease (Schiavi et al., 2021), among others (**Table 1**). For its diversity and abundance, cellulose is an outstanding material with a list of properties yet to be explored as a nanopesticide thus, understanding better its composition and potential interactions with agrochemicals and non- target and target organisms is essential to the future design of sustainable nano-enabled agriculture.

Lignin-Based Nanopesticides

Lignin is a three-dimensional and complex aromatic biopolymer that is bound to cellulose and hemicellulose within the plant cell wall microstructure (**Figure 2A**). Furthermore, it has attracted great attention due to its availability at large scales (Lizundia et al., 2021). In the last years, lignin-based nanoparticles (LNPs) have been used in agriculture against fungus, and insects due to their eco-friendly properties, low cost, and good encapsulating properties; however, this formulation is insoluble in the aqueous environment, which raises some technical difficulties when producing nanocarriers or promoting cargo delivery. Nevertheless, production of LNPs has been demonstrated to be possible for upscaling at reasonable cost (Abbati de Assis et al., 2018; Bangalore Ashok et al., 2018). For instance, stem lignin nanoparticles have been used as matrix in the controlled release of the herbicide diuron (Yearla and Padmasree, 2016). Chemical modifications in lignin to control their interactions with water and solubility (Balakshin and Capanema, 2015; Agustin et al., 2019; Falsini et al., 2019; Ma et al., 2020; Machado et al., 2020), also facilitate their use in nano-enabled strategies for agriculture. For instance, sodium lignosulfonate can electrostatically interact with other polymers [e.g., chitosan (Li et al., 2019)], and cationic surfactant [e.g., dodecyl dimethyl benzyl ammonium chloride (Zhang et al., 2021a), cetyltrimethylammonium bromide (Peng et al., 2020)] by self-assembly to form stimuli-responsive nanopesticides (**Table 1**). Kraft lignin (KL) has a tunable amphiphilic nature due to the abundant phenolic hydroxyl groups capable of forming a stable double-layered nanomaterial with ionic surfactants (Ela et al., 2020), nanocapsules with olive oil (Falsini et al., 2020), and is also able to chelate cationic metals (Sipponen et al., 2017). Other nanopesticides have also been synthesized with alkali lignin (AL) (Yin et al., 2020), organosolv lignin (Zhang et al., 2020a), and methacrylate lignin (Yiamsawas et al., 2021).

In this regard, some interesting studies have been using lignin nanoparticles for the controlled release of fungicide to target Esca (a type of grapevine trunk disease that negatively impacts grape yields and the wine industry around the world). For instance, Machado et al. (2020) developed several fungicide-loaded lignin nanocarriers (**Figure 2B$_{1,2}$**) to be applied in a single injection into *Vitis vinifera* ("Portugieser") plants, and the results showed successfully inhibition of lignase-producing fungi (e.g., *Phaeomoniella chlamydospora* and *Phaeoacremonium minimum*) as well as fungicide efficiency for at least 4 years against Esca (**Figure 2B$_3$**). Furthermore, two other stimuli-responsive lignin-based nanocarriers were developed for the treatment of Esca (Fischer et al., 2019; Peil et al., 2020). In both studies, the fungi associated with Esca degraded lignin through secretion of ligninolytic enzymes (e.g., laccases and peroxidases) and, thus, released fungal spores (*Trichoderma reesei*) (Peil et al., 2020) and the hydrophobic fungicide pyraclostrobin (Fischer et al., 2019) loaded in lignin nanocarriers (**Figure 2B$_{4,5}$**). Moreover, another triggered strategy is based on the controlled release of micronutrients , such as copper and iron, to fertilize and protect plants against various pathogens (Gazzurelli et al., 2020; Li et al., 2021b).

Despite the development of numerous lignin-based nanocarriers for agriculture, the great challenge of these nanoformulations is still the complexity and variability of chemical structure of this resource given the batch-to-batch variations in the extraction process. In this context, studies such as those by Beckers et al. (2021) have been important as it is possible to synthesize lignin-like monomers (e.g., phenylcoumaran and β-O-4-aryl ether) able to comprise linkages found in native lignin with promising results. Nevertheless, lignin-first biorefining approaches have recently been proposed to produce well-defined lignin structures that can be further utilized in a more systematic way (Lourencon et al., 2019).

Hemicellulose-Based Nanopesticides

Hemicellulose is a biopolymer with a degree of polymerization of ca. 50–200 and molecular weight below 90 kDa, thus a much smaller building block when compared to cellulose or lignin (Ye et al., 2021). Hemicelluloses represent 15–25% of the wood cell-wall but can reach up to 45% in annual, seasonal plants. Such biopolymers include xyloglucans, xylans (**Figure 2A**), mannans and glucomannans, and beta-glucans. A wide range of applications has been associated with hemicellulose, such as the generation of chemical products, packaging materials, drug delivery systems, and more recently as pesticide delivery systems (Naidu et al., 2018; Wijaya et al., 2021). The extraction of hemicellulose comes from lignocellulosic biomass, wood, foliage, grass, and agricultural residues and can be carried out using organic solvent but more commonly with hydrothermal extractions (Naidu et al., 2018).

Due to the low water solubility of hemicelluloses, there are still some challenges to produce stable hemicellulose-based nanocarriers for the controlled release of agrochemicals. However, several examples have been demonstrated in recent years. Beckers et al. (2020a) described the first synthesis of nanocarriers built from xylan extracted from corn cobs to contain the fungicide pyraclostrobin, by interfacial polymerization method of diisocyanate of toluene (TDI) in an inverse emulsion. Hence, such nanopesticide was colloidally stable in water and cyclohexane for several weeks as well as it was efficient against phytopathogenic fungi (*Botrytis cinerea*) as the biocide release from the xylan nanocarriers was stimulated by the fungi. In another study, xylan-based nanoparticles (without active ingredients) were fabricated and their antifungal effect was studied on corn husk fiber and on the high-density polyethylene (HDPE) composite. Such nanoparticles prevented the formation of hyphae in wood as well as increased the strength of the composite (Gao et al., 2021b). Additionally, lignin sulfonate-based nanocarriers containing hemicellulose residues showed potential for controlled delivery of agrochemicals such as the fungicides pyraclostrobin or prothioconazole (Beckers et al., 2020b). In addition, xylan-based nanoparticles are advantageous for their biocompatibility, biodegradability, and low-cost biological material (Beckers et al., 2020b). Recently, lignin-xylan and arabinoxylan nanoparticles were also reported as an enzymatic-responsive for pesticides release (Jiang et al., 2020) (**Table 1**) as well as a gene delivery system for CRISR-Cas9 DNA (Sarker et al., 2020), respectively.

β-Glucan is a homopolymer, an abundant class of polysaccharides in plants, fungi, and bacteria. Most recently, ß-Glucan-based nanocarriers have been extensively studied as drug delivery systems (Su et al., 2021b). For instance, Kaziem et al. (2022) developed a smart-delivery formulation based on carboxymethylated-β-glucans on the mesoporous silica nanoparticles (MSNs) surfaces after loading chlorothalonil (CHT) fungicide, with bioactivity against phytopathogens better than commercial formulation and lower toxicity to manure worm (*Eisenia fetida*) and zebra fish (*Danio rerio*). In another study with the same formulation, the authors observed that CHT@MSNs-β-glucans showed 2.6 times lower toxicity to the planktonic crustacean (*Daphnia magna*) and also exhibited lower effects on soil microbial abundance than commercial chlorothalonil (Kaziem et al., 2021), which improves its use as a nano-enabled agrochemical.

Other Lignocellulosic Materials-Based Nanopesticides

Other lignocellulosic materials, even in minor quantities, are rising in agriculture as compounds of nanocarriers. Pectin (Pec), a structural compound present in the primary cell walls of higher plants has been applied for the development of nano-enabled delivery systems for agrochemicals. Pectin has been used to configure an intelligent stimuli-responsive carrier triggered by pectinase, an enzymes produced by plants, filamentous fungi, bacteria, and yeasts. Moreover, a hybrid system comprising mesoporous silica nanoparticles and pectin (MSN-Pec) could delivery prochloraz (a fungicide) slowly, showing potential to be used in rice crops (Abdelrahman et al., 2021). Pectin-based nanocarriers showed promising behavior to mitigate drought stress in plants of arid and semi-arid environments (Sharma et al., 2017). Carbendazim-loaded chitosan-pectin nanoparticles showed a good response against pathogenic fungi *Fusarium pxysporum* and *Aspergillus parasiticus* (Kumar et al., 2017). Composite systems, such as chitosan/tripolyphosphate/pectin nanoparticles, were reported as a delivery system for paraquat herbicide to reduce the toxic behavior to alveolar and mouth cell lines, as well as to enhance the herbicidal activity against maize and mustard plants (Rashidipour et al., 2019). Thus, the nanoencapsulation of paraquat improves its herbicidal activity and reduces its toxic and mutagenic effects (Grillo et al., 2015; Pontes et al., 2021; Rashidipour et al., 2021).

Tannins, especially tannic acid, have been used in nanopesticide formulations (**Table 1**) as an additive to promote better foliage adhesion of particulates (Yu et al., 2019; Zhi et al., 2020). The ability of tannins to promote multiple and diverse secondary interactions towards virtually any surface has warranted their utilization to modify nanocarriers surfaces while adding UV protection and antioxidant properties (both useful to increase the lifetime of the active ingredient) (Guo et al., 2016). Finally, acids such as rosin (abietic acid) and salicylic acid are used in the attempt to create efficient nanocarriers (**Table 1**) (Zhao et al., 2021b; Su et al., 2021c).

CONCLUDING REMARKS AND CHALLENGES AHEAD

Current research on the smart nano-enabled delivery systems for pesticides has opened a new way to view the stimuli-responsive controlled release of crop protectants and to the development of novel agro-technological products. Despite the complexity of biomolecules and the challenges on generating stable nanoformulations, lignocellulosic-based nanocarriers have shown promising features that can be further explored in advanced, and renewable nanocarriers for agriculture. These carriers display unique properties (e.g., targeting wood-destroying pests), low cost, and good biodegradability rate. However, the number of studies on the mechanism of action of these nanopesticides as well as their toxicity impacts in the environment is still very limited (Grillo et al., 2021b). Moreover, little is known about the biodegradation of biopolymers after their modification or compositing, which still restricts their wider utilization in large-scale platforms such as crop protection. Therefore, further research on lignocellulosic nanomaterials is necessary in order to improve the efficient use of biomass resources as well as achieving environmental sustainability in agriculture.

AUTHOR CONTRIBUTIONS

PL, DA, and MF writing, review and editing the manuscript, MP and BM review and editing the manuscript, and RG conceptualization, writing, review, editing and supervision the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.