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Review

The Exploitation of Nanotechnology in Herbicides and Bioherbicides: A Novel Approach for Sustainable Weed Management

Mirko La Iacona [1], Aurelio Scavo [2,*], Sara Lombardo [1] and Giovanni Mauromicale [1]

[1] Department of Agriculture, Food and Environment (Di3A), University of Catania, 95123 Catania, Italy; mirko.laiacona@phd.unict.it (M.L.I.); saralomb@unict.it (S.L.); g.mauromicale@unict.it (G.M.)
[2] Department of Veterinary Sciences, University of Messina, Polo Universitario dell'Annunziata, 98168 Messina, Italy
* Correspondence: aurelio.scavo@unime.it

Abstract: The growing global demand for food security requires a paradigm shift towards sustainable agricultural practices, particularly in weed management. Nanotechnology is emerging in agriculture as a useful tool to reduce the dosage and the negative effects of herbicides on the one side and to improve the bioherbicides efficiency on the other side. This review provides an in-depth analysis of the literature available on the topic, with particular reference to the main characteristics of nanoparticles for weed control and the main nanoformulations for herbicides and bioherbicides. Nanoformulations such as nanoemulsions, nanocapsules, nanospheres, silver nanoparticles and organic materials protect the active ingredients from environmental degradation and enable their controlled release, enhance foliar adhesion and facilitate the penetration into plant tissues while at the same time minimizing the off-target effects. The last paragraph reviews the recent advancements in the field of nanobioherbicides. Moreover, examples of nanoherbicide and nanobioherbicide application in laboratory, greenhouse and field conditions are collected and discussed. This review highlights the increasing efficiency and diffusion of nanoherbicides and nanobioherbicides, suggesting their introduction into sustainable and integrated weed management strategies. However, further research is still required to assess their effectiveness under natural conditions, improve their stability over time and study their bioaccumulation and toxicity toward non-target organisms.

Keywords: allelochemicals; nanoparticles; nanoformulation; nanoencapsulation; sustainability; weed control

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1. Introduction

According to the United Nations Department of Economic and Social Affairs [1], the world's population is expected to reach over 9.7 billion by 2050. Nowadays, about 50% of the global usable land is dedicated to agriculture [2]. To ensure food security for the increasing population, a 70% increase in agricultural productivity is required due to the challenges encountered by farmers, including raising temperature, water scarcity and pesticides, which are becoming more impacting as a consequence of climate change [2]. Among biotic factors, weeds cause the highest yield losses, esteemed in 20 to 50% (corresponding to a USD 32 billion per year economic loss) depending on their intensity [3]. Weeds are also considered one of the main threats to biodiversity in various agricultural systems as the changing climate creates conditions for the emergence of new invasive species that will impose a radical change in their ecological management [4]. Although several weed control methods are today available (cultural, mechanical, physical, biological and ecological), even with improved efficiency, synthetic herbicides are still the most adopted in both developed and developing countries [5]. Currently, about 4.2 million tons of pesticides are used annually in agriculture worldwide, of which the herbicide consumption touched 1.7 million tons [6]. However, the prolonged, intensive and indiscriminate use of synthetic herbicides posed serious risks to human and environmental health. The main issues related to herbicide application are the development of herbicide resistance in many weed species [7], the harmful effects towards nontarget organisms and the high persistence in plants, soils and groundwater [8,9]. From the study of Zhao and co-workers [10], it emerged that less than 10% of pesticides reach their targets, and only 0.1% stay long enough to exert a biological activity.

Given that these repercussions started appearing only in recent years, integrated weed management strategies are now trying to meet the objectives set by the Sustainable Use of Pesticides Directive in 2009, the Paris Agreement on climate change, the United Nations 2030 Agenda for Sustainable Development in 2015, the European Green Deal and the Farm to Fork strategy in 2019, which aim to reduce the use of hazardous chemical pesticides [11]. Various alternative strategies for weed management have, therefore, emerged around the basic principle that this problem demands a holistic approach based on the combination of different preventive and curative weed control methods within a context-specific weed management strategy [12]. Thanks to the efforts of the agrichemical industry, allelochemical-based bioherbicides have attracted interest due to their environmentally friendly chemical structure, high degradability, water solubility, etc. [13]. However, they still have low efficacy and high degradability in the field, which makes them a promising alternative to synthetic formulations for the future but a not-resolutive solution at present.

Nanotechnology is gaining popularity as an effective tool to improve the efficiency of bioherbicides and reduce the dosage and the negative effects provided by herbicides, together with the possibility of re-evaluating some banned active ingredients [14,15]. Many industries have been revolutionized by the use of nanotechnology, and agriculture is not an exception. These technologies promise to increase the efficiency and reduce the environmental impact in the field of the nanofertilization and control of weeds, insects and pathogens [16]. Nanoparticles (NPs) are classified as aggregates or components ranging from 1 to 100 nm, which have specific physical, chemical and optical properties compared to their bulk counterparts [17]. Electron microscopy and polymer engineering provide advanced tools for designing NPs with optimized characteristics for the controlled release of the active ingredients [18]. Nanoherbicides are a category of nanopesticides produced by using nanometer-scale techniques, exploiting the physical, physicochemical and chemical properties of nanomaterials [19]. Wilkins [20] firstly proposed natural nanomaterials like cellulose and chitin for this application. Recent research has expanded to include more complex structures such as metal–organic frameworks [21]. Moreover, NPs can be used to create structures called nanocarriers that allow the controlled release of active ingredients, a greater penetration into target plant tissues and a higher selectivity [22]. Despite there still not being a globally recognized criterion, nanopesticide classification is primarily based on the particle size [23]. Forini et al. [24] categorized nanoherbicides into organic nano-enabled herbicides (in which the active ingredient is encapsulated into organic nanocarriers), inorganic nano-enabled herbicides and hybrid nanostructures.

This review provides an overview on the recent advances in the field of nanoformulations for the improvement of herbicide and bioherbicide efficiency, analyzing the main types of nanoparticles and nanoformulations employed in weed control while also providing examples of applications. This article is structured into five main sections. Section 1 delves into the methodology adopted for the review. Section 2 discusses the main characteristics of NPs for weed control. Section 3 presents the main characteristics of organic and inorganic nanoformulations, while Section 4 is focused on the main nanoformulations. Section 5 discusses the new frontiers in nanobioherbicides. The last section concludes the review, summarizing the main findings and limitations on the application of nanotechnology to weed control and highlighting the possible future perspectives.

2. Methodology

To address the objectives of this review, the Preferred Reporting Items for Systematic Review and Meta-Analysis (PRISMA) methodology [25] was adopted, which shows clear guidelines and allows us to gather all the necessary information. We firstly conducted a preliminary search with the Google Scholar database to identify the main nanotechnologies and build the core idea. Then, the PRISMA protocol started with a bibliographic search that was carried out on the Scopus and Science Direct databases by using the following keywords: “nanotechnology” AND “weed management” OR “herbicide” OR “bioherbicides”. The keywords were strategically chosen to yield the maximum number of articles relevant to the scope of this review. In addition to a preliminary analysis of the title and abstract, the following exclusion criteria have been defined:

- Papers not written in English;
- Not original research (reviews, conference papers and book chapters);
- Unrelated articles with different treatment (neither herbicides nor bioherbicides) or different issue.

From this first search, the article selection resulted in 426 chosen documents in Scopus and 606 documents in Science Direct. A second screening was then carried out by thoroughly analyzing the documents and applying the following additional exclusion criteria:

- Papers that reported trials on nanoparticle’s role in the detoxification of environment parts (water, soil and air);
- Papers that reported ecotoxicological profile of NPs;
- Mini reviews considered an experimental trial by Scopus database.

Only the articles that contain quantitative data on the efficiency of nanoherbicides and nanobioherbicides were selected. From the last search performed on September 2024, only 30 documents were eligible as the remaining 155 articles reported irrelevant contents for the aim of this review. The complete information on the screening procedure is available in the PRISMA flowchart (Figure 1) (Table S1).

Figure 2 shows the time progression of published papers on nanotechnology application in weed control. Except for 2014, the number of journal papers was always below 30 per year, while since 2018, the publications increased exponentially to almost 100 in 2023 and 2024, denoting significant interest in the topic.

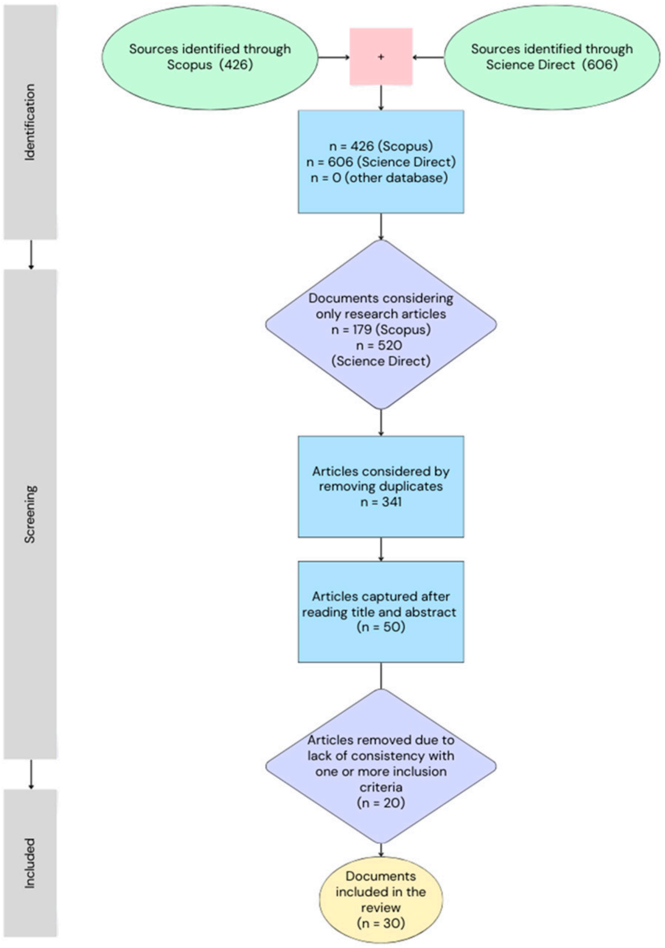

Figure 1. Inclusion–exclusion flowchart of the PRISMA diagram adopted in this review.

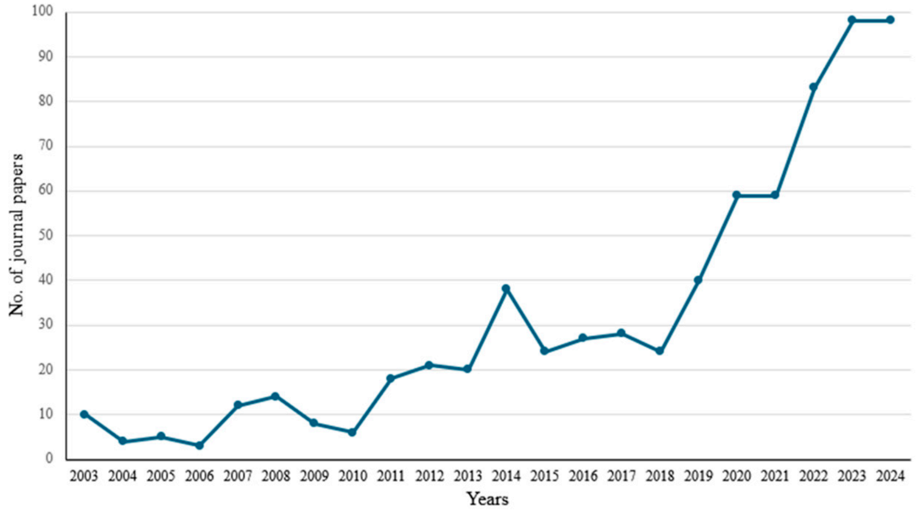

Figure 2. Number of journal papers per year on the Scopus® and Science Direct® databases using the search terms "nanotechnology", "weed management", "herbicide" and "bioherbicides".

3. Characteristics of NPs for Weed Control

The dimension of nanoparticles is the most important aspect that should be considered to fully understand the usefulness of nanotechnology for weed control. Ditta [26] reported that the US Environmental Protection Agency (EPA) defines a nanomaterial as a substance containing particles with at least one dimension in the approximate range of 1 to 100 nanometers. Indeed, it is thanks to nanoscale dimensions and chemical composition that nanostructures can penetrate the cellular wall and release the active ingredients at cellular level [17]. NPs or micelles, in nanoemulsion, often show sizes that exceed the 100 nm threshold. In Table 1 are reported some chemical herbicides loaded in different nanocarriers and their main characteristics including dimension range, zeta potential, shape and specific surface area measured in those works considered eligible from the PRISMA analysis.

Table 1. Main characteristics of common nanocarriers loaded with chemical herbicides.

Type of NPs	**Characteristic**				**Type of Tested Herbicides**	**Reference**
	Size (nm)	**Shape**	**Z Potential (mV)**	**Specific Surface Area (m^2/g)**		
Nanoemulsion	20–200	Spherical	from −44.17 to −1.84	–	Glyphosate isopropylamine	[15,27]
Polysaccharide pectin NPs	50–90	Spherical	−35.9	–	Metsulfuron methyl	[28]
Poly(ε-caprolactone) nanocapsules	200–300 (with atrazine or pretilachlor)	Spherical with atrazine, irregular polyhedral with pretilachlor	from −30 to −23	–	Atrazine; ametrine; simazine; pretilachlor	[14,29–35]
Poly(lactic-co-glycolic acid) NPs	204–520	Spherical	–	–	Atrazine	[36]
Chitosan NPs (CN) Chitosan/Alginate NPs (C/AN)	40–70 (CN); 197–305 (C/AN)	Spherical	−22.8 ± 2.3 (C/AN)	–	Mesosulfuron methyl and mesosulfuron methyl + florasulam + MCPA (2-methyl-4-chlorophenoxyacetic acid) isooctylic acid; clodinofop-propargyl and fenoxaprop-P-ethyl	[37–39]
Anionic Synthetic Clay (ASC) and Cationic Organic Clay (COC)	225–306	Lamellar	22 (ASC); 125 (COC)	19–91.8	Imazamox, 2,4-D, bentazone and dicamba	[40,41]
Metal–organic frameworks	252–280	Regular polyhedrons	−15.3	1600–2000	Paraquat and diquat	[42,43]
Silver NPs	10–30	Spherical, semi-spherical or cubic	from −5.6 to −3.65	–	Used alone and in combination with glyphosate	[44,45]

Note: NPs: nanoparticles; Z potential quantifies the electrical charge present at the interface between a particle's surface and the surrounding liquid. A high Z absolute value, regardless of its sign, indicates strong electrostatic repulsion between particles, promoting stability in dispersions. Conversely, a low Z potential implies weak electrostatic repulsion, increasing the likelihood of particle aggregation and destabilization of the system [37].

In general, the useful technological characteristics of NPs are summarized in Table 2:

Table 2. Main technological characteristics of nanoparticles (NPs).

Characteristic	**Description**	**Reference**
Higher specific surface area (SSA) to volume ratio	There are more atoms on the surface of an NP than in the internal part. The increased SSA leads to enhanced reactivity and enhanced catalytic activity	[46–48]
Reduced size	The small size of NPs allows their penetration into the stomata of leaves	[49]

Table 2. *Cont.*

Characteristic	Description	Reference
Controlled release	NPs can be engineered to release herbicides measuredly, reducing the need for frequent applications and minimizing their environmental impact	[50,51]
Enhanced bioavailability	NPs can enhance the bioavailability of herbicide active ingredients, leading to a greater uptake and increased efficacy	[52]
Multifunctional characteristics	Hybrid nanomaterials can combine the advantages of organic and inorganic materials into a single structure, offering properties such as a good targeting ability and reactivity	[24,42,43]
Biosynthesis	Some types of NPs, such as silver-based NPs, can be biosynthesized using plant extracts, offering an eco-friendly approach for weed control	[53]
Nanoencapsulation	NPs can be used to encapsulate the herbicidal metabolites extracted from microorganisms, improving their efficacy	[54]

Nanoencapsulation offers numerous advantages for herbicide formulations. By protecting the active ingredient from degradation, enabling controlled release and enhancing foliar adhesion, nanoherbicides can improve the efficacy and reduce the application rates. Moreover, their small size and surface properties facilitate an increased uptake and penetration into plant tissues, while their potential for targeted delivery can minimize the off-target effects. These attributes, combined with the possibility of synergistic interactions with other pest management strategies, make nanoherbicides a promising technology for sustainable weed control [24]. More sophisticated approaches involve functionalizing the nanocarrier surface with recognition molecules such as antibodies or DNA probes, targeting specific biological entities and triggering the controlled release of the encapsulated cargo [22,55].

Unfortunately, both nanoherbicides and nanobioherbicides still face criticisms. Key concerns include the bioaccumulation in soils and plants, particularly in edible parts, leading to phytotoxicity and potential chromosomal aberrations. There are also worries about the food safety of products treated with nanopesticides and the safety of workers handling them. NPs can trigger harmful biochemical reactions, such as an increased production of Reactive Oxygen Species (ROS), leading to oxidative stress. Additionally, they affect water uptake, and transport in plants, and impact the metabolic pathways and photosynthesis [56]. Assessing risks and identifying hazards of nanomaterials, including their life cycle and use in fertilizers, is therefore crucial. It is also important to prioritize toxicological research, especially considering the accumulation of NPs in plants and the potential health risks. NPs persist in soil due to their limited mobility, resulting in higher concentrations compared to those in air and water [54]. For these reasons, the assessment of the potential effects of NPs on human health and environment is of central importance before their widespread marketing.

4. Nanoformulations for Enhancing Traditional Herbicides and Bioherbicides

The main goals set for the synthesis of herbicides or bioherbicides at a nanoscale are the increasing solubility (to enhance the assimilation by plants) and the high selectivity. NPs are used to improve formulations through the use of nanoemulsions, nanocapsules, nanospheres and metal–organic NPs like silver NPs that enhance both the herbicidal effect of some chemical and biological active ingredients (Figure 3).

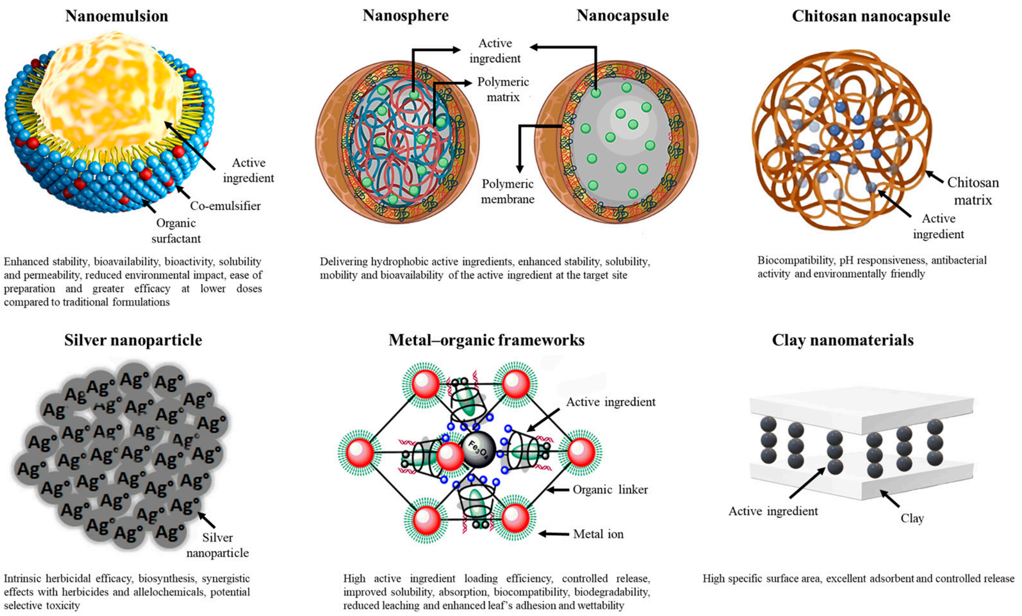

Figure 3. Common structures for nanoherbicides and nanobioherbicides. Nanoemulsion modified from https://www.genizer.com/art/nanoemulsion_a0060.html (accessed on 5 October 2024); nanosphere and nanocapsule modified from Baldim et al. [57]; chitosan nanocapsule modified from Chuah et al. [58]; silver nanoparticle modified from Li et al. [59]; metal–organic framework modified from Saklan et al. [43].

4.1. Nanoemulsions

Nanoemulsions are defined as kinetically stable dispersions of oil in water, composed of oil, water and surfactants, with droplet sizes ranging from 20 to 200 nm [60]. Nanoemulsions can be considered a form of colloidal release system [61]. They have several beneficial characteristics determined by the small droplet size, including dynamic stability, transparent or translucent appearance and capacity to improve the active ingredient penetration, solubility and stability [62]. These characteristics enable a higher bioavailability, a longer release of active ingredients and an improved penetration into plant tissues, which in turn may enhance the herbicidal efficacy and lessen the environmental impact [63]. Nanoemulsions are increasingly recognized as promising carriers for the encapsulation and controlled release of agrochemicals, particularly for herbicide applications, due to their greater stability and effectiveness compared to conventional emulsions [61].

Main Methodologies for the Preparation of Nanoemulsions

The selection of the appropriate emulsification method depends on several factors, such as the properties of the oil and water phases and the type and concentration of the used surfactant, as well as the desired size and distribution of the nanoemulsion droplets. Somala et al. [63] indicated that the main emulsification methodologies can be grouped into low-energy and high-energy methods:

- Low-energy methods generally employ only chemicals and normal agitation to create the nanoemulsion. These methods include phase inversion, spontaneous emulsification and solvent displacement. However, low-energy methods require a high concentration of emulsifying agents, which can impact the environmental safety [63]. An example of a low-energy method is reported in the experiment conducted by Hazrati et al. [60], namely, the catastrophic phase inversion method, who produced a stable nanoemulsion of *Satureja hortensis* L. essential oil without heating the oil, which could lead to a loss of the substance's properties. This method consists of gradually adding water to a mixture of essential oil and surfactant while stirring at a specific rate. Water is added until the mixture undergoes a phase inversion from a water-in-oil emulsion to an oil-in-water emulsion. According to Kumar et al. [64], although low-energy methods are less energy-intensive, they require high concentrations of emulsifying agents that are not environmentally safe.

- High-energy methods are widely used to produce nanoemulsions. High-energy methods, such as sonication, microfluidization and high-pressure homogenization, require a machine to induce intense forces to produce smaller emulsions. These technologies allow saving on the use of emulsifiers and surfactants to obtain smaller, more stable and more efficient droplets from an herbicidal point of view. This was demonstrated by Somala et al. [63], who adopted microfluidization to prepare a nanoemulsion based on citronella essential oil, and by Dimak et al. [65], who applied microfluidization to prepare a nanoemulsion of peppermint essential oil.

4.2. Nanocapsules and Nanospheres

In recent years, nanoencapsulation has been growing in interest for improving the herbicides efficiency and, at the same time, for reducing the risk of bioaccumulation in plants, animals, soil and groundwater. Various biodegradable and biocompatible polymers are used to produce nanocapsules, including poly(ε-caprolactone) (PCL), poly(lactic-co-glycolic acid) PLGA, chitosan, lignin and pectin, as well as inorganic materials such as metal, silica, etc. [24]. Nanoencapsulation (i) shields the active ingredients from environmental degradation by UV radiation, temperature, humidity and microbial activity; (ii) enables the controlled release of active ingredients over time, thus reducing their environmental impact; (iii) facilitates the root uptake; (iv) eliminates the possibility of off-target effects [54]. The encapsulation methods, with particular reference to organic formulations, have been already extensively reviewed by Rodríguez-Mejías et al. [18].

Although the terms “nanocapsules” and “nanospheres” are sometimes used interchangeably, they indicate slightly different structures in the context of the controlled release of herbicides. Both are nanoscale-delivery systems, but they differ primarily in the spatial arrangement of the encapsulating material and the active ingredient. Nanocapsules have a core–shell structure where the herbicide is enclosed in a core surrounded by a polymeric or lipidic shell. This shell acts as a protective barrier, controlling the release rate of the active ingredient and protecting it from environmental degradation. In the nanospheres, the active ingredient is dispersed uniformly within a solid polymeric matrix, and there is no a clear separation between the core and the shell. The release of the active ingredient occurs by diffusion through the polymeric matrix or by matrix degradation.

4.2.1. Poly(ε-Caprolactone) (PLC) Nanocapsules

PCL is a biodegradable and biocompatible aliphatic polyester. It degrades by the hydrolysis of its ester bond under physiological conditions, making it suitable for agricultural applications where a low environmental impact is desirable [33]. The size of the nanocapsules depends on the preparation method, with hydrodynamic sizes reported from 100 nm to 240 nm [35]. PCL nanocapsules have a core–shell structure in which the herbicide is encapsulated in a polymer core surrounded by a shell. This structure allows for the targeted and sustained release of the herbicide [30].

4.2.2. Poly(Lactic-co-Glycolic Acid) (PLGA) Nanospheres

PLGA is a copolymer showing a “hybrid” structure formed by lactic acid and glycolic acid, which endow the nanocapsules with valuable properties [36]. Among these properties, the most important are biodegradability and biocompatibility. The degradation of lactic acid into the environment has been reviewed in detail by Teixeira et al. [66], who stated that its biodegradability is linked to the environment in which it is released. For instance, lactic acid degradation in soils is generally quite slow due to the high moisture content that increases its hydrolysis and assimilation by thermophilic microorganisms [66]. It is important to highlight, however, that research into the environmental impact of biodegradable polymers such as PLGA is ongoing, and, in many cases, there are still no definitive answers. Both lactic acid and glycolic acid are natural metabolites present in the human body. Therefore, when PLGA degrades, it breaks down into these two innocuous and easily metabolizable substances. The presence of lactic acid and glycolic acid makes PLGA highly biocompatible, meaning it is well tolerated by living tissues and unlikely to trigger adverse reactions. However, while nanospheres are attractive because of their lower synthesis costs compared to nanocapsules, their stability is lower than the previously described structures [51]. PLGA-NPs are commonly prepared with the emulsion-solvent evaporation method. This method involves the build-up of an oil-in-water emulsion where the active ingredient is dissolved in the oil phase along with the PLGA polymer and an organic solvent [36]. The size of the PLGA nanospheres is controlled by varying the preparation conditions such as sonication time, surfactant content, solvent fraction and polymer content. The reported sizes of these nanospheres range from 204 to 520 nm. PLGA nanospheres are characterized using techniques like dynamic light scattering and scanning electron microscopy. The encapsulation efficiency and the bioherbicide release profile from the nanospheres can be evaluated using a model herbicide like atrazine [36].

4.2.3. Chitosan and Pectin-Based Matrices

Chitosan is a linear polysaccharide produced by the deacetylation of chitin, a natural polymer present in the exoskeletons of crustaceans such as shrimp and in other organisms like insects and fungi. It is a natural polymer that can be synthesized and obtained at a low cost from the exoskeleton of crustaceans; moreover, both purchase and synthesis allow the obtainment of considerable quantities [22]. Chitosan can form stable NPs by encapsulating herbicides (such as clodinafop-propargyl and fenoxaprop-P-ethyl) and also bioherbicides from the leaf extracts and the shells of *Carya illinoinensis* (Wangenh.) K. Koch, *Ruta graveolens* L. and *Solanum rostratum* Dunal [67] through the ionic gelation technique. This technique suggests that the formation of NPs occurs through the ionic interaction between chitosan, which is positively charged, and a negatively charged crosslinking agent like tripolyphosphate [38,39]. The same authors report that chitosan, being a natural polymer, is also both biodegradable and biocompatible.

From the literature, it is not possible to state with certainty whether the nanomatrices loaded with herbicides belong to the group of nanospheres or NPs. Nanospheres are of interest for their low synthesis costs compared to nanocapsules; however, their stability is lower compared to the previously described methodologies [51]. The method of preparing chitosan nanospheres begins with ionotropic gelation, which exploits the ability of polyelectrolytes to form three-dimensional networks in the presence of ions using a solution of sodium alginate and calcium chloride to obtain a pre-gel of calcium alginate [37]. Then, polyelectrolyte complexation is carried out where a chitosan solution is added to the pre-gel to reinforce the nanospheres through electrostatic interactions, obtaining alginate–chitosan nanospheres with a diameter in the order of nanometers. Lastly, the active ingredient is mixed with the sodium alginate solution before adding calcium chloride to obtain alginate–chitosan nanospheres loaded with the active ingredient [68].

Pectins are anionic polysaccharides widely present in plant cell walls. Their ability to gel in the presence of acids and sugars is well known, making them widely used in the food industry as thickeners and stabilizers. Moreover, as natural compounds, they are safe for plants and animals. The size of pectin nanocapsules is slightly larger; in fact, in the experiments performed by Khan et al. [38,39] and Tucuch-Pérez et al. [67], sizes between 40 and 70 nm were recorded, while Kumar et al. [28] reported sizes of 50–90 nm. The methodologies for the formation of these NPs are the same as those used to produce chitosan NPs (ionotropic gelation using the crosslinking agent TTP), whereas Kumar et al. [28] used calcium chloride as a crosslinking agent.

4.2.4. Metal–Organic Framework-Based NPs

A novel technology exploited to construct nanocarriers is based on the metal–organic frameworks (MOFs), which are porous materials with a high surface area where the active ingredients of phytopharmaceuticals, including herbicides, can be inserted and released in a controlled manner [69]. In the last two years, two experiments that exploit MOFs to synthesize nano-herbicides based on traditional chemical herbicides have been found. Dong et al. [42] used the Material Institute Lavoisier-101(Fe), abbreviated as MIL-101(FeIII), a mesoporous structure capable of hosting paraquat molecules. The herbicide-loaded nanocapsules are then coated with a carboxymethylcellulose hydrogel cross-linked with calcium anions (CMC-CaII). More recently, another experiment has been published describing the creation of nanocomposites for the controlled release of diuron by using Zeolitic Imidazolate Framework-8 (ZIF-8) MOFs [43]. They work synergistically with the p-sulfocalix [4] arenedicarboxylic acid (SCX4) complex to release diuron in a controlled manner and make it less permeable in the soil compared to free diuron. Unfortunately, based on the literature and considering the complexity of the process leading to the synthesis of the two different nanocarriers, the applicability of these technologies is still prohibitive due to the high knowledge and economic inputs required. Furthermore, studies on the safety of these structures are still preliminary as there is insufficient information regarding bioaccumulation in soil and plant tissues, although they improve the safety of otherwise dangerous herbicides.

4.3. Silver NPs

Silver nanoparticles (AgNPs) are one of the most prevalent nanomaterials employed for industrial and agricultural applications, owing to their exceptional antimicrobial efficacy and other advantageous physicochemical attributes [70].

Within the context of weed control through nanotechnology, AgNPs represent an interesting alternative as they are synthesized using plant extracts as reducing agents (green synthesis) and tested for their herbicidal activity alone and without being associated with any active principle, whether synthetic or organic. Two experiences have been selected from the bibliographic search and are summarized in Table 3.

Table 3. Two green syntheses of silver nanoparticles (AgNPs) from two common spontaneous species.

Steps for the Synthesis	**Method with *Zanthoxylum nitidum* (Roxb.) DC. [71]**	**Method with *Haplophyllum tuberculatum* (Forssk.) A. Juss [53]**
Donor plant	Dried and ground *Z. nitidum* roots	Dried vegetative part of *H. tuberculatum*
Extract preparation	Sonication at room temperature for 30 min, followed by centrifugation and filtration	Immersion in distilled water for 24 h at 25 °C in the dark, followed by centrifugation. Adjustment of pH to 6.8
Extract concentration	Not mentioned, but a ratio of 0.5 g powder to 50 mL water is used for extraction	Preparation of 5%, 10% and 20% dilutions of the crude extract
Reducing agent	Bioactive compounds present in the aqueous extract	Bioactive compounds present in the crude aqueous extract
AgNPs synthesis	Addition of 0.1 mol L^{-1} $AgNO_3$ dropwise to the extract, stirring continuously for 3 h at room temperature	Addition of 10 mL extract to 100 mL of 3 mM $AgNO_3$, shaking for 2 h and, then, stirring at room temperature for 24 h

Unfortunately, based on the two studies, it is not possible to determine whether AgNPs pose a risk to the environment and human health as toxicity tests were not conducted during the characterization phases. Nevertheless, Feng et al. [45] analyzed the effects of the AgNps and glyphosate combination on wheat growth compared to AgNps and glyphosate alone.

4.4. Clay's Nanocarrier

Clays are layered minerals that can be classified as either anionic or cationic based on their net surface charge. This surface charge arises from isomorphic substitutions within the crystal lattice structure. Anionic clays, such as layered double hydroxides (LDHs), possess a net negative surface charge and can be utilized to host anionic species (such as acidic herbicides) between their layers through electrostatic interactions [72]. Moreover, LDHs can be synthesized in the laboratory using low-cost methods [73].

Cationic clays such as montmorillonite and organic clays have a net-positive surface charge. Organic clays are modified montmorillonite clays with organic cations [74]. The strengths of these classes of NPs lie in their ability to adsorb anionic or cationic chemical species between their lamellae, controlled release of active ingredients, and biocompatibility with soil.

These aspects are supported by the work of Granetto et al. [41], which investigated some methods to reduce the leaching and volatilization of dicamba for improving its efficacy and environmental sustainability. Specifically, tests were conducted comparing four different natural clays capable of adsorbing dicamba (two Na-montmorillonites, one Ca-montmorillonite and one zeolite) subsequently coated with a carboxymethylcellulose-based biopolymer. The experiment successfully demonstrated the potential of natural clays, particularly K10 montmorillonite coated with CMC, as nanocarriers for dicamba. This nanoformulation effectively reduced the volatilization and mobility of dicamba in the subsoil while maintaining an herbicidal efficacy comparable or superior to commercial formulations against *S. nigrum* and *Amaranthus retroflexus* L.

In a recent work published by Khatem and co-workers [40], two synthetic clays, a cationic (Cloisite 10A (Clo10A)) and an anionic (anionic layered double hydroxide (LDH)) one, were loaded with the chemical herbicide imazamox (Imz) to reduce leaching and Imz doses while maintaining its herbicidal activity against *Brassica nigra* L. Furthermore, the Imz–clay complexes acted as intelligent release systems, slowly releasing Imz over time.

Despite these advantages, the extraction and processing of clays can pose several environmental risks, including soil erosion and the subsequent destruction of natural habitats. Additionally, the potential bioaccumulation of some smectite clay classes in water cannot be underestimated [75]. In recent years, nano-clays have been the subject of extensive research due to their adsorbent properties, which have applications in various sectors. After the release of an active principle, nano-clays could adsorb and retain nutrients essential for plants, such as sulfates and phosphates, leading to severe deficiencies in already nutrient-poor soils [76]. To minimize environmental risks, it is crucial to continue research to develop more sustainable extraction and production methods, to thoroughly assess the toxicity and long-term effects of nano-clays and to promote responsible disposal and reuse practices.

5. Plant-Based Nanobioherbicides

In recent years, numerous pilot studies aimed to identify sustainable alternatives for weed control such as the development of nanobioherbicides derived from plant allelochemicals [77]. The majority of these studies were conducted in vitro, whereas just one study was carried out in open-field conditions [78] to the best of our knowledge (Table 4). Nanotechnology offers a promising solution to enhance the efficacy and sustainability of bioherbicides. Nanoemulsified essential oils, plant extracts combined with NPs and nanocapsules loaded with natural compounds are the most promising formulations for future research [66,78,79].

Table 4. In vitro and in vivo examples of nanobioherbicide application.

Nanotechnology	Active Ingredient	Target Weeds	% of Weed Suppression	Type of Experiment	Reference
Nanoemulsion	*S. hortensis* L. essential oil	*Amaranthus retroflexus* L. and *Chenopodium album* L.	*A. retroflexus* and *C. album* seed germination: −95% and −70.7%, respectively. Total mortality of both species at 4000 μL L^{-1}	In vitro and greenhouse	[60]
Nanoemulsion	*Cymbopogon nardus* L. essential oil	*Echinochloa cruss-galli* (L.) P. Beauv and *A. tricolor*	*E. crus-galli* and *A. tricolor* growth: −80% and −85%, respectively	Greenhouse	[63]
Nanoemulsion	*Foeniculum vulgare* Mill. essential oil	*Phalaris minor* Retz., *Avena ludoviciana* Durieu, *Rumex dentatus* L. and *Medicago denticulata* Willd	Seed germination: total inhibition at 0.05 wt% and 0.1 wt%	In vitro	[80]
Nanoemulsion	*Rosmarinus officinalis* L. essential oil	*Lactuca sativa* L.	Seed germination: −61%, −60% and −30% at concentrations of 10, 7 and 5 mg mL^{-1}, respectively	In vitro	[81]
Nanoemulsion	*Mentha* × *piperita* L. essential oil	*A. tricolor*	Seed germination (−82.5%) and root growth (−59.92%) at 800 μL L^{-1}	In vitro	[65]
Nanoemulsion with two different surfactants: cremophor EL and polyoxyethylene lauryl ether	*Artemisia argyi* H.Lév. and Vaniot essential oil	*Setaria viridis* (L.) P. Beauv., *E. crus-galli*, *Portulaca oleracea* L. and *A. retroflexus*	Fresh biomass weight: more than −80%	Greenhouse and pot trial in open air	[61]
Nanocapsules of Arabic gum, Persian gum/gelatin and Persian gum	*S. hortensis* essential oil	*A. retroflexus*	Injury: nearly 100% damage after 7 days 15 mL L^{-1} (except for Arabic gum)	Greenhouse	[79]
Polimeric NPs	DiS-NH_2 (2,2′-disulfanediyldianiline)	Durum wheat's weed flora	Aboveground biomass: −51.3% at 0.75 g m^{-2} and −40.9% at 1.5 g m^{-2}	Field	[78]
Chitosan and alginate NPs	Ethanolic extracts of *Carya illinoinensis* (Wangenh.) K.Koch, *Ruta graveolens* L. and *Solanum rostratum* Dunal	*Sorghum bicolor* (L.) Moench and *Phaseolus vulgaris* L.	Seed germination: −96 to −100% by most of the extracts at 12.5% and 25% concentrations. Root and hypocotyl growth were completely inhibited by the majority of extracts	In vitro	[67]
AgNPs	Green synthetized AgNPs from *H. tuberculatum* (Forssk.) A. Juss.	*P. minor*	Seed germination: total inhibition compared to the crude aqueous extract of *H. tuberculatum*	Pot trial	[53]
AgNPs	*Z. nitidum*	*Bidens pilosa* L.	Seed germination: −11.86% by *Z. nitidum* aqueous extract, −18.64% by *Z. nitidum* AgNPs. Seedling growth: −19.38% of root length and −23.33% of shoot length by *Z. nitidum* AgNPs	In vitro	[71]

NPs: nanoparticles; AgNPs: silver nanoparticles.

Hazrati et al. [60] investigated the herbicidal activities of *S. hortensis* essential oil nanoemulsion against two common Mediterranean weeds, *A. retroflexus* and *Chenopodium album* L., both in vitro and in greenhouse trials. By interfering with seed germination, growth, and weed physiological processes, the *S. hortensis* nanoemulsion demonstrated a high herbicidal efficacy, thus representing a promising strategy for the development of bioherbicides. Building upon previous work, Taban et al. [79] studied the selective herbicidal effects of *S. hortensis* essential oil nanoencapsulated into organic polymer-based nanocarriers, focusing on tomato and *A. retroflexus*. The nanocapsules, prepared using gum Arabic, gum tragacanth and a gum tragacanth–gelatin mixture, showed a significant herbicidal activity against *A. retroflexus* while exhibiting a milder effect on tomato plants. These findings suggest that nanoencapsulation enhances the selectivity of *S. hortensis* essential oil.

Tucuch-Pérez et al. [67] focused on the herbicidal activity of *C. illinoinensis*, *R. graveolens* and *S. rostratum* plant extracts nanoencapsulated in chitosan and alginate nanocarriers and on the seed germination and seedling growth of *Sorghum bicolor* L. and *Phaseolus vulgaris* L. The presence of secondary metabolites such as phenolic acids and flavonoids in the plant extracts explains their allelopathic activity, which affected various physiological processes in target plants including membrane permeability, photosynthesis, respiration, hormonal activity and ion uptake. The encapsulation of the plant extracts in biopolymer-based nanocapsules enhanced their herbicidal efficacy, likely due to an improved stability, solubility and cellular uptake of bioactive compounds when encapsulated in biopolymer matrices.

The nanoemulsion of citronella essential oil tested by Somala et al. [63] also demonstrated enhanced post-emergence herbicidal activity on both *A. retroflexus* and *Echinochloa crus-galli* L.) P. Beauv. in greenhouse conditions, causing necrosis, visible leaf burns, reduction in photosynthetic pigments and an increase in malondialdehyde (MDA). The same study also showed that damage increased proportionally with the concentration of the nanoemulsion. Subsequently, the authors found promising results with peppermint essential oil tested in vitro on *A. tricolor* seeds and seedlings, detecting inhibitions of α-amylase in seeds and reductions in seedling growth with dose-dependent effects [65].

A key aspect in the evaluation of nanobioherbicides lies in their selectivity. In this regard, Chen et al. [61] evaluated the nanoemulsion of *Artemisia argyi* L. essential oil at two concentrations (5 and 12.5 mg g^{-1}) against two monocotyledonous (*Setaria viridis* (L.) P. Beauv. and *E. crus-galli*) and two dicotyledonous (*Portulaca oleracea* L. and *A. retroflexus*) weeds, two medicinal species (*A. argyi* and *Chrysanthemum* × *morifolium* (Ramat.) Hemsl) and three crops (rice, cotton and soybean). No negative effects were observed on non-target crops at 5 mg g^{-1}, but significant herbicidal effects were observed on weeds; however, at 12.5 mg g^{-1}, damages were observed in medicinal species and cotton, and slight wilting in rice and soybean plants, in addition to an extensive herbicidal effect on weeds.

The sole field study performed with nanobioherbicide is the research by Scavo et al. [78], who tested a nanoparticle formulation of DiS-NH_2 (2,2′-disulfanediyldianiline) applied as post-emergence foliar herbicide at two dosages (0.75 and 1.5 g m^{-2}) for weed management in durum wheat. The authors reported that the nanoencapsulated DiS-NH_2 not only showed a higher weed-suppressive ability than chemical control (51.3% and 40.9% by DiS-NH_2 at 0.75 and 1.5 g m^{-2}, respectively, vs. 33.5% by herbicides) but also improved durum wheat growth and yield, thus denoting a good selectivity.

AgNPs represent a further opportunity to enhance the effectiveness of bioherbicides. As described in the previous section, they can be synthesized from plant extracts [53] and enhance the herbicidal action of chemical and biological substances [71,82]. Eldarier et al. [53] compared the herbicidal activity of *H. tuberculatum* crude aqueous extract and the same extract enriched with AgNPs on *Phalaris minor* L. and *T. aestivum*. The authors reported that *H. tuberculatum* aqueous extract enriched with AgNPs completely inhibited *P. minor* seed germination at all the tested concentrations. Furthermore, the analysis of photosynthetic pigments revealed an interesting biphasic effect: at low concentrations, it stimulated the production of pigments in *T. aestivum*, thus favoring its growth, while at higher concentrations, it inhibited photosynthesis in *P. minor*. In the use of AgNPs as bioherbicides, the size of these NPs should be also considered since different sizes of AgNPs have differentiated effects on target plants. For instance, Wang et al. [82], comparing the phytotoxicity of AgNPs at different sizes (30 and 70 nm) and AgNPs combined with *Solidago canadensis* L. extracts in controlling *Lactuca sativa* L., found that AgNPs at 70 nm showed greater phytotoxicity than AgNPs at 30 nm and that the AgNPs increased the allelopathic activity of *S. canadensis* extracts. In a recent publication, Jiang et al. [71] described another ecological method for AgNP synthesis (Table 2) by using an aqueous extract of *Z. nitidum* roots and evaluated their herbicidal activity against *Bidens pilosa* L. Compared to previous works, the NPs were not tested in combination with the aqueous extract from which they were derived but were tested alone. The results confirmed that the synthesis model can represent a sustainable solution for the synthesis of AgNPs usable as nanobioherbicides.

6. Conclusions and Future Perspectives

The present review indicates that nanotechnology offers a promising approach to enhance the efficacy and sustainability of weed control. The reduced size, high surface area and unique chemical properties of NPs enable the controlled release of active ingredients, the improved penetration into plant tissues and the reduced environmental impact. Nanoformulations of conventional herbicides can increase their efficacy and reduce their environmental dispersion. Nanobioherbicides based on natural substances such as essential oils, plant extracts or plant allelochemicals offer a viable alternative to synthetic products. AgNPs synthesized from plant extracts, for example, show great potential as bioherbicides. However, a thorough assessment of the risks associated with the use of nanotechnology in agriculture is essential. Further research is needed to evaluate the bioaccumulation of NPs in soil and plant tissues, their toxicity to non-target organisms and their long-term impact on human health and the environment. Another urgent need is the set-up of field experiments to assess the effectiveness and selectivity of nanoherbicides and nanobioherbicides under open-field conditions. Technical aspects such as the method of application (directly to the plants or to the soil) or the timing of nanoherbicides' effects, especially with nanocapsules and nanospheres, should be also addressed in the future. Nevertheless, NPs still require efforts by scientists and agrochemical industry to improve their stability over time and efficiency, especially in the field of nanobioherbicides, in order to launch commercial formulates on the market.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/agronomy15010228/s1. Table S1. PRISMA 2020 checklist.

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