agronomy

Review

Perspectives and Advances in Organic Formulations for Agriculture: Encapsulation of Herbicides for Weed Control

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Abstract: This article offers a critical analysis of the evolution of encapsulation methods for herbicides and natural products, with a main focus on organic formulations. It extols the possibilities presented by these micro- and nanomaterials, such as their slow release, stability, bioavailability, water solubility, and stability for classical and natural herbicides from their origins to the present.

Keywords: nanoencapsulation; allelochemical; organic nanoparticle; weed management; bioherbicides; allelopathy; polymeric nanoparticles; formulation

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1. Introduction

"There is need for the development of safe and effective controlled release formulations of pesticides. [. . .] formulations could make it possible to use smaller amounts of pesticides and perhaps even improve performance efficiency [1]." These were the words of Richard G. Sinclair, the author of the first research paper on the encapsulation of agrochemicals in 1973. The paper was entitled 'Polymers of Lactic and Glycolic Acids as Ecologically Beneficial, Cost-Effective Encapsulating Materials' and was based on the pillars established by the Pennwalt Corporation in 1972, whose development of Penncap-M shook up the agricultural field. This first agro-material was based on polyamide spheres in which methyl parathion was encapsulated, and the spheres were spread by spraying an aqueous suspension. This was a broad-spectrum pesticide that was mainly used to control insects, such as caterpillars, beetles, and grasshoppers [2]. However, it was the starting point for the encapsulation of agrochemicals, and these techniques were recently applied for herbicides. The commercial pesticide Penncap-M® (O,O-dimethyl-O-p-nitrophenyl phosphorothioate) is currently being recalled, as it is a health risk for humans and is banned from sale and import in nearly all countries around the world [3,4].

Other renowned enterprises, such as 3M Corp and National Cash Register (currently known as NCR Corporation), also began large-scale field trials in 1973. The systems tested include 'biodegradable plastic compositions' and 'proteinaceous films' [2]. These companies started a race to develop the safest, cheapest, and most profitable encapsulation system, and this race continues today.

Scientific research on the encapsulation of agrochemicals has been influenced by market demands, but this is always with some delay. The scientific community is focused on advancing knowledge and humanity, and studies have been carried out to identify natural products as alternatives to classical herbicides and to replace field-persistent encapsulation structures with ecologically sound materials. In this respect, the number of studies focused on this topic has markedly increased over the last decade and, particularly, in the last four years, i.e., 2018–2022 (Figure 1); this has maintained the high impact of this subject.

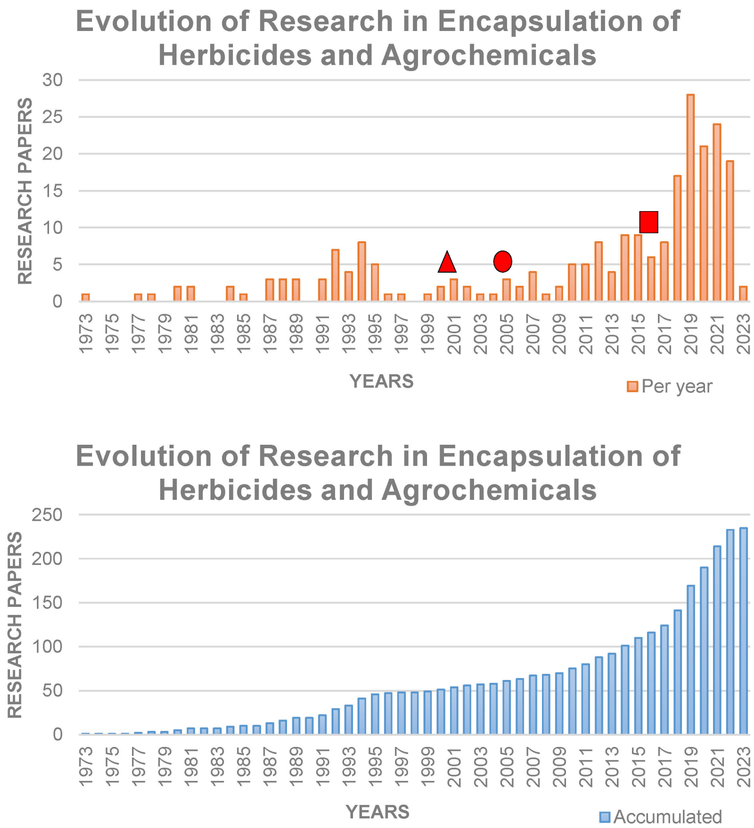

Figure 1. Evolution of research on the encapsulation of herbicides/bioherbicides according to Scifinder® (Keywords: Encapsulation, Herbicide, Agrochemicals, Nanoecapsulation, Natural Products). (Triangle) First publication about atrazine contamination of drinking water in the USA (2001) [5]. (Circle) The use of Atrazine and Alachlor in the European Union is banned (2004) [6]. (Square) Plan to ban glyphosate in most countries of the European Union within two years, and some states of the USA start to evaluate the adverse effects (2016) [7]. (**Top**) Papers published per year. (**Bottom**) Cumulative papers published per year.

The use of encapsulation has been very successful in terms of property modification, the application of smaller amounts of herbicides, and enhancements in stability. These modifications also result in higher water solubility, lower soil and environmental pollution, and more targeted products. Since the 1970s, this approach has been applied to classical herbicides. Such chemicals have very limited pollution control and little specificity in terms of their mode of action. This undisciplined approach has led to a rapid increase in herbicide-resistant weed species worldwide, which has led to higher herbicide application rates and the use of other active principles with longer environmental persistence [8]. Furthermore, Hulme stated that the number of herbicide-resistant weeds is probably underestimated and that agronomic drivers suggest that, in many countries, the number of resistant weeds will increase [9]. As a consequence, in recent decades, the use of natural alternatives for weed control, crop protection, and increased production has been promoted. In this respect, organic encapsulation has been successfully applied to these new natural and nature-inspired options.

The benefits associated with bioherbicides/allelochemicals can be summarized as follows: natural origin of the chemical compounds, low impact on the environment, new modes of action against weeds, and public acceptance [10–12]. However, there are still barriers that limit the use of these systems under natural conditions, and these include their low water solubility, rapid biodegradation in the environment, and high cost of synthesis, among others [13]. Roberts et al. stated that, in order to be successfully integrated within weed management systems, bioherbicides should have a suitable formulation, be economically sustainable, cause a high mortality rate for target plants, and lead to very limited or zero impact on the surrounding natural environment and human health [14]. Current examples include the encapsulation of phytotoxic sesquiterpene lactones in organic nanotubes that show activity against *Phalaris arundinacea* L., *Lolium perenne* L., and *Portulaca oleracea* L. weeds or monoterpenes encapsulated in organoclays for the prevention of volatilization [15,16]. The release rate is another important factor; in general, larger sizes facilitate a gradual and prolonged release of the active substances, while smaller particles allow a more homogeneous dispersion, increase the release rate, and facilitate the transport and absorption of the substances. This results in a controlled release of the active substance. For this reason, among others, different technologies that allow increasingly smaller encapsulation sizes have been developed. In general, one can speak of microencapsulation when the particles are between 1 and 1000 μm and of nanoencapsulation when the particle size is smaller, down to 10 nm [17,18].

The aim of this paper is to provide a perspective on how encapsulation systems have evolved and discuss the experimental results that have been obtained in field studies. The main focus is on the most relevant and promising organic encapsulation systems that have been studied to develop safer, non-persistent, and ecological agrochemicals.

2. Perspectives and Analysis of Organic Encapsulation Systems Employed for Weed Control

2.1. Cyclodextrins and Macrocycles

A large number of compounds encapsulated with cyclodextrins (CDs) have been used in the field of medicinal chemistry, but the use of these systems for weed control and crop enhancement is very limited. Szejtli was the first to report the safe application of CDs to plants by analyzing the physiological effect of this macrocycle on seeds from crops of interest [19]. He studied the phytotoxic effect of β-CD, and two years later, in 1985, he applied the encapsulation method to several herbicides (e.g., molinate, dichlobenil, and benthiocarb, among others), pesticides, and fungicides [20]. Since then, several studies have focused on the complexation of a range of CDs and herbicides, although these have only concerned supramolecular properties, such as solubility or soil stability, and biological applications have not been considered [21,22]. Lezcano et al. reported the complexation of fungicides with these macrocycles—specifically, with the three natural CDs (α, β, and γ) [23,24]. However, only complex production and characterization were described, without reference to biological applications. Comparable results were published by Benfeito et al., who used 2-hydroxypropyl-β-cyclodextrin to host Oxadiargyl (5-tert-butyl-3-[2,4-dichloro-5-(prop-2-ynyloxy)phenyl]-1,3,4-oxadiazol-2(3*H*)-one) [25]. Interestingly, CDs were also tested as soil remediators, but these were not combined with applications for crop protection or enhancement purposes [26,27].

The first experimental application of this formulation method was not reported until 2017. Cala et al. encapsulated three sesquiterpene lactones (Figure 2), and these showed phytotoxic effects against parasitic plants (*Orobanche cumana* Wallr., *Orobanche minor* Sm., *Orobanche ramosa* L. (syn.: *Phelipanche ramosa* (L.) Pomel), *Orobanche aegyptiaca* Pers. (syn.: *Phelipanche aegyptiaca* (Pers.) Pomeland) *Striga hermonthica* (Delile) Benth.) of the Fabaceae and Asteraceae families, but also tomato, maize, and sugar cane. This study revealed that β-CD encapsulation improved the water solubility of these allelochemicals and enhanced their bioactivity when compared to that of free sesquiterpenes, and it also highlighted this as a potential pre-emergence herbicide for food production [28]. Another sesquiterpene lactone, Inuloxin A (Figure 2), was also tested against *Orobanche ramosa* L. (syn.: *Phelipanche ramosa* (L.) Pomel) after complexation with β-CD [29].

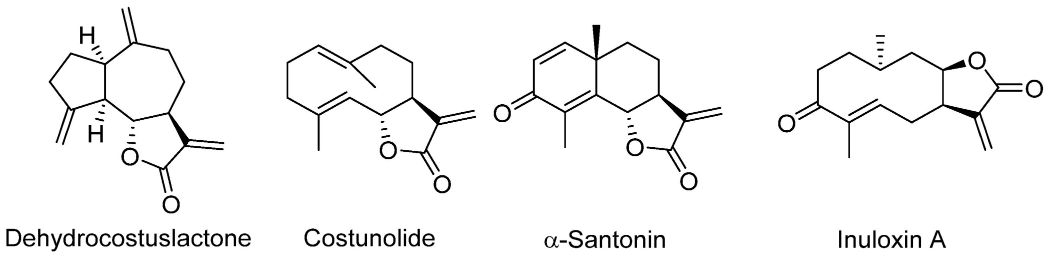

Figure 2. Sesquiterpene lactones encapsulated with cyclodextrins to fight parasitic plants.

In addition to those used against parasitic plants, formulations for combatting *Echinochloa crus-galli* (L.) P.Beauv. are the second main focus for the agrochemical application of cyclodextrin formulations in crop protection. Atrazine [30], butachlor [31], cyanazine [32], and diuron [33] have been complexed with β-CD or its 2-hydroxypropyl derivative. In all cases, the inhibition of different plant parameters was higher when compared to that obtained with free herbicides. For example, plant height, root length, and fresh weight were directly affected by encapsulation with CDs. HP-β-CD and γ-CD were recently employed to encapsulate 2,2′-disulfanediyldianiline (DiS-NH_2), an aminophenoxazinone mimic, to target *Portulaca oleracea* L., *Plantago lanceolata* L., and *Lolium rigidum* Gaudin, which are problematic weeds in rice, wheat, and barley cultures, respectively. The results showed an enhancement of the water solubility and bioactivity for the γ-CD complex, with inhibition values higher than 80% with respect to the control for germination, shoot length, and root formation of *P. lanceolata* [34].

Interestingly, there is a significant gap in the information concerning the use of CDs in field experiments and the more dominant in vitro tests. The results in the literature support the application of these systems in field experiments, but there is a lack of further research focused on this area. Furthermore, most research has focused on β-CD, and the other natural CDs have been largely overlooked (Figure 3). β-CD is approved by the EFSA (Food code: E459), and this fact has encouraged research on crops for human consumption [35]. However, β-CD has the lowest water solubility of the CD family. The inclusion in the structure of 2-hydroxypropyl substituents improves solubility, and this explains why there are some research papers on this macrocycle. Many authors seem to be attracted by new nanostructures, and natural formulation methods are often overlooked, though we should, in fact, seek to rediscover them. γ-CD, which allows the generation of higher-order complexes (1:2) with respect to the guest, seems to be a particularly economically interesting option due to the lower amount of cyclodextrin that is required.

Other macrocycles have recently been studied for weed control, but these are synthetic materials. One example is cucurbit[*n*]urils (CB*n*), whose main structural motifs are glycoluril units, and these can usually be obtained with 5–8 subunits. Most of the studies on herbicide encapsulation concern physicochemical characterization, as in the cases of ametryn [36], atrazine, and imazapyr [37,38], but their biological activity was not described. Nevertheless, the encapsulation of natural phytotoxic aminophenoxazinones and their sulfur mimics by complexation with CB7 has recently been reported, and these displayed improved phytoactivity in the growth of wheat (*Triticum aestivum* L.) models when compared with the free compounds [39].

The formulation process for using CDs as host materials is rather simple, and no extra adjuvants or steps are needed, apart from mixing the correct concentrations once the binding constant is known. They are also natural products, so this is a green approach for formulations. Current biotechnological production makes their obtention cheap. Furthermore, the main units of CDs are glucose units, which have been demonstrated to enhance the bioavailability of the drugs/herbicides encapsulated.

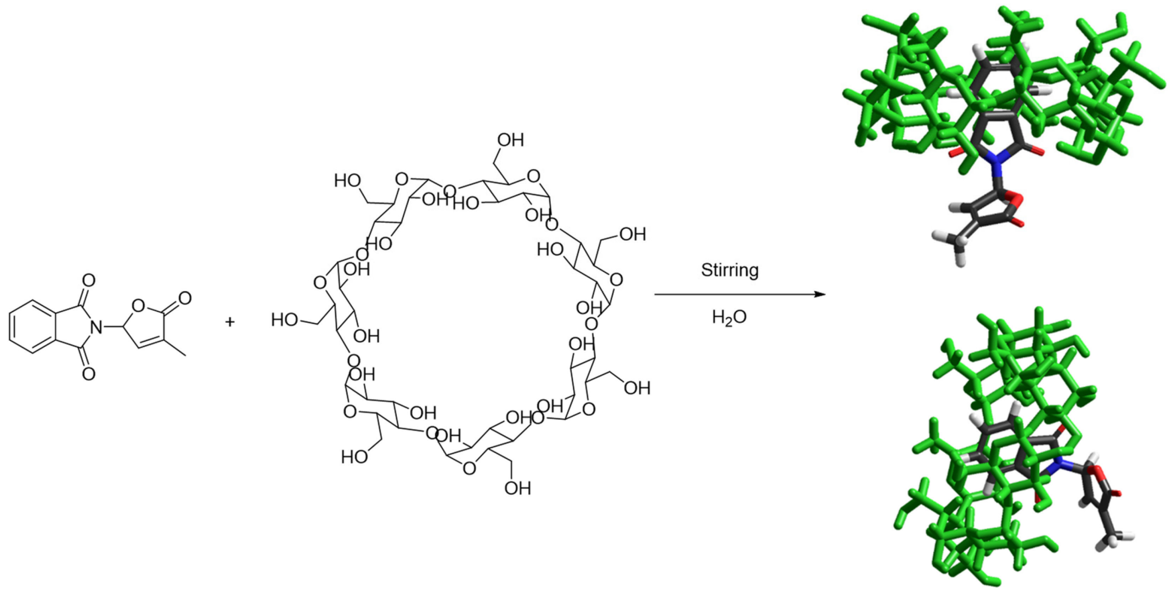

Figure 3. Scheme of the procedure of encapsulation with cyclodextrins and herbicides. This example includes the formation of PL01@βCD. Reprinted/adapted with permission from Ref. [36]. Copyright 2023, copyright owner Royal Society of Chemistry.

2.2. Clays

Clays have been extensively studied in an agronomic context, as they are porous materials that are present in soil. There are several research papers on the adsorption of herbicides onto soil clays and on how this reduces the efficacy of herbicides. In contrast, the use of clays as carriers has not been widely investigated, but this has changed over the last decade. The main advantage of this approach is the biocompatibility of the material with the medium in which the crop and weeds grow. In most cases, this is a green approach because the encapsulating or carrier material is already present as part of the soil.

The first applications of clays were reported in 1984, i.e., around ten years after the first use of encapsulation in agrochemistry. Connick et al. employed a kaolin clay to adsorb 2,6-dichlorobenzonitrile and studied its properties as a carrier to control common purslane (*Portulaca oleracea* L.), broadleaf signalgrass (*Brachiaria platyphylla* (Munro ex C.Wright) Nash), goosegrass (*Eleusine indica* Gaertn.), and large crabgrass (*Digitaria sanguinalis* (L.) Scop.) in vitro [40]. These weeds occur in corn, cotton, soybean, rice, and wheat cultures, and they cause yield losses of up to 20% [41–44]. Further research on clays for herbicide/weed control was not carried out until 1994, when Carr et al. developed an interesting method with montmorillonite to support starch with encapsulated metolachlor and atrazine [45]. However, these formulations were not applied in the field or in vitro. Montmorillonite has also been used to encapsulate chloridazon and metribuzin [46], glyphosate [47], paraquat [48,49], and picloram [50], but these studies are limited to the characterization of the encapsulated agrochemical compound in terms of release, stability, and water solubility. Generally, the encapsulation method involves the preparation of the clay in the presence of the herbicide to enhance the probabilities of capture in the clay pores, as observed in Figure 4.

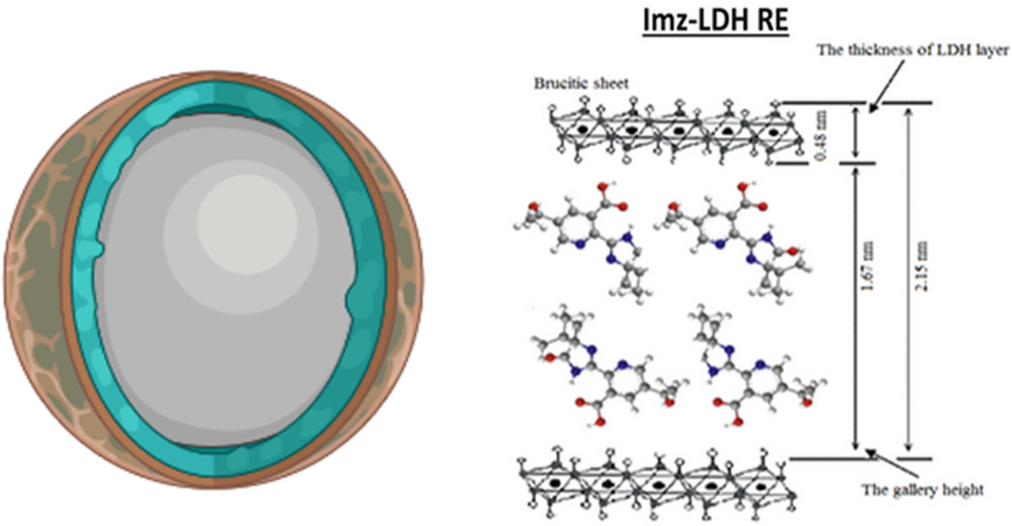

Figure 4. Encapsulation method of imazamox in a cationic nanoclay (Cloisite 10A). Partially reproduced from [51] with permission from Elsevier (license number: 5522980963504).

Mixtures of starch with different clays/organoclays, inspired by the work of Carr et al., have also been reported in recent years. These materials showed interesting properties. For example, isoproturon encapsulated in sodium montmorillonite with carboxymethyl starch-based micro-particles gave a reduction of around 90% in the herbicide released per irrigation of the soil [52]. This enabled the long-term delivery of the herbicide and, thus, reduced the pollution effect. In addition, a similar starch/montmorillonite nanocomposite with encapsulated ametryne displayed an interesting photoprotective effect on the herbicide [53]. This prolonged the action time for weed control, thus avoiding an extra application of the herbicide for days.

Chitosan has been employed as a matrix to be dispersed on the surface of clays. For example, the herbicide imazamox has been encapsulated in a chitosan matrix and adsorbed on sodium-enriched montmorillonite. This system showed good in vitro phytotoxicity for standard target species, such as cauliflower (*Brassica oleracea* var. botrytis L.) [54]. Similar results were obtained with imazamox encapsulated in cloisite clay and a modified quaternary alkylammonium montmorillonite clay in combating the invasive plant *Brassica nigra* W.D.J.Koch [51,55].

In terms of nanomaterials mixed with clays, additives other than starch have been employed, and these include phosphatidylcholine vesicles. In this case, atrazine and alachor were encapsulated in vesicles and supported on sodium montmorillonite. The resulting materials were tested in vitro against green foxtail (*Setaria viridis* (L.) P.Beauv.) germination [56]. This weed affects late-seeded wheat (*Triticum aestivum* L.), sugarbeet (*Beta vulgaris* L.), and maize (*Zea mays* L.) [57]. An experiment was designed to determine the content of the herbicide and its efficacy. The authors prepared a soil column and added the nanocomposite, which was then eluted with water. Green foxtail seeds were distributed at different heights in the column, and germination was evaluated to assess the release of the herbicide. A similar technique was employed for atrazine and imidacloprid encapsulated in chitosan and supported on bentonite clay [58], as well as for sulfosulfuron encapsulated in montmorillonite to target green foxtail [59]. This approach provided interesting data about the release profile from the clay. Other cases of mixed nanomaterials have been published, and these include encapsulation of the herbicide in micelles with subsequent adsorption on clays. Research on alkylpolyglucosides, ethoxylated amines [60], and octadecyltrimethylammonium bromide micelles (ODTMs) [61–64] has been published, with sepiolite and sodium montmorillonite acting as carriers. Pendimethalin was encapsulated with ODTMs and montmorillonite, and it was shown to be effective in reducing the root penetration of tomato (*Solanum lycopersicum* L.) into greenhouse drippers, thus enhancing the yield of this fruit.

Natural bioherbicides based on allelochemicals have been encapsulated in clays. *S*-Carvone, a monoterpene that is usually isolated from spearmint (*Mentha spicata* L.) or caraway (*Carum carvi* L.), was encapsulated in an organobentonite clay modified with dimethyl, benzyl, and hydrogenated alkyl tallow quaternary ammonium salts [15]. Its bioactivity was tested in vitro on standard target species (specifically, *Lactuca sativa* L.) in terms of general phytotoxicity, and it was found that the formulation improved the inhibition of shoots and germination when compared to the free compound. Similar results were obtained by Galán-Pérez et al. when encapsulating scopoletin in montmorillonite clays with the same modifications as those outlined for the previous organobentonite. This formulation also showed phytotoxic effects on *Lactuca sativa* L. germination and root length, and the results were better than those for free scopoletin [65].

More biological studies have been carried out on clay encapsulation than on macrocycle complexation, and there is, therefore, more knowledge on these systems for both classical herbicides and allelochemicals. However, despite the ecofriendly nature of this approach, field experiments have not been widely employed. The most remarkable results were reported by Galán-Jiménez et al. on the encapsulation of the herbicide mesotrione in sepiolite clays. These materials were applied post-emergence on a maize (*Zea mays* L.) crop to target broadleaf weeds between maize rows. The authors performed the experiment on an area of 0.216 ha and observed better results in terms of maize yield when compared to the positive control mesotrione/atrazine. The formulation was applied by directly spraying on the weeds [66]. The potential applications of this encapsulation technique remain unexploited when compared with currently available systems. Novel encapsulation methods could be interesting, but the biocompatibility of clay particles with the soil is a key factor in terms of a green approach, and these carriers have shown interesting properties for slow release and in-depth soil applications.

2.3. Matrices from Starch to Hybrids

Starch matrices were among the most relevant systems for encapsulation in the early research into this approach in agriculture. The modification of starch with xanthates or alkali chlorides generates microporous organic materials that are useful for the encapsulation of herbicides. The earliest system was developed with butylate and diazinon as bioactive compounds in the fight against foxtail (*Hordeum murinum* L.), which infests barley crops [67]. Other herbicides, such as EPTC [68,69] and trifluralin [70–72], were later encapsulated. Starch is readily available and cheap, and methods for chemical modification are well established. It is noteworthy that the application of this method leads to an enhancement in the persistence of the herbicide as the volatility is decreased. The increased interest in starch has allowed more in-depth characterization, and authors have studied how different levels of amylose/amylopectin in starch improve herbicide release in soil [73,74]. Bioassays were carried out, especially via field testing, with trials on encapsulated trifluralin against *Echinochloa crus-galli* L., which infests soybean (*Glycine max* L.) [75], and against foxtail (*Hordeum murinum* L.) [76]. In the latter case, different ions were evaluated, and it was found that calcium and borate were the best combination for achieving slow release.

There were reports about the environmental risks of trifluarin [77,78], and research over the following decade focused more on other classical herbicides, e.g., atrazine [79–83] and alachlor [82,84–86]. Strategies other than adduct formation were studied, e.g., twin-screw extrusion. However, the use of these techniques to produce starch for herbicide encapsulation generates slurries that, despite showing promise in vitro, were ruled out in subsequent research papers due to their problematic soil distribution in field experiments [87–90]. Ion adducts with starch were produced by Fleming et al. [91] and Reed et al. [92], who obtained interesting results through the encapsulation of alachlor/metribuzin with a starch–borate matrix and EPTC/butylate with a starch–iron ($FeCl_3$) matrix, respectively. In the former case, the encapsulated system led to an enhancement in soybean crop yield and protection against large crabgrass (*Digitaria sanguinalis* (L.) Scop.), foxtail millet (*Setaria italica* (L.) P.Beauv.), and longspine sandbur (*Cenchrus longispinus* (Hack.) Fernald). The application of starch–iron inhibited several weeds, such as johnsongrass (*Sorghum halepense* Pers.), giant foxtail (*Setaria faberi* R.A.W.Herrm.), and redroot pigweed (*Amaranthus retroflexus* L.), due to the enhanced release of the herbicides. However, this approach could cause high iron accumulation in the soil. Green approaches should take precedence over the efficacy of the formulation, and fortunately, this is the current trend.

In recent years, interest in starch as an encapsulation system for agrochemicals has decreased due to increased research on new materials, such as nanoparticles, new polymers, or biomaterials that offer different physicochemical properties. In terms of applications, starch materials are still very interesting due to their low cost, biocompatibility, and low soil pollution. However, this material does suffer from some drawbacks, such as low thermal stability and strong retention of the encapsulated bioactive compound. Researchers have, therefore, studied the hybridization of starch to enhance these properties. One such example is the use of starch-coated clay (montmorillonite) to encapsulate ametryn [93] and a mixed starch–alginate matrix to encapsulate 2,4-D [94,95]. However, the biological efficacy of these hybrids was not studied.

The first application of allelochemicals encapsulated in starch is an interesting example. This system was developed by Alipour et al. in 2019 and involved the encapsulation of rosemary essential oil (*Rosmarinus officinalis* L.) to control weeds such as amaranth (*Amaranthus retroflexus* L.), common purslane (*Portulaca oleracea* L.), and knapweed (*Acroptilon repens* (L.) DC.) [96]. The oil was trapped in the starch matrix, and this allowed its application as a solid. The same strategy was employed with savory (*Satureja hortensis* L.) essential oils, albeit encapsulated in a different type of matrix, namely, an Arabic gum matrix and apple pectin. This approach also led to high growth inhibition in the pre-emergence mode for amaranth weed [97]. Further studies on matrices in agriculture for weed control were carried out last year. Carboxymethyl chitosan [58,98], carboxymethyl [99], or ethyl-cellulose [100,101] and lignin [102,103] are the most interesting materials for herbicide and bioherbicide encapsulation on the basis of properties such as their release, delivery, and stability. These matrices were used in conjunction with metolachlor, 2,4-D, and atrazine, amongst others, but biological results were not obtained in vitro or in the field to demonstrate their efficacy.

Other matrices are currently under investigation, as they are readily available from natural sources and they show appropriate physicochemical properties a priori. Examples include β-CD nanosponges, which are obtained by crosslinking cyclodextrins [104], and biochars, which are stable carbon-rich materials formed through the pyrolysis of biomass under oxygen-limited conditions [105]. These materials were used to encapsulate the post-emergence herbicide nicosulfuron and natural coumarins, respectively. Only in the case of biochar@coumarin was phytotoxicity evaluated in *Lactuca sativa* L. models.

Similarly to the encapsulation method for clay systems, current formulation systems with matrices apply an in situ method to keep the bioactive component inside. The polymeric grid or structure is self-assembled while the herbicide is dispersed in the media. This increases the encapsulation efficiency and conveniently reduces the number of steps in the formulation. Figure 5 shows an example of the methodology for the encapsulation of agrochemicals with new polymers based on polyethylene glycol.

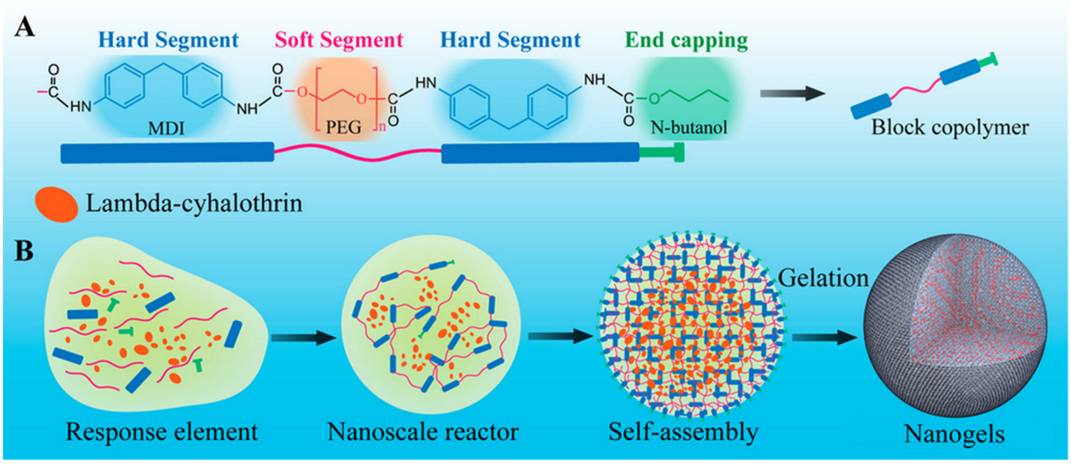

Figure 5. (**A**) Synthesis of block copolymers through the self-assembly of reaction elements. (**B**) Schematic of one-step synthesis of herbicide-loaded flexible nanogels. Reprinted (adapted) with permission from [106]. Copyright 2021 American Chemical Society.

Matrices, particularly starch, are still of great interest for field applications in weed control. The possibility of combining matrices with new biomaterials that are under development could improve properties and applications, especially in the case of allelochemicals. However, many more biological studies on the new matrices are required and are a prerequisite for future applications.

2.4. Micro- and Nanoparticles

The relevance of organic micro- and nanoparticles can be seen in Figure 6. These types of particle are the major contributors in the representation of the most widely employed methods for encapsulation. These contributions have undergone exponential growth in the last 15 years, and this is much more than any other formulation method for weed control. This increase is due to improvements in characterization techniques, such as electron microscopy, and the boost in polymer engineering.

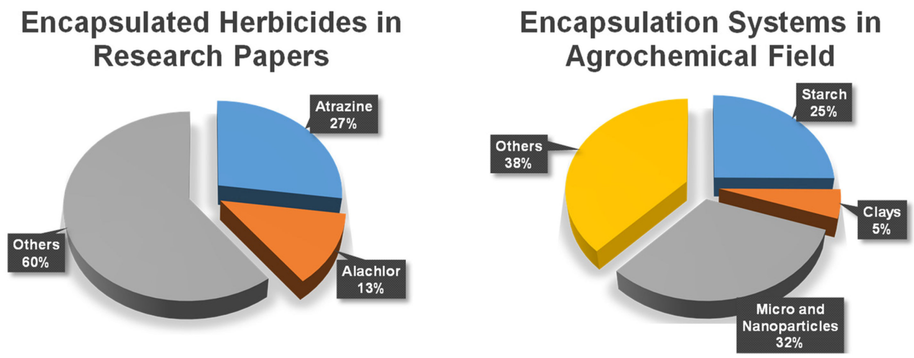

Figure 6. (**Left**) Most commonly studied herbicides for encapsulation. (**Right**) Most widely used systems for encapsulating agrochemicals.

The first use of microparticles for weed control involved the encapsulation of chlorpropham to target several grass weeds that infect tomatoes, safflowers, and onions [107]. It is interesting to note that this encapsulation was inspired by the volatilization issues associated with this herbicide. Therefore, the intention of the authors was to improve the persistence of the bioactive compound, as in the case of the early starch encapsulation approach. This idea contrasts with the current approach of nano- and microparticle encapsulation of various kinds of herbicides. However, Petersen and Shea exploited this idea for slow release and established the modern concepts of encapsulated herbicides for crop protection. Polyurea polymers were used to encapsulate alachlor, and the efficacy was demonstrated on *Triticum aestivum* L., which was protected for a longer time than with free alachlor [108].

Researchers subsequently employed different organic polymers, such as polylactic acid [109–111], polyvinyl alcohol [112], chitosan [112–115], poly(hydroxyvalerate) [116,117], and ethyl cellulose [118–122], for encapsulation in weed control. Norfluorazon, alachlor, and 2,4-D are the most widely studied herbicides, but it is worth highlighting the study by Chang et al., which is one of the first field studies on the bioactivity of organic nanoparticles/microparticles without an encapsulated bioactive compound [109]. These authors showed that the carriers alone can also stimulate the growth and yield of soybeans. This finding established the interesting pillars of new encapsulation models that address the dual effect of the phytotoxicity of the core and the synergistic properties of the shell.

The work by Quiñones et al. is worth highlighting, as it is the first report on allelochemical encapsulation with this system [114]. Brassinosteroids, which are usually isolated from *Brassica napus* L., were encapsulated in chitosan microparticles. The resulting materials were characterized, but they were not biologically tested. A similar approach was employed by Cho et al. [123] with the encapsulation of a vitamin B1 derivate in lecithin nanoparticles. However, the biological evaluation only showed good results against fungal infection prevention on white radish (*Raphanus sativus* L.), and relevant activities against weeds were not observed.

In the last ten years, nanoparticle encapsulation in agrochemistry has been improved by using new polymers that had already been tested for biological purposes. Poly(ε-caprolactone) [124–129] or alginate polymers [130–132] have attracted attention, and, for example, they have been applied against invasive plants such as *Brassica* spp. It is curious, however, that the increase in the number of publications about the encapsulation of herbicides with these structures does not necessarily correlate with a higher number of in vitro or field experiments [125,132–134]. Several papers were only concerned with the characterization or physicochemical properties, and any enhancement in weed control activity was only assumed. However, this trend changed dramatically around 2018 with the new requirements for publications, and most of the papers published later contain data from biological evaluations. As a consequence, more papers have been published on the encapsulation of new commercially available herbicides. Polymers have been explored in greater detail, and they have been tested on a variety of weeds and invasive plants. For example, poly(methylmethacrylate) has been employed to encapsulate haloxyfop and Gallant® in the fight against duckweed (*Lemna minor* L.) and greater duckweed (*Spirodela polyrhiza* (L.) Schleid.), both of which are invasive aquatic plants that particularly affect crops that have a high water demand [135–138]. The published papers describe the better efficacy of the herbicide in the encapsulated version and a reduction in water pollution. Several interesting mechanistic studies have been described in which the delivery processes in plant cells were examined to understand the mode of transport. One such example is atrazine encapsulated by poly(ε-caprolactone) nanoparticles, which were tested for the control of *Brassica juncea* (L.) Czern., which infests spring grain crops. The authors discovered that the formulation allowed penetration into the leaf tissue, with the formulation reaching the mesophyll through the stomata. This encapsulation improved the efficacy of the herbicide more than ten-fold, and side effects due to the capsule were not observed. In the same context, Falsini et al. explored the delivery mechanism of gibberellic acid encapsulated in lignin nanoparticles. This represents the first application of natural polymers for encapsulating a natural product, and the authors showed how the lignin nanoparticles entered the root of the seedling through cortical cells to enhance the growth of tomatoes (*Solanum lycopersicum* L.) and arugula (*Eruca vesicaria* (L.) Cav.) [139].

The trend in the application of allelochemicals has subsequently increased, but the isolation and synthesis of natural products still limit industrial approaches. For this reason, natural extracts are more commonly encapsulated with organic nanoparticles than with pure compounds. For example, Synowiec et al. employed maltodextrin nanoparticles to encapsulate caraway (*Carum carvi* L.) essential oil and obtained good results against

Echinochloa crus-galli (L.) P.Beauv. and *Galinsoga parviflora* Cav. Weeds, which infect rice and potato crops [140]. Taban et al. also encapsulated essential oil for agrochemical application, but this was sourced from savory (*Satureja hortensis* L.) and encapsulated with Arabic gum nanoparticles. This agro-nanomaterial showed high specificity in the control of *Amaranthus retroflexus* L. in post-emergence treatment without harming tomato crops [141]. This new strategy facilitates the desired green approach in agriculture for the replacement of classical herbicides, and in vitro and field experiments are currently supporting fully organic bioherbicides from the core (allelochemical) to the shell (formulation).

2.5. Metal–Organic Systems

In the past, metal–organic systems for encapsulation were inspired by the use of metalloids such as boron in starch–borate systems for butylate and *S*-ethyl dipropylthiocarbamate [142,143]. Currently, organometallic approaches have also been applied in formulations, especially in recent years since the discovery of metal–organic frameworks (MOFs). These materials are synthesized with zinc [144–146], iron [147–149], or gadolinium [150] as metal cores, and they display interesting properties in terms of their stability, delivery, and pH-responsiveness. Wang et al. tested 2,4-D encapsulated in Fe-MOFs in vitro against *Cichorium intybus* L. and found improved growth inhibition in comparison with that of the free herbicide. Similar phytotoxicity results were obtained with Zn-MOFs in which disulfide herbicides were encapsulated in tests against *Lolium rigidum* Gaudin, *Echinochloa crus-galli* (L.) P.Beauv., and *Amaranthus blitum* L. (syn.: *Amaranthus viridis* All.). These weeds mainly affect rice, corn, and potato crops, and the aforementioned formulation method led to a reduction in the root formation of the weeds that was twice as good as that of commercial herbicides and 5–10 times better than that of the non-encapsulated compound (Figure 7).

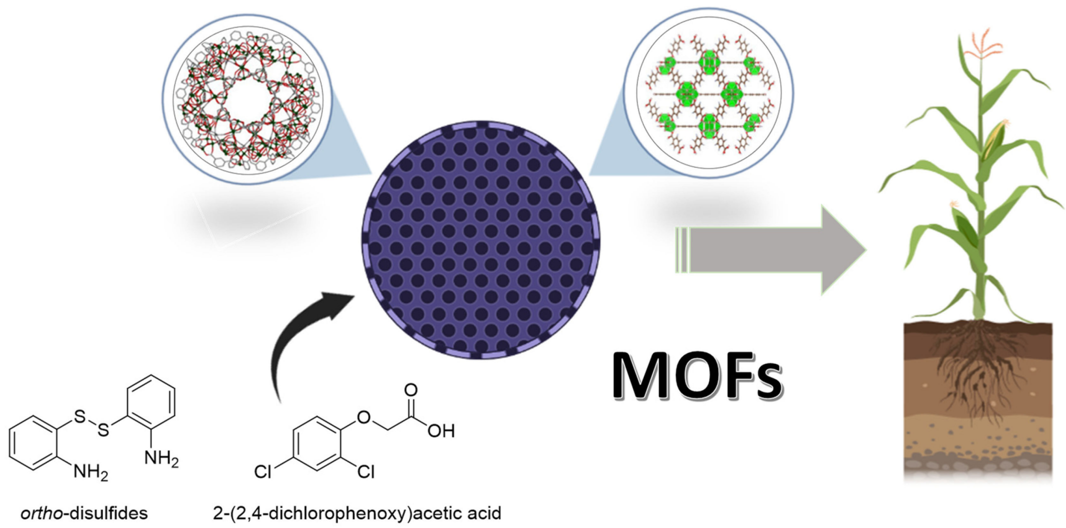

Figure 7. Scheme of encapsulation with *o*-disulfides and 2,4-D in metal–organic frameworks based on Fe and Zn, respectively [144,146]. Those agromaterials displayed phytotoxicity against weeds and protective effects on the crops.

Copper and silver are the metals that are most widely employed to generate encapsulation systems after those employed for MOFs. Copper can be found in agrochemical applications in stabilizers with biological polymers such as alginate [151] and incorporated into other nanoparticles to enhance their properties [152] or to enhance delivery to the surface of 2D graphene materials [153]. In a copper alginate carrier, this system was employed to encapsulate sodium selenate, which improved cherry radish (*Raphanus sativus* L.) yield and showed inhibitory effects on the fungus *Fusarium oxysporum* Schltdl [151]. Silver nanoparticles have been used to support paraquat encapsulated in chitosan polymer, and this nanomaterial was tested against the invasive plant *Eichhornia crassipes* (Mart.) Solms with enhanced results. The authors also tested its phytotoxicity in crops of interest, such as black gram (*Vigna mungo* (L.) Hepper), but inhibitory effects were not observed [154].

Different organometallic nanomaterials, such as metallacrowns [155], sandwich nanohybrid complexes [156], and organosilica vesicles [157], have been considered for weed control or other agrochemical purposes. In reality, the use of metal cores increases the cost of formulations and increases the environmental risk of soil and water pollution. Researchers have clarified the potential use of these systems and obtained good results even when using trace metals that are essential for plant development in the nanomaterial design. However, the lack of field experiments with these formulation methods is the best explanation for the limited use of this approach.

2.6. New Trends

New encapsulation methods in medicinal chemistry have been exploited to develop new formulations in agriculture in recent years, especially in the last decade. Applications in agrochemistry require low-cost and large-scale production not only for bioactive compounds, but also for carriers. However, it is important to note that a good formulation method can decrease the concentration of the herbicide/bioherbicide required in the field. Enhancements in water solubility, stability, or targeting could decrease the amount required for weed control by 10–50 times according to current research papers [11].

One of the main encapsulation techniques reported in the scientific literature involves the use of nanotubes. The first use of nanotubes for agrochemical purposes was in 2014 with the application of carbon nanotubes containing a polycitric acid surface shell. This matrix was adsorbed onto the surface of the nanotubes, followed by encapsulation of zineb and mancozeb, two pesticides that act against the fungus *Alternaria alternate* (Fr.) Keissl. (Fr.), which infects most cereal plants [158]. However, some level of toxicity has been associated with carbon nanotubes, and this approach does not seem to represent a green method [159]. It was not until 2019 that the first application of nanotubes in phytotoxicity studies was reported. In this case, nanotubes were formed with lithocholic acid, a natural product that is produced by the human body, and these nanotubes were employed to encapsulate disulfide herbicides [160] and natural sesquiterpene lactones (Figure 8) [16]. The authors demonstrated an enhancement in water solubility and in vitro efficacy against *Phalaris arundinacea* L., *Lolium perenne* L., and *Portulaca oleracea* L. The bioactivity was higher than for the free compounds and the positive control (Logran®) at higher concentrations (1000–300 μM) of the allelochemicals (aguerin B, cynaropicrin, and grosheimin). More specifically, the activity was mainly observed in the root formation of the weeds, and this system was more active against dicotyledons [16]. The data obtained—as well as the method itself—are of great interest for future field applications, particularly in the case of the natural sesquiterpene lactones due to their encapsulation with nanotubes generated by natural products. This would represent a green approach to weed control and food enhancement. In terms of natural/biological encapsulation systems, other interesting methods have been reported, and these include polymers generated by coumarin moieties for the encapsulation of 2,4-D [161]. This method was tested in vitro in *Cucurbita maxima* Duchesne models, and a boost in the activity was observed in comparison with the non-encapsulated herbicide. In addition to the idea of 'natural product carriers', apple pectin and Arabic gum have been employed [162]. There are other interesting ideas, such as the use of plant virus nanoparticles to deliver herbicides. Chariou et al. employed the icosahedral cowpea mosaic virus and the physalis mosaic virus to encapsulate nematocidal abamectin inside a virus capsule [163]. The results showed better soil mobility when compared to other encapsulation methods (e.g., silica nanoparticles) and a higher loading capacity.

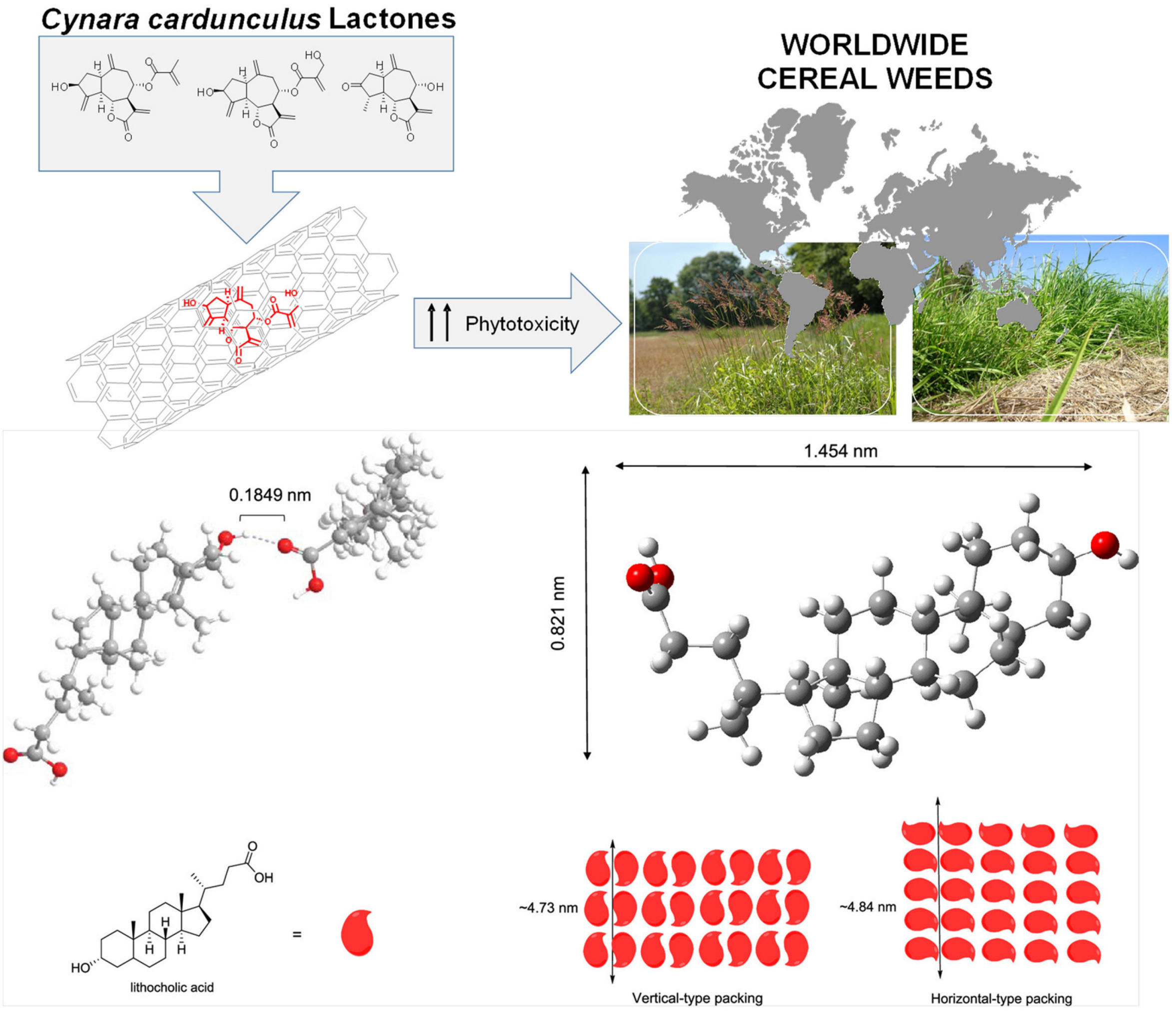

Figure 8. Nanotubes generated with lithocholic acid, a natural bile acid, to encapsulate *Cynara cardunculus* sesquiterpene lactones. Adapted with permission from [16,160]. Copyright 2019 and 2022, American Chemical Society.

In the last few years, allelopathy has gained some momentum, and natural products (allelochemicals) are seen as valid options for weed control. However, as outlined above, a good formulation without structural modification is important for retaining the role of a 'natural herbicide'. Some of the new methods presented here are promising in terms of formulation, but real applications in the field are still underexplored. It is our belief that the possibilities offered by organic encapsulation systems will meet with success, especially those employing other natural components as carriers for their formulation.

3. Conclusions

The most relevant advances in the encapsulation and formulation of herbicides and allelochemicals for weed control have been presented. Several methods have been successfully applied since this method was established in 1973. Some of these approaches have been extensively studied, e.g., that using starch, but they are now less widely studied due to new advances in nanotechnology and polymers. These advances have allowed the emergence of nanoparticle encapsulation, as well as the use of new materials, such as nanotubes and metal–organic hybrids. However, there is a lack of biological studies on these materials, and they must be analyzed in vitro and in the field before their large-scale application. Most of the knowledge on the encapsulating materials presented here has been applied to classical herbicides, with enhanced results being obtained for their physicochemical and biological properties. Nevertheless, in the future, it is expected that this technique will be applied to natural products/allelochemicals to achieve green approaches in agriculture. In the last five years, advances have been made in this respect, but challenges remain in terms of formulation and before industrial applications are developed. The authors suggest that the methods presented here indicate that applications using organic nanoparticles are very promising due to their biodegradability, ecological materials, slow-release properties, and greater potential for surface functionalization. In general, nanoparticles have three dimensions at the nanoscale, which offers more options for bioavailability compared to microstructures or 2D nanomaterials. Recognition, assimilation, and transport by and through plant cells are easier for 3D nanomaterials.

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References

1. Sinclair, R.G. Slow-Release Pesticide System. Polymers of Lactic and Glycolic Acids as Ecologically Beneficial, Cost-Effective Encapsulating Materials. *Environ. Sci. Technol.* **1973**, *7*, 955–956. [CrossRef]
2. Pennwalt to Test Encapsulated Pesticide. *Chem. Eng. News Arch.* **1972**, *50*, 68–69. [CrossRef]
3. Jaga, K.; Dharmani, C. Methyl Parathion: An Organophosphate Insecticide Not Quite Forgotten. *Rev. Environ. Health* **2006**, *21*, 57–68. [CrossRef] [PubMed]
4. CNN News Monsanto Pleads Guilty to Illegally Spraying Banned Pesticide in Maui. Available online: https://edition.cnn.com/2019/11/22/us/monsanto-maui-pesticide-guilty-plea/index.html (accessed on 2 June 2023).
5. Gilliom, R.J.; Barbash, J.E.; Crawford, C.G.; Hamilton, P.A.; Martin, J.D.; Nakagaki, N.; Nowell, L.H.; Scott, J.C.; Stackelberg, P.E.; Thelin, G.P.; et al. Occurrence and Distribution in Streams and Ground Water. In *Pesticides in the Nation's Streams and Ground Water, 1992–2001*; Geological Survey (USGS): Reston, VA, USA, 2001; pp. 41–66.
6. Law, E.U. Commission Decision of 10 March 2004 Concerning the Non-Inclusion of Atrazine in Annex I to Council Directive 91/414/EEC and the Withdrawal of Authorisations for Plant Protection Products Containing This Active Substance. Available online: https://eur-lex.europa.eu/eli/dec/2004/248/oj (accessed on 12 June 2023).
7. Hedlund, B. Flemish Government Approves Belgium Glyphosate Ban for Individuals. Available online: https://www.baumhedlundlaw.com/belgium-glyphosate-ban-individuals/ (accessed on 12 June 2023).
8. Peterson, M.A.; Collavo, A.; Ovejero, R.; Shivrain, V.; Walsh, M.J. The Challenge of Herbicide Resistance around the World: A Current Summary. *Pest Manag. Sci.* **2018**, *74*, 2246–2259. [CrossRef] [PubMed]
9. Hulme, P.E. Weed Resistance to Different Herbicide Modes of Action Is Driven by Agricultural Intensification. *Field Crops Res.* **2023**, *292*, 108819. [CrossRef]
10. Scavo, A.; Mauromicale, G. Crop Allelopathy for Sustainable Weed Management in Agroecosystems: Knowing the Present with a View to the Future. *Agronomy* **2021**, *11*, 2104. [CrossRef]
11. Macías, F.A.; Mejías, F.J.; Molinillo, J.M. Recent Advances in Allelopathy for Weed Control: From Knowledge to Applications. *Pest Manag. Sci.* **2019**, *75*, 2413–2436. [CrossRef]
12. Macías, F.A.; Durán, A.G.; Molinillo, J.M.G. Allelopathy: The Chemical Language of Plants. In *Progress in the Chemistry of Organic Natural Products*; Springer: Berlin/Heidelberg, Germany, 2020; Volume 112, pp. 1–84.
13. Harding, D.P.; Raizada, M.N. Controlling Weeds with Fungi, Bacteria and Viruses: A Review. *Front. Plant Sci.* **2015**, *6*, 659. [CrossRef]
14. Roberts, J.; Florentine, S.; Fernando, W.G.D.; Tennakoon, K.U. Achievements, Developments and Future Challenges in the Field of Bioherbicides for Weed Control: A Global Review. *Plants* **2022**, *11*, 2242. [CrossRef]
15. Gámiz, B.; Celis, R. S-Carvone Formulation Based on Granules of Organoclay to Modulate Its Losses and Phytotoxicity in Soil. *Agronomy* **2021**, *11*, 1593. [CrossRef]

16. Mejías, F.J.R.; Fernández, I.P.; Rial, C.; Varela, R.M.; Molinillo, J.M.G.; Calvino, J.J.; Trasobares, S.; Macías, F.A. Encapsulation of *Cynara Cardunculus* Guaiane-Type Lactones in Fully Organic Nanotubes Enhances Their Phytotoxic Properties. *J. Agric. Food Chem.* **2022**, *70*, 3644–3653. [CrossRef] [PubMed]
17. Suganya, V.; Anuradha, V. Microencapsulation and Nanoencapsulation: A Review. *Int. J. Pharm. Clin. Res.* **2017**, *9*, 233–239. [CrossRef]
18. Scavo, A.; Mejías, F.J.R.; Chinchilla, N.; Molinillo, J.M.G.; Schwaiger, S.; Lombardo, S.; Macías, F.A.; Mauromicale, G. Wheat Response and Weed-Suppressive Ability in the Field Application of a Nanoencapsulated Disulfide (DiS-NH_2) Bioherbicide Mimic. *Agronomy* **2023**, *13*, 1132. [CrossRef]
19. Szejtli, J. Physiological Effects of Cyclodextrins on Plants. *Starch* **1983**, *35*, 433–438. [CrossRef]
20. Szejtli, J. Cyclodextrins in Pesticides. *Starch* **1985**, *37*, 382–386. [CrossRef]
21. Gines, J.M.; Perez-Martinez, I.; Arias, M.J.; Moyano, J.R.; Morillo, E.; Ruiz-Conde, A.; Sachez-Soto, P.J. Inclusion of the Herbicide 2,4-Dichlorophenoxyacetic Acid (2,4-D) with β-Cyclodextrin by Different Processing Methods. *Chemosphere* **1996**, *33*, 321–334. [CrossRef]
22. Hosangadi, B.; Asgaonkar, A. Inclusion of Acaricides by Complexation with β-Cyclodextrin. *J. Incl. Phenom. Mol. Recognit. Chem.* **1995**, *23*, 35–39. [CrossRef]
23. Lezcano, M.; Novo, M.; Al-Soufi, W.; Rodríguez-Núñez, E.; Tato, J.V.; Vázquez Tato, J. Complexation of Several Fungicides with β-Cyclodextrin: Determination of the Association Constants and Isolation of the Solid Complexes. *J. Agric. Food Chem.* **2003**, *51*, 5036–5040. [CrossRef]
24. Lezcano, M.; Al-Soufi, W.; Novo, M.; Rodríguez-Núñez, E.; Vázquez Tato, J. Complexation of Several Benzimidazole-Type Fungicides with α- and β-Cyclodextrins. *J. Agric. Food Chem.* **2002**, *50*, 108–112. [CrossRef]
25. Benfeito, S.; Rodrigues, T.; Garrido, J.; Borges, F.; Garrido, E.M. Host-Guest Interaction between Herbicide Oxadiargyl and Hydroxypropyl-β-Cyclodextrin. *Sci. World J.* **2013**, *2013*, 1–6. [CrossRef]
26. Perez-Martinez, J.I.; Morillo, E.; Gines, J.M. β-CD Effect on 2,4-D Soil Adsorption. *Chemosphere* **1999**, *39*, 2047–2056. [CrossRef]
27. Cai, X.; Liu, W.; Chen, S. Environmental Effects of Inclusion Complexation between Methylated β-Cyclodextrin and Diclofop-Methyl. *J. Agric. Food Chem.* **2005**, *53*, 6744–6749. [CrossRef] [PubMed]
28. Cala, A.; Molinillo, J.M.G.G.; Fernández-Aparicio, M.; Ayuso, J.; Álvarez, J.A.; Rubiales, D.; Macías, F.A.; Delavault, P. Complexation of Sesquiterpene Lactones with Cyclodextrins: Synthesis and Effects on Their Activities on Parasitic Weeds. *Org. Biomol. Chem.* **2017**, *15*, 6500–6510. [CrossRef]
29. Moeini, A.; Masi, M.; Zonno, M.C.; Boari, A.; Cimmino, A.; Tarallo, O.; Vurro, M.; Evidente, A. Encapsulation of Inuloxin A, a Plant Germacrane Sesquiterpene with Potential Herbicidal Activity, in β-Cyclodextrins. *Org. Biomol. Chem.* **2019**, *17*, 2508–2515. [CrossRef] [PubMed]
30. Zhang, J.; Li, B.; Bi, H.; Zhang, P. Synthesis of Atrazine-HPCD Inclusion and Its Bioactivity. *Trans. Tianjin Univ.* **2014**, *20*, 350–357. [CrossRef]
31. Geng, Q.; Xie, J.; Wang, X.; Cai, M.; Ma, H.; Ni, H. Preparation and Characterization of Butachlor/(2-Hydroxypropyl)-β-Cyclodextrin Inclusion Complex: Improve Soil Mobility and Herbicidal Activity and Decrease Fish Toxicity. *J. Agric. Food Chem.* **2018**, *66*, 12198–12205. [CrossRef] [PubMed]
32. Gao, S.; Jiang, J.; Li, X.; Liu, Y.; Zhao, L.; Fu, Y.; Ye, F. Enhanced Physicochemical Properties and Herbicidal Activity of an Environment-Friendly Clathrate Formed by β-Cyclodextrin and Herbicide Cyanazine. *J. Mol. Liq.* **2020**, *305*, 112858. [CrossRef]
33. Gao, S.; Jiang, J.Y.; Liu, Y.Y.; Fu, Y.; Zhao, L.X.; Li, C.Y.; Ye, F. Enhanced Solubility, Stability, and Herbicidal Activity of the Herbicide Diuron by Complex Formation with β-Cyclodextrin. *Polymers* **2019**, *11*, 1396. [CrossRef]
34. Mejías, F.J.R.; Carrasco, Á.; Durán, A.G.; Molinillo, J.M.G.; Macías, F.A.; Chinchilla, N. On the Formulation of Disulfide Herbicides Based on Aminophenoxazinones: Polymeric Nanoparticle Formulation and Cyclodextrin Complexation to Combat Crop Yield Losses. *Pest Manag. Sci.* **2022**, *79*, 1547–1556. [CrossRef]
35. Mortensen, A.; Aguilar, F.; Crebelli, R.; Di Domenico, A.; Dusemund, B.; Frutos, M.J.; Galtier, P.; Gott, D.; Gundert-Remy, U.; Leblanc, J.C.; et al. Re-Evaluation of β-Cyclodextrin (E 459) as a Food Additive. *EFSA J.* **2016**, *14*, e04628. [CrossRef]
36. Mokhtar, M.S.; Suliman, F.O.; Elbashir, A.A. Investigation of Inclusion Complexes of Ametryne and Atrazine with Cucurbit[n]Urils (n = 6–8) Using Experimental and Theoretical Techniques. *J. Incl. Phenom. Macrocycl. Chem.* **2019**, *94*, 31–43. [CrossRef]
37. Mokhtar, M.S.; Suliman, F.O.; Elbashir, A.A. The Binding Interaction of Imazapyr with Cucurbit[n]Uril (n = 6–8): Combined Experimental and Molecular Modeling Study. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2018**, *194*, 67–75. [CrossRef]
38. Mokhtar, M.S.; Elbashir, A.A.; Suliman, F.O. Spectroscopic and Molecular Simulation Studies on the Interaction of Imazaquin Herbicide with Cucurbiturils (n = 6–8). *J. Mol. Struct.* **2023**, *1274*, 134444. [CrossRef]
39. Mejías, F.J.R.; He, S.; Varela, R.M.; Molinillo, J.M.G.; Barba-Bon, A.; Nau, W.M.; Macías, F.A. Stability and PKa Modulation of Aminophenoxazinones and Their Disulfide Mimics by Host–Guest Interaction with Cucurbit[7]Uril. Direct Applications in Agrochemical Wheat Models. *J. Agric. Food Chem.* **2023**, *71*, 480–487. [CrossRef] [PubMed]
40. Connick, W.J.; Bradow, J.M.; Wells, W.; Steward, K.K.; Van, T.K. Preparation and Evaluation of Controlled-Release Formulations of 2,6-Dichlorobenzonitrile. *J. Agric. Food Chem.* **1984**, *32*, 1199–1205. [CrossRef]
41. Qasem, J.R. Nutrient Accumulation by Weeds and Their Associated Vegetable Crops. *J. Hortic. Sci.* **1992**, *67*, 189–195. [CrossRef]
42. Chauhan, B.S.; Johnson, D.E. Germination Ecology of Goosegrass (*Eleusine indica*): An Important Grass Weed of Rainfed Rice. *Weed Sci.* **2008**, *56*, 699–706. [CrossRef]

43. Zhang, S.-Z.; Li, Y.-H.; Kong, C.-H.; Xu, X.-H. Interference of Allelopathic Wheat with Different Weeds. *Pest Manag. Sci.* **2016**, *72*, 172–178. [CrossRef]
44. Zhou, B.; Kong, C.H.; Li, Y.H.; Wang, P.; Xu, X.H. Crabgrass (*Digitaria sanguinalis*) Allelochemicals That Interfere with Crop Growth and the Soil Microbial Community. *J. Agric. Food Chem.* **2013**, *61*, 5310–5317. [CrossRef]
45. Carr, M.E.; Wing, R.E.; Doane, W.M. Clay as a Carrier in Starch Encapsulated Herbicides Prepared by Extrusion Processing. *Starch-Stärke* **1994**, *46*, 9–13. [CrossRef]
46. Flores Céspedes, F.; Villafranca Sánchez, M.; Pérez García, S.; Fernández Pérez, M. Modifying Sorbents in Controlled Release Formulations to Prevent Herbicides Pollution. *Chemosphere* **2007**, *69*, 785–794. [CrossRef] [PubMed]
47. Rivoira, L.; Frassati, S.; Cordola, S.; Castiglioni, M.; Onida, B.; Ronchetti, S.; Ingrando, I.; Bruzzoniti, M.C. Encapsulation of the Glyphosate Herbicide in Mesoporous and Soil-Affine Sorbents for Its Prolonged Release. *Chem. Eng. J.* **2022**, *431*, 134225. [CrossRef]
48. Han, Y.-S.; Lee, S.-Y.; Yang, J.-H.; Soo Hwang, H.; Park, I. Paraquat Release Control Using Intercalated Montmorillonite Compounds. *J. Phys. Chem. Solids* **2010**, *71*, 460–463. [CrossRef]
49. Rashidzadeh, A.; Olad, A.; Hejazi, M.J. Controlled Release Systems Based on Intercalated Paraquat onto Montmorillonite and Clinoptilolite Clays Encapsulated with Sodium Alginate. *Adv. Polym. Technol.* **2017**, *36*, 177–185. [CrossRef]
50. Marco-Brown, J.L.; Undabeytia, T.; Torres Sánchez, R.M.; dos Santos Afonso, M. Slow-Release Formulations of the Herbicide Picloram by Using Fe–Al Pillared Montmorillonite. *Environ. Sci. Pollut. Res.* **2017**, *24*, 10410–10420. [CrossRef]
51. Khatem, R.; Celis, R.; Hermosín, M.C. Cationic and Anionic Clay Nanoformulations of Imazamox for Minimizing Environmental Risk. *Appl. Clay Sci.* **2019**, *168*, 106–115. [CrossRef]
52. Wilpiszewska, K.; Spychaj, T.; Paździoch, W. Carboxymethyl Starch/Montmorillonite Composite Microparticles: Properties and Controlled Release of Isoproturon. *Carbohydr. Polym.* **2016**, *136*, 101–106. [CrossRef]
53. Giroto, A.S.; De Campos, A.; Pereira, E.I.; Ribeiro, T.S.; Marconcini, J.M.; Ribeiro, C. Photoprotective Effect of Starch/Montmorillonite Composites on Ultraviolet-Induced Degradation of Herbicides. *React. Funct. Polym.* **2015**, *93*, 156–162. [CrossRef]
54. Cabrera, A.; Celis, R.; Hermosín, M.C. Imazamox-Clay Complexes with Chitosan- and Iron(III)-Modified Smectites and Their Use in Nanoformulations. *Pest Manag. Sci.* **2016**, *72*, 1285–1294. [CrossRef]
55. Cal-IPC (California Invasive Plant Council). *Cal-IPC Plant Assessment Form for Brassica Nigra*; Cal-IPC: Berkeley, CA, USA, 2004.
56. Sánchez-Verdejo, T.; Undabeytia, T.; Nir, S.; Villaverde, J.; Maqueda, C.; Morillo, E. Environmentally Friendly Formulations of Alachlor and Atrazine: Preparation, Characterization, and Reduced Leaching. *J. Agric. Food Chem.* **2008**, *56*, 10192–10199. [CrossRef]
57. Wall, D.A.; Friesen, G.H. Effect of Duration of Green Foxtail (*Setaria viridis*) Competition on Potato (*Solanum tuberosum*) Yield Effect of Duration of Green Foxtail (*Setaria viridis*) Competition on Potato (*Solanum tuberosum*) Yield. *Weed Technol.* **1990**, *4*, 539–542. [CrossRef]
58. Li, J.; Yao, J.; Li, Y.; Shao, Y. Controlled Release and Retarded Leaching of Pesticides by Encapsulating in Carboxymethyl Chitosan/Bentonite Composite Gel. *J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes* **2012**, *47*, 795–803. [CrossRef] [PubMed]
59. Mishael, Y.G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S. Sulfosulfuron Incorporated in Micelles Adsorbed on Montmorillonite for Slow Release Formulations. *J. Agric. Food Chem.* **2003**, *51*, 2253–2259. [CrossRef] [PubMed]
60. Galán-Jiménez, M.D.C.; Mishael, Y.-G.; Nir, S.; Morillo, E.; Undabeytia, T. Factors Affecting the Design of Slow Release Formulations of Herbicides Based on Clay-Surfactant Systems. A Methodological Approach. *PLoS ONE* **2013**, *8*, e59060. [CrossRef] [PubMed]
61. Zait, Y.; Segev, D.; Schweitzer, A.; Goldwasser, Y.; Rubin, B.; Mishael, Y.G. Development and Employment of Slow-Release Pendimethalin Formulations for the Reduction of Root Penetration into Subsurface Drippers. *J. Agric. Food Chem.* **2015**, *63*, 1682–1688. [CrossRef]
62. Goldreich, O.; Goldwasser, Y.; Mishael, Y.G. Effect of Soil Wetting and Drying Cycles on Metolachlor Fate in Soil Applied as a Commercial or Controlled-Release Formulation. *J. Agric. Food Chem.* **2011**, *59*, 645–653. [CrossRef]
63. Hermosin, M.C.; Calderón, M.J.; Aguer, J.P.; Cornejo, J. Organoclays for Controlled Release of the Herbicide Fenuron. *Pest Manag. Sci.* **2001**, *57*, 803–809. [CrossRef]
64. Mishael, Y.G.; Undabeytia, T.; Rabinovitz, O.; Rubin, B.; Nir, S. Slow-Release Formulations of Sulfometuron Incorporated in Micelles Adsorbed on Montmorillonite. *J. Agric. Food Chem.* **2002**, *50*, 2864–2869. [CrossRef]
65. Galán-Pérez, J.A.; Gámiz, B.; Celis, R. Granulated Organoclay as a Sorbent to Protect the Allelochemical Scopoletin from Rapid Biodegradation in Soil. *Environ. Technol. Innov.* **2022**, *28*, 102707. [CrossRef]
66. del Carmen Galán-Jiménez, M.; Morillo, E.; Bonnemoy, F.; Mallet, C.; Undabeytia, T. A Sepiolite-Based Formulation for Slow Release of the Herbicide Mesotrione. *Appl. Clay Sci.* **2020**, *189*, 105503. [CrossRef]
67. Doane, W.M.; Shasha, B.S.; Russell, C.R. Encapsulation of Pesticides within a Starch Matrix. *Control. Release Pestic.* **1977**, *53*, 74–83.
68. Schreiber, M.M.; White, M.D. Effect of Formulation Technology on the Release of Starch Encapsulated EPTC. *Proc. Br. Crop Prot. Conf. Weeds* **1980**, *15*, 225–229.
69. Schreiber, M.M.; White, M.D. Granule Structure and Rate of Release with Starch-Encapsulated Thiocarbamates. *Weed Sci.* **1980**, *28*, 685–690. [CrossRef]

70. Shasha, B.S.; Trimnell, D.; Otey, F.H. Encapsulation of Pesticides in a Starch-Calcium Adduct. *J. Polym. Sci. Part A Polym. Chem.* **1981**, *19*, 1891–1899. [CrossRef]
71. Trimnell, D.; Shasha, B.S.; Doane, W.M. Release of Trifluralin from Starch Xanthide Encapsulated Formulations. *J. Agric. Food Chem.* **1981**, *29*, 637–640. [CrossRef]
72. Trimnell, D.; Shasha, B.S.; Otey, F.H. The Effect of α-Amylases upon the Release of Trifluralin Encapsulated in Starch. *J. Control. Release* **1985**, *1*, 183–190. [CrossRef]
73. Wing, R.E.; Doane, W.M. The Role of Retrogradation on Starch Encapsulation and Release of Active Agents. *Polym. Prepr.* **1987**, *28*, 108–109.
74. Wing, R.E.; Maiti, S.; Doane, W.M. Effectiveness of Jet-cooked Pearl Cornstarch as a Controlled Release Matrix. *Starch-Stäke* **1987**, *39*, 422–425. [CrossRef]
75. White, M.D.; Schreiber, M.M. Herbicidal Activity of Starch Encapsulated Trifluralin. *Weed Sci.* **1984**, *32*, 387–394. [CrossRef]
76. Trimnell, D.; Shasha, B.S. Autoencapsulation: A New Method for Entrapping Pesticides within Starch. *J. Control. Release* **1988**, *7*, 25–31. [CrossRef]
77. Grover, R.; Wolt, J.; Cessna, A.; Schiefer, B. Environmental Fate of Trifluralin. In *Reviews of Environmental Contamination and Toxicology*; Springer: Berlin/Heidelberg, Germany, 1997; pp. 1–64.
78. European Union European Union-Final Regulatory Action. Available online: http://archive.pic.int/view_displayFRA.php?id=1186&back=viewB_FRAchems.php?sort=chemical (accessed on 7 June 2023).
79. Schreiber, M.M.; Hickman, M.V.; Vail, G.D. Starch-encapsulated Atrazine: Efficacy and Transport. *J. Environ. Qual.* **1993**, *22*, 443–453. [CrossRef]
80. Vail, G.D.; Hickman, M.V.; Schreiber, M.M. Atrazine Dissipation and Carryover from Commercial and Starch-Encapsulated Atrazine Formulations. *Weed Sci.* **1997**, *45*, 842–847. [CrossRef]
81. Fleming, G.F.; Wax, L.M.; Simmons, F.W. Leachability and Efficacy of Starch-Encapsulated Atrazine. *Weed Technol.* **1992**, *6*, 297–302. [CrossRef]
82. Buhler, D.D.; Schreiber, M.M.; Koskinen, W.C. Weed Control with Starch-Encapsulated Alachlor, Metolachlor, and Atrazine. *Weed Technol.* **1994**, *8*, 277–284. [CrossRef]
83. Williams, C.F.; Nelson, S.D.; Gish, T.J. Release Rate and Leaching of Starch-Encapsulated Atrazine in a Calcareous Soil. *Soil Sci. Soc. Am. J.* **1999**, *63*, 425–432. [CrossRef]
84. Gish, T.G.; Shirmohammadi, A.; Wienhold, B.J. Field-Scale Mobility and Persistence of Commercial and Starch-Encapsulated Atrazine and Alachlor. *J. Environ. Qual.* **1994**, *23*, 355–359. [CrossRef]
85. Wienhold, B.J.; Sadeghi, A.M.; Gish, T.J. Effect of Starch Encapsulation and Temperature on Volatilization of Atrazine and Alachlor. *J. Environ. Qual.* **1993**, *22*, 162–166. [CrossRef]
86. Wienhold, B.J.; Gish, T.J. Effect of Formulation and Tillage Practice on Volatilization of Atrazine and Alachlor. *J. Environ. Qual.* **1994**, *23*, 292–298. [CrossRef]
87. Wing, R.E.; Maiti, S.; Doane, M. Amylose Content of Starch Control the Release of Encapsulated Bioactive Agents. *J. Control. Release* **1988**, *7*, 33–37. [CrossRef]
88. Trimnell, D.; Wing, R.E.; Carr, M.E.; Doane, W.M. Encapsulation of EPTC in Starch by Twin-screw Extrusion. *Ind. Crops Prod.* **1991**, *43*, 146–151. [CrossRef]
89. Wing, R.E.; Carr, M.E.; Trimnell, D.; Doane, W.M. Comparison of Steam Injection Cooking versus Twin-Screw Extrusion of Pearl Cornstarch for Encapsulation of Chloroacetanilide Herbicides. *J. Control. Release* **1991**, *16*, 267–277. [CrossRef]
90. Carr, M.E.; Wing, R.E.; Doane, W.M. Encapsulation of Atrazine within a Starch Matrix by Extrusion Processing. *Cereal Chem.* **1991**, *68*, 262–266.
91. Fleming, G.F.; Wax, L.M.; Simmons, F.W.; Felsot, A.S. Movement of Alachlor and Metribuzin from Controlled Release Formulations in a Sandy Soil. *Weed Sci.* **1992**, *40*, 606–613. [CrossRef]
92. Reed, J.P.; Hall, F.R.; Trimnell, D. Effect of Encapsulating Thiocarbamate Herbicides within Starch for Overcoming Enhanced Degradation in Soils. *Starch-Stärke* **1989**, *41*, 184–186. [CrossRef]
93. Giroto, A.S.; de Campos, A.; Pereira, E.I.; Cruz, C.C.T.; Marconcini, J.M.; Ribeiro, C. Study of a Nanocomposite Starch-Clay for Slow-Release of Herbicides: Evidence of Synergistic Effects between the Biodegradable Matrix and Exfoliated Clay on Herbicide Release Control. *J. Appl. Polym. Sci.* **2014**, *131*, 41188. [CrossRef]
94. Riyajan, S.A. Physical Property Testing of a Novel Hybrid Natural Rubber-Graft-Cassava Starch/Sodium Alginate Bead for Encapsulating Herbicide. *Polym. Test.* **2017**, *58*, 300–307. [CrossRef]
95. Riyajan, S.A. A Novel Hybrid 2,4-Dichlorophenoxy Acetate Bead from Modified Cassava Starch and Sodium Alginate with Modified Natural Rubber Coating. *J. Polym. Environ.* **2018**, *26*, 1950–1961. [CrossRef]
96. Alipour, M.; Saharkhiz, M.J.; Niakousari, M.; Seidi Damyeh, M. Phytotoxicity of Encapsulated Essential Oil of Rosemary on Germination and Morphophysiological Features of Amaranth and Radish Seedlings. *Sci. Hortic.* **2019**, *243*, 131–139. [CrossRef]
97. Taban, A.; Saharkhiz, M.J.; Naderi, R. A Natural Post-Emergence Herbicide Based on Essential Oil Encapsulation by Cross-Linked Biopolymers: Characterization and Herbicidal Activity. *Environ. Sci. Pollut. Res.* **2020**, *27*, 45844–45858. [CrossRef]
98. Dong, H.; Li, F.; Li, J.; Li, Y. Characterizations of Blend Gels of Carboxymethylated Polysaccharides and Their Use for the Controlled Release of Herbicide. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2012**, *49*, 235–241. [CrossRef]

99. Li, J.; Jiang, M.; Wu, H.; Li, Y. Addition of Modified Bentonites in Polymer Gel Formulation of 2,4-D for Its Controlled Release in Water and Soil. *J. Agric. Food Chem.* **2009**, *57*, 2868–2874. [CrossRef] [PubMed]
100. Flores-Céspedes, F.; Daza-Fernández, I.; Villafranca-Sánchez, M.; Fernández-Pérez, M. Use of Ethylcellulose To Control Chlorsulfuron Leaching in a Calcareous Soil. *J. Agric. Food Chem.* **2009**, *57*, 2856–2861. [CrossRef] [PubMed]
101. Fernández-Pérez, M.; Villafranca-Sánchez, M.; Flores-Céspedes, F.; Daza-Fernández, I. Ethylcellulose and Lignin as Bearer Polymers in Controlled Release Formulations of Chloridazon. *Carbohydr. Polym.* **2011**, *83*, 1672–1679. [CrossRef]
102. Fernández-Pérez, M.; Villafranca-Sánchez, M.; Flores-Céspedes, F.; Daza-Fernández, I. Lignin-Polyethylene Glycol Matrices and Ethylcellulose to Encapsulate Highly Soluble Herbicides. *J. Appl. Polym. Sci.* **2014**, *132*, 41422. [CrossRef]
103. Yiamsawas, D.; Kangwansupamonkon, W.; Kiatkamjornwong, S. Lignin-Based Nanogels for the Release of Payloads in Alkaline Conditions. *Eur. Polym. J.* **2021**, *145*, 110241. [CrossRef]
104. Liu, X.; Li, W.; Xuan, G. Preparation and Characterization of β-Cyclodextrin Nanosponges and Study on Enhancing the Solubility of Insoluble Nicosulfuron. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *774*, 012108. [CrossRef]
105. Gámiz, B.; López-Cabeza, R.; Velarde, P.; Spokas, K.A.; Cox, L. Biochar Changes the Bioavailability and Bioefficacy of the Allelochemical Coumarin in Agricultural Soils. *Pest Manag. Sci.* **2021**, *77*, 834–843. [CrossRef]
106. Luo, J.; Gao, Y.; Liu, Y.; Huang, X.; Zhang, D.; Cao, H.; Jing, T.; Liu, F.; Li, B. Self-Assembled Degradable Nanogels Provide Foliar Affinity and Pinning for Pesticide Delivery by Flexibility and Adhesiveness Adjustment. *ACS Nano* **2021**, *15*, 14598–14609. [CrossRef] [PubMed]
107. Turner, B.C.; Glotfelty, D.E.; Taylor, A.W.; Watson, D.R. Volatilization of Microencapsulated and Conventionally Applied Chlorpropham in the Field. *Agron. J.* **1978**, *70*, 933–937. [CrossRef]
108. Petersen, B.B.; Shea, P.J. Microencapsulated Alachlor and Its Behavior on Wheat (*Triticum aestivum*) Straw. *Weed Sci.* **1989**, *37*, 719–723. [CrossRef]
109. Chang, Y.N.; Mueller, R.E.; Iannotti, E.L. Use of Low MW Polylactic Acid and Lactide to Stimulate Growth and Yield of Soybeans. *Plant Growth Regul.* **1996**, *19*, 223–232. [CrossRef]
110. Stloukal, P.; Kucharczyk, P.; Sedlarik, V.; Bazant, P.; Koutny, M. Low Molecular Weight Poly(Lactic Acid) Microparticles for Controlled Release of the Herbicide Metazachlor: Preparation, Morphology, and Release Kinetics. *J. Agric. Food Chem.* **2012**, *60*, 4111–4119. [CrossRef]
111. Boehm, A.L.; Martinon, I.; Zerrouk, R.; Rump, E.; Fessi, H. Nanoprecipitation Technique for the Encapsulation of Agrochemical Active Ingredients. *J. Microencapsul.* **2003**, *20*, 433–441. [CrossRef] [PubMed]
112. Yeom, C.K.; Oh, S.B.; Rhim, J.W.; Lee, J.M. Microencapsulation of Water-Soluble Herbicide by Interfacial Reaction. I. Characterization of Microencapsulation. *J. Appl. Polym. Sci.* **2000**, *78*, 1645–1655. [CrossRef]
113. Wang, X.; Zhao, J. Encapsulation of the Herbicide Picloram by Using Polyelectrolyte Biopolymers as Layer-by-Layer Materials. *J. Agric. Food Chem.* **2013**, *61*, 3789–3796. [CrossRef]
114. Quiñones, J.P.; García, Y.C.; Curiel, H.; Covas, C.P. Microspheres of Chitosan for Controlled Delivery of Brassinosteroids with Biological Activity as Agrochemicals. *Carbohydr. Polym.* **2010**, *80*, 915–921. [CrossRef]
115. Yeom, C.K.; Kim, Y.H.; Lee, J.M. Microencapsulation of Water-Soluble Herbicide by Interfacial Reaction. II. Release Properties of Microcapsules. *J. Appl. Polym. Sci.* **2002**, *84*, 1025–1034. [CrossRef]
116. Grillo, R.; de Melo, N.F.S.; de Lima, R.; Lourenço, R.W.; Rosa, A.H.; Fraceto, L.F. Characterization of Atrazine-Loaded Biodegradable Poly(Hydroxybutyrate-Co-Hydroxyvalerate) Microspheres. *J. Polym. Environ.* **2010**, *18*, 26–32. [CrossRef]
117. Lobo, F.A.; De Aguirre, C.L.; Silva, M.S.; Grillo, R.; De Melo, N.F.S.; De Oliveira, L.K.; De Morais, L.C.; Campos, V.; Rosa, A.H.; Fraceto, L.F. Poly(Hydroxybutyrate-Co-Hydroxyvalerate) Microspheres Loaded with Atrazine Herbicide: Screening of Conditions for Preparation, Physico-Chemical Characterization, and in Vitro Release Studies. *Polym. Bull.* **2011**, *67*, 479–495. [CrossRef]
118. Pérez-Martínez, J.I.; Morillo, E.; Maqueda, C.; Ginés, J.M. Ethyl Cellulose Polymer Microspheres for Controlled Release of Norfluazon. *Pest Manag. Sci.* **2001**, *57*, 688–694. [CrossRef]
119. Dailey, O.D.J. Volatilization of Alachlor from Polymeric Formulations. *J. Agric. Food Chem.* **2004**, *52*, 6742–6746. [CrossRef] [PubMed]
120. Dowler, C.C.; Dailey, O.D.; Mullinix, B.G. Polymeric Microcapsules of Alachlor and Metolachlor: Preparation and Evaluation of Controlled-Release Properties. *J. Agric. Food Chem.* **1999**, *47*, 2908–2913. [CrossRef] [PubMed]
121. Elbahri, Z.; Taverdet, J.L. Optimization of an Herbicide Release from Ethylcellulose Microspheres. *Polym. Bull.* **2005**, *54*, 353–363. [CrossRef]
122. Sopeña, F.; Cabrera, A.; Maqueda, C.; Morillo, E. Controlled Release of the Herbicide Norflurazon into Water from Ethylcellulose Formulations. *J. Agric. Food Chem.* **2005**, *53*, 3540–3547. [CrossRef]
123. Cho, J.; Seo, Y.; Yim, T.; Lee, H. Effect of Nanoencapsulated Vitamin B1 Derivative on Inhibition of Both Mycelial Growth and Spore Germination of *Fusarium oxysporum* f. sp. Raphani. *Int. J. Mol. Sci.* **2013**, *14*, 4283–4297. [CrossRef] [PubMed]
124. Clemente, Z.; Grillo, R.; Jonsson, M.; Santos, N.Z.P.; Feitosa, L.O.; Lima, R.; Fraceto, L.F. Ecotoxicological Evaluation of Poly(ε-Caprolactone) Nanocapsules Containing Triazine Herbicides. *J. Nanosci. Nanotechnol.* **2014**, *14*, 4911–4917. [CrossRef]
125. Grillo, R.; Rosa, A.H.; Fraceto, L.F. Poly(ε-Caprolactone) Nanocapsules Carrying the Herbicide Atrazine: Effect of Chitosan-Coating Agent on Physico-Chemical Stability and Herbicide Release Profile. *Int. J. Environ. Sci. Technol.* **2014**, *11*, 1691–1700. [CrossRef]

126. Pereira, A.E.S.; Grillo, R.; Mello, N.F.S.; Rosa, A.H.; Fraceto, L.F. Application of Poly(Epsilon-Caprolactone) Nanoparticles Containing Atrazine Herbicide as an Alternative Technique to Control Weeds and Reduce Damage to the Environment. *J. Hazard. Mater.* **2014**, *268*, 207–215. [CrossRef]
127. Diyanat, M.; Saeidian, H. The Metribuzin Herbicide in Polycaprolactone Nanocapsules Shows Less Plant Chromosome Aberration than Non-Encapsulated Metribuzin. *Environ. Chem. Lett.* **2019**, *17*, 1881–1888. [CrossRef]
128. Preisler, A.C.; Pereira, A.E.S.; Campos, E.V.R.; Dalazen, G.; Fraceto, L.F.; Oliveira, H.C. Atrazine Nanoencapsulation Improves Pre-Emergence Herbicidal Activity against Bidens Pilosa without Enhancing Long-Term Residual Effect on Glycine Max. *Pest Manag. Sci.* **2020**, *76*, 141–149. [CrossRef]
129. Sousa, B.T.; Santo Pereira, A.D.E.; Fraceto, L.F.; de Oliveira, H.C.; Dalazen, G. Effectiveness of Nanoatrazine in Post-Emergent Control of the Tolerant Weed Digitaria Insularis. *J. Plant Prot. Res.* **2020**, *60*, 185–192. [CrossRef]
130. Babaei, S.; Kahrizi, D.; Nosratti, I.; Karimi, N.; Arkan, E.; Tahir, M.B. Preparation and Characterization of Chloridazon-Loaded Alginate/Chitosan Nanocapsules. *Cell. Mol. Biol.* **2022**, *68*, 34–42. [CrossRef] [PubMed]
131. Artusio, F.; Casà, D.; Granetto, M.; Tosco, T.; Pisano, R. Alginate Nanohydrogels as a Biocompatible Platform for the Controlled Release of a Hydrophilic Herbicide. *Processes* **2021**, *9*, 1641. [CrossRef]
132. Faria, D.M.; Dourado Júnior, S.M.; Nascimento, J.P.L.D.; Nunes, E.D.S.; Marques, R.P.; Rossino, L.S.; Moreto, J.A. Development and Evaluation of a Controlled Release System of TBH Herbicide Using Alginate Microparticles. *Mater. Res.* **2016**, *20*, 225–235. [CrossRef]
133. Kumar, S.; Bhanjana, G.; Sharma, A.; Sarita; Sidhu, M.C.; Dilbaghi, N. Herbicide Loaded Carboxymethyl Cellulose Nanocapsules as Potential Carrier in Agrinanotechnology. *Sci. Adv. Mater.* **2015**, *7*, 1143–1148. [CrossRef]
134. Maruyama, C.R.; Guilger, M.; Pascoli, M.; Bileshy-José, N.; Abhilash, P.C.; Fraceto, L.F.; De Lima, R. Nanoparticles Based on Chitosan as Carriers for the Combined Herbicides Imazapic and Imazapyr. *Sci. Rep.* **2016**, *6*, 19768–19781. [CrossRef]
135. Gerardo, R.; de Lima, I.P. Monitoring Duckweeds (*Lemna minor*) in Small Rivers Using Sentinel-2 Satellite Imagery: Application of Vegetation and Water Indices to the Lis River (Portugal). *Water* **2022**, *14*, 2284. [CrossRef]
136. Torbati, S.; Mahmoudian, M.; Alimirzaei, N. Nanocapsulation of Herbicide Haloxyfop-R-Methyl in Poly(Methyl Methacrylate): Phytotoxicological Effects of Pure Herbicide and Its Nanocapsulated Form on Duckweed as a Model Macrophyte. *Turk. J. Chem.* **2018**, *42*, 132–145. [CrossRef]
137. Torbati, S.; Mahmoudian, M.; Alimirzaei, N. Toxicological Effects of a Post Emergent Herbicide on Spirodela Polyrhiza as a Model Macrophyte: A Comparison of the Effects of Pure and Nano-Capsulated Form of the Herbicide. *Iran. J. Toxicol.* **2018**, *12*, 45–54. [CrossRef]
138. Mahmoudian, M.; Torbati, S.; AliMirzayi, N.; Nozad, E.; Kochameshki, M.G.; Shokri, A. Preparation and Investigation of Poly(methylmethacrylate) Nano-Capsules Containing Haloxyfop-R-Methyl and Their Release Behavior. *J. Environ. Sci. Health Part B* **2019**, *55*, 301–309. [CrossRef]
139. Falsini, S.; Clemente, I.; Papini, A.; Tani, C.; Schiff, S.; Salvatici, M.C.; Petruccelli, R.; Benelli, C.; Giordano, C.; Gonnelli, C.; et al. When Sustainable Nanochemistry Meets Agriculture: Lignin Nanocapsules for Bioactive Compound Delivery to Plantlets. *ACS Sustain. Chem. Eng.* **2019**, *7*, 19935–19942. [CrossRef]
140. Synowiec, A.; Lenart-Boroń, A.; Bocianowski, J.; Lepiarczyk, A.; Kalemba, D. How Soil-Applied Maltodextrin with Caraway (*Carum carvi* L.) Oil Affects Weed and Soil Microbiological Activity in Maize (*Zea mays* L.) Stands. *Pol. J. Environ. Stud.* **2019**, *29*, 817–826. [CrossRef] [PubMed]
141. Taban, A.; Saharkhiz, M.J.; Khorram, M. Formulation and Assessment of Nano-Encapsulated Bioherbicides Based on Biopolymers and Essential Oil. *Ind. Crops Prod.* **2020**, *149*, 112348. [CrossRef]
142. Wing, R.E.; Maiti, S.; Doane, M. Factors Affecting Release of Butylate from Calcium Ion-Modified Starch-Borate Matrices. *J. Control. Release* **1987**, *5*, 79–89. [CrossRef]
143. Shasha, B.S.; Trimnell, D.; Otey, F.H. Starch–Borate Complexes for EPTC Encapsulation. *J. Appl. Polym. Sci.* **1984**, *29*, 67–73. [CrossRef]
144. Mejías, F.J.R.; Trasobares, S.; Varela, R.M.; Molinillo, J.M.G.; Calvino, J.J.; Macías, F.A. One-Step Encapsulation of Ortho-Disulfides in Functionalized Zinc MOF. Enabling Metal–Organic Frameworks in Agriculture. *ACS Appl. Mater. Interfaces* **2021**, *13*, 7997–8005. [CrossRef] [PubMed]
145. Raju, P.; Natarajan, S. Investigation of Pesticidal and Anti-Biofilm Potential of Calotropis Gigantea Latex Encapsulated Zeolitic Imidazole Nanoframeworks. *J. Inorg. Organomet. Polym. Mater.* **2022**, *32*, 2771–2780. [CrossRef]
146. Ma, S.; Wang, Y.; Yang, X.; Ni, B.; Lü, S. MOF Hybrid for Long-Term Pest Management and Micronutrient Supply Triggered with Protease. *ACS Appl. Mater. Interfaces* **2022**, *14*, 17783–17793. [CrossRef] [PubMed]
147. Wang, Y.; Ma, S.; Yang, X.; Li, Y.; Lü, S. Facile Synthesis of the Dual Pesticide-Loaded Metal–Organic Framework Hybrid for PH-Responsive Release. *ACS Agric. Sci. Technol.* **2022**, *2*, 1267–1275. [CrossRef]
148. Shan, Y.; Xu, C.; Zhang, H.; Chen, H.; Bilal, M.; Niu, S.; Cao, L.; Huang, Q. Polydopamine-Modified Metal–Organic Frameworks, NH_2-Fe-MIL-101, as PH-Sensitive Nanocarriers for Controlled Pesticide Release. *Nanomaterials* **2020**, *10*, 2000. [CrossRef]
149. Dong, J.; Chen, W.; Feng, J.; Liu, X.; Xu, Y.; Wang, C.; Yang, W.; Du, X. Facile, Smart, and Degradable Metal–Organic Framework Nanopesticides Gated with Fe III-Tannic Acid Networks in Response to Seven Biological and Environmental Stimuli. *ACS Appl. Mater. Interfaces* **2021**, *13*, 19507–19520. [CrossRef]

150. Lunn, R.D.J.; Tocher, D.A.; Sidebottom, P.J.; Montgomery, M.G.; Keates, A.C.; Carmalt, C.J. Encapsulation of Aromatic Compounds and a Non-Aromatic Herbicide into a Gadolinium-Based Metal–Organic Framework via the Crystalline Sponge Method. *Cryst. Growth Des.* **2020**, *20*, 7238–7245. [CrossRef]
151. Ma, X.; Zhang, S.; Yang, Y.; Tong, Z.; Shen, T.; Yu, Z.; Xie, J.; Yao, Y.; Gao, B.; Li, Y.C.; et al. Development of Multifunctional Copper Alginate and Bio-Polyurethane Bilayer Coated Fertilizer: Controlled-Release, Selenium Supply and Antifungal. *Int. J. Biol. Macromol.* **2023**, *224*, 256–265. [CrossRef] [PubMed]
152. Liang, Y.; Song, J.; Dong, H.; Huo, Z.; Gao, Y.; Zhou, Z.; Tian, Y.; Li, Y.; Cao, Y. Fabrication of PH-Responsive Nanoparticles for High Efficiency Pyraclostrobin Delivery and Reducing Environmental Impact. *Sci. Total Environ.* **2021**, *787*, 147422. [CrossRef] [PubMed]
153. Sharma, S.; Singh, B.; Bindra, P.; Panneerselvam, P.; Dwivedi, N.; Senapati, A.; Adholeya, A.; Shanmugam, V. Triple-Smart Eco-Friendly Chili Anthracnose Control Agro-Nanocarrier. *ACS Appl. Mater. Interfaces* **2021**, *13*, 9143–9155. [CrossRef] [PubMed]
154. Karthick Raja Namasivayam, S.; Aruna, A. Gokila Evaluation of Silver Nanoparticles-Chitosan Encapsulated Synthetic Herbicide Paraquate (AgNp-CS-PQ) Preparation for the Controlled Release and Improved Herbicidal Activity against *Eichhornia crassipes*. *Res. J. Biotechnol.* **2014**, *9*, 19–27.
155. Dendrinou-Samara, C.; Alevizopoulou, L.; Iordanidis, L.; Samaras, E.; Kessissoglou, D.P. 15-MC-5 Manganese Metallacrowns Hosting Herbicide Complexes. Structure and Bioactivity. *J. Inorg. Biochem.* **2002**, *89*, 89–96. [CrossRef]
156. Hussein, M.Z.; Hashim, N.; Yahaya, A.H.; Zainal, Z. Synthesis of an Herbicides-Inorganic Nanohybrid Compound by Ion Exchange-Intercalation of 3(2-Chlorophenoxy)Propionate into Layered Double Hydroxide. *J. Exp. Nanosci.* **2010**, *5*, 548–558. [CrossRef]
157. Liang, Y.; Gao, Y.; Wang, W.; Dong, H.; Tang, R.; Yang, J.; Niu, J.; Zhou, Z.; Jiang, N.; Cao, Y. Fabrication of Smart Stimuli-Responsive Mesoporous Organosilica Nano-Vehicles for Targeted Pesticide Delivery. *J. Hazard. Mater.* **2020**, *389*, 122075. [CrossRef]
158. Sarlak, N.; Taherifar, A.; Salehi, F. Synthesis of Nanopesticides by Encapsulating Pesticide Nanoparticles Using Functionalized Carbon Nanotubes and Application of New Nanocomposite for Plant Disease Treatment. *J. Agric. Food Chem.* **2014**, *62*, 4833–4838. [CrossRef]
159. Francis, A.P.; Devasena, T. Toxicity of Carbon Nanotubes: A Review. *Toxicol. Ind. Health* **2018**, *34*, 200–210. [CrossRef] [PubMed]
160. Mejías, F.J.R.; Trasobares, S.; López-Haro, M.; Varela, R.M.; Molinillo, J.M.G.; Calvino, J.J.; Macías, F.A. In Situ Eco Encapsulation of Bioactive Agrochemicals within Fully Organic Nanotubes. *ACS Appl. Mater. Interfaces* **2019**, *11*, 41925–41934. [CrossRef] [PubMed]
161. Atta, S.; Paul, A.; Banerjee, R.; Bera, M.; Ikbal, M.; Dhara, D.; Singh, N.P. Photoresponsive Polymers Based on a Coumarin Moiety for the Controlled Release of Pesticide 2,4-D. *RSC Adv.* **2015**, *5*, 99968–99975. [CrossRef]
162. Taban, A.; Saharkhiz, M.J.; Kavoosi, G. Development of Pre-Emergence Herbicide Based on Arabic Gum-Gelatin, Apple Pectin and Savory Essential Oil Nano-Particles: A Potential Green Alternative to Metribuzin. *Int. J. Biol. Macromol.* **2021**, *167*, 756–765. [CrossRef]
163. Chariou, P.L.; Dogan, A.B.; Welsh, A.G.; Saidel, G.M.; Baskaran, H.; Steinmetz, N.F. Soil Mobility of Synthetic and Virus-Based Model Nanopesticides. *Nat. Nanotechnol.* **2019**, *14*, 712–718. [CrossRef]