Nano-Enabled Weed Management Using Poly(Epsilon-Caprolactone)-Based Nanoherbicides

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The number of effective herbicides available to farmers is steadily decreasing due to increasing herbicide resistance. It seems very important to address and effectively deal with the main weed management challenges (low crop yield and environmental pollution) by investigating the potential of newly introduced materials, such as biocompatible polymer-based nanoparticles. It has been indicated that some polymeric nanocarriers can penetrate biological barriers, including membranes and plant cell walls, and translocate across vascular tissues, resulting in a more efficient delivery of active ingredients. Poly(epsilon-caprolactone) is a biocompatible material that is easily decomposable by enzymes and fungi. Poly ε-caprolactone (PCL) nanoparticles could be applied as nanocarriers of herbicides in agriculture due to their low toxicity, their potential for large-scale synthesis from inexpensive materials, their ability to dissolve herbicides, their high loading capacity, and their ability to help minimize the chemical decomposition of herbicides.

biocompatible polymer | controlled release | environmental contamination | nanocarrier | nanoencapsulation | poly(epsilon-caprolactone) | polymeric nanoparticles

1. Introduction

Weeds are one of the main factors threatening agriculture, and in vulnerable agro-ecosystems, they may endanger the entire harvest. Today, most herbicides on the market are designed to eradicate or control the weed plants' above-ground portions. Rhizomes and tubers, which serve as propagation sources for new weeds during the evolving season, are active below-ground plant portions that are unaffected by any of these herbicides. In this regard, Field bindweed (*Convolvulus arvensis* L.), Canada thistle (*Cirsium arvense* L.), purple nutsedge (*Cyperus rotundus* L.), and Johnsongrass (*Sorghum halepense* L.) could be mentioned as some of the main problematic perennial weeds [1][2]. Compared to soils where weeds are controlled, soils that are infested with weeds and weed seeds are likely to produce lower crop yields. Hence, increased crop yield might be the result of enhanced herbicide efficacy brought about by nanotechnology [3]. The use of new technology in several aspects of agriculture, including the development of effective monitoring systems, smart chemicals, and gene delivery systems for crops, nanoherbicides, and nanoformulations, among many other applications, will transform the agricultural system. By reducing the effects of environmental contamination, it will boost productivity and decrease agricultural waste that arises indirectly. Therefore, it seems necessary to introduce nanotechnology into all agricultural systems, along with further research and field application [4][5][6]. Nanotechnology involves the manipulation or self-assembly of single atoms, molecules, or molecular clusters into structures to produce materials and products with novel or different features. One of the most exciting areas of science and technology in recent years is the study of the unique features of materials that arise at the nanoscale.

Nanoherbicides are created with the aid of nanosized preparations or nanomaterial-based herbicide formulations. Nanoherbicides are characterized as herbicide formulations based on nanomaterials that make use of the potential for effective chemical delivery to a target site. The widespread concerns about food and environmental contamination have been gradually brought on by the excessive and improper use of chemical herbicides. In comparison to conventional herbicides, formulations based on nanomaterials could increase the herbicide's efficacy, increase its solubility, and decrease its toxicity. To increase bioavailability and improve weed eradication, herbicides are coated with nanomaterials. Nanoherbicides are made up of tiny particles containing the herbicide's active components and have a high affinity for their target due to their huge specific surface area. The wettability and dispersion of agricultural formulations are also improved by nanoherbicides. Some of the formulations used in nanoherbicides include nanoemulsions, nanocapsules, nanocontainers, and nanocages [7].

There is a necessity to create and develop nanoherbicides that can safeguard the environment and function as both subsurface and above-ground pretenders of weeds and that truly imitate the agricultural system. The development of a target-specific herbicide chemical enclosed in a nanoparticle is directed toward a specific receptor in the roots of the target weeds, where it enters the root system and translocates to areas that block the hydrolysis of food reserves. This can cause certain weed plants to starve and eventually result in their death [3][8].

2. Weed Control System

Weeds are plants that establish themselves in addition to crops. Any plant, regardless of its economic value, can become a weed if it grows on cropland against the will of the landowner. Currently, there are about 2000 agricultural weeds in the world that reduce crop yields; release harmful substances into the soil; create intense competition for light, moisture, nutrients, and water; create shade; and serve as a breeding ground for most crop diseases and pests. Globally, weeds cause about a 31.5% reduction in crop production and result in economic losses of USD 32 billion per year [9]. Herbicides are most widely used as pesticides, which account for more than 40% of their total use, whilst insecticides and fungicides account for about 30% and 20%, respectively [10].

The toxicity of the herbicides used in agriculture depends on their chemical stability, photodegradability, solubility, bioavailability, and sorption in soil. There are several possible solutions to minimize toxicity, including the development of carrier systems capable of modifying the properties of a compound and providing controlled release. Controlled release provides a safer environment for pesticide use and minimizes the potential threat to the environment. At the same time, by reducing the amount of pesticide used, its effectiveness is increased [11]. The major interest of these nano-objects lies in the inherent properties (biodegradability, biocompatibility, and better stability) of their morphology and size. Indeed, a reduction in the size of various structures that are below the micrometer has allowed for new properties that are not observed at more conventional sizes to be highlighted. Aliphatic polyesters, such as poly (lactic acid) (PLA), poly (lactic acid-co-glycolic acid) (PLGA), or poly(epsilon-caprolactone) (PCL), are the most commonly used to develop active substance carriers.

3. Challenges in Weed Management

3.1. Herbicide Resistance

With the intensive use of herbicides, it has become clear that the effectiveness of these preparations has diminished over time due to the appearance of weeds, which are resistant to their effects. The number of efficient herbicides available to farmers is steadily declining as a result of herbicide resistance. According to Heap's [12] recent surveys, there are currently 523 unique cases (species × site of action) of herbicide-resistant weeds globally, comprising 269 species (154 dicots and 115 monocots). Weeds have evolved resistance to 21 of the 31 known herbicide sites of action and to 167 different herbicides (reported in 99 crops in 72 countries) [12]. Herbicide resistance has a significant impact on weed control, especially following the development of weeds that are resistant to numerous herbicides with various modes of action (MOAs). Following the idea of the "pesticide treadmill", growers then adopt other classes of herbicides to supplement or replace those that have decreased in efficacy due to the evolution of herbicide resistance. This has led to the process of the continuous use of new herbicides, or combining new herbicides, and the herbicidal resistance also posed by newer herbicides is a driver of the research on herbicidal systems [13][14][15].

3.2. Herbicide Residues

The violation of hygienic standards in the storage, transport, and massive application of herbicides in their translational forms leads to their accumulation in the environment, food raw materials, and food products, which presents a threat to humans and animals, specifically pollinators. Based on their application modalities, between 10% and 75% of pesticides do not reach their targets, resulting in the frequent contamination of terrestrial and aquatic environments [10]. However, herbicides that act selectively on weeds can cause symptoms in crops.

The evolution of pesticides in the environment depends on their physicochemical properties, as well as on the pedoclimatic and topographic characteristics of the land. After application, they reach the soil, where they can be subjected to retention processes, transfer to groundwater, and transfer to the atmosphere via volatilization or erosion. Some pesticides such as organochlorines are persistent in soil, remaining from a few hours to several years. 2-Methyl-4-chlorophenoxyacetic acid was detected at 93% of 68 water sites surveyed along the Danube River by Loos et al. [16]. From a dust sampling campaign conducted in 2012 in 239 homes in the Rhône-Alpes Auvergne region, Béranger et al. [17] detected 125 distinct pesticides, at least once, among the 276 searched for. Several researches have indicated that glyphosate can adsorb to sediments, constituting a pathway for its dispersion in aquatic environments [18][19].

4. Nanotechnology in Weed Management

According to previous research, only a small portion of herbicides is absorbed by plants. The rest is lost through one or more of the following ways: volatilization, adsorption, leaching, photodecomposition, chemical degradation, and microbial breakdown. The continuous use of herbicides results in the development of resistance in weeds toward that herbicide [12]. The science of nanoherbicide technology can be used as a tool to fabricate a slow-release nanoencapsulated pre-emergence herbicide for achieving season-long weed-free conditions without hampering the environment. Nanoherbicides are being developed to address the problems in perennial weed management and exhausting the weed seed bank. Encapsulation by nanomaterials can protect active ingredients from premature degradation and unnecessary losses.

Studies have shown that the nanoencapsulation of herbicides can produce more targeted and less toxic formulations for agricultural applications. Due to enhanced herbicidal activity in comparison with commercial formulations, the use of nanoencapsulated herbicides would allow for the application of lower dosages of the herbicide [20]. The use of lower doses of herbicides is desirable, as it reduces the long-term effects of the residues of herbicides in agricultural areas and their toxicity to the environment. Nanoherbicides can aid in the easy delivery of herbicides to weed plants, reducing the residual accumulation in soil [20].

nanoencapsulation. The membrane system controls diffusion, ion exchange, and other mechanisms that allow the release of the toxicant [21]. Also, with the aid of nanotechnology, water chemicals can travel through the cracks created in weed seeds by the use of nano-carbon tubes, causing them to germinate quickly. As a result, this decreases the weed seed bank and interferes with the weed seed dormancy feature, which allows weeds to develop in wash out. Eliminating naturally occurring germination inhibitors in some weeds also improves germination.

Target-specific release is also helpful in killing weeds, without even interacting with crops, and ultimately results in a high crop yield. Nanoherbicides have the advantage that they can be further developed for the target site inhibition of the biochemical reactions of weeds [20]. Nanoencapsulations decrease herbicide buildup in soil and prevent the emergence of weeds that are resistant to them. This is because employing herbicides that are encapsulated in nanoparticles or using nanoparticles as herbicide carriers allows the active ingredient of the herbicide to be delivered directly to the target location of weeds. This lessens the likelihood of soil herbicide buildup. The extremely small dimensions of nanoherbicides allow them to blend with soil particles and prevent the growth of weed species that have grown resistant to traditional herbicides. Smart delivery systems reduce the amount of active ingredient needed.

In summary, using nanoformulations could potentially increase the stability, shelf life, bioavailability, environmental sustainability, and safety of the active ingredients for sustained release. The modification of surface or bulk properties at the nanoscale has a great potential for effective improvement in agricultural productivity. Some nanomaterials enhance the mechanisms of tolerance in plants under stress conditions. In this regard, these nanomaterials could be considered as effective promising tools for overcoming some of the main problems in sustainable agricultural production. Due to their unique qualities and applications, nanoformulated agricultural products are enforced in different areas [22].

5. Types of Nanomaterials for Assembling Nanoherbicides

5.1. Nanoherbicides Based on Inorganic Nanomaterials

Silica, metal–organic frameworks, mesoporous silica nanoparticles, clay minerals, and other inorganic materials can be used for the preparation of nanoherbicides. Some of these nanoherbicides can release ions, though some can enclose organic molecules and release them gradually [20][23][24][25][26]. For example, inorganic nanomaterials for the synthesis of nanoherbicides based on double-layer aluminum hydroxides or zinc [27], or sepiolite clay linked with magnesium–aluminum, have been extensively used for herbicide alliance since they may reduce herbicide leaching through soil and, hence, increase the transportation of the functional materials to the plant [28][29]. They can also aid the system in encapsulating hydrophobic herbicides among their layers and are used for combating *Chlamydomonas reinhardtii Dang* algae. Clay elements can possibly form nano-assembling herbicides since they can be biocompatible and inexpensive and have a pertinent potential for reduction [30]. Water-bearing silicates or aluminosilicates, such as kaolinite, montmorillonite, attapulgite, diatomite, and hydrotalcite, are the principal types of clay minerals. Clay minerals are often crystalline and capable of being altered by inorganic or organic cations and have a high specific surface area. These modified derivatives work well as adsorbents for a variety of organic chemicals, and their release into the environment can be regulated by their adsorption of active ingredients [31].

Recently, metal–organic frameworks (MOFs) have also been employed to regulate the release of pesticides, which has become a research hotspot. Metal–organic structures are continuously repeating periodic systems made of porous crystalline substances with metal ions or clusters as the center atom and one or more organic ligands. Since MOFs have distinct benefits over other materials, including huge surface areas, customizable apertures, and a variety of structural options, they are widely used in a variety of industries [32][33]. The types of organic molecules and metal ions utilized and the techniques for connecting them are very specialized, but the composition of MOF materials defines the flexible diversity of their metal ions and ligands. As a result, the structures and properties of MOF materials are quite varied. Organic ligands that are highly stable are carboxylic acids, which are often employed in the manufacture of MOF materials. Almost all metal elements, including transitional elements and lanthanide metals, are included in the range of metal centers that is employed. Copper, iron, and zinc are often and extensively used [34][35].

5.2. Nanoherbicides Based on Organic Nanomaterials

Organic nanomaterials are exceptional materials for the synthesis of nanoherbicides, and they can be built on polymers, synthetic organic materials [36][37], lipids, lignocellulosic materials, proteins, and complex macromolecules such as dendrimers [38][39][40][41][42]. Generally, various techniques have been reported to create nanoherbicides, but the nanoemulsion method is the most often used method [43][44][45][46]. Polymers are broadly used in nanoherbicides for preparation because of their biodegradability, affordability, and biocompatibility [47][48].

A type of natural polymer is chitosan, a natural deacetylation of chitin that displays good characteristics like biodegradability, biocompatibility, and environmental friendliness. Chitosan can be utilized as a bacteriostatic material to control plant diseases and pests, and they can be formulated with pesticides to prepare nanopesticides

[49][50][51]. Liang et al. [52] prepared chitosan nanomaterials that were loaded with avermectin using an ion-crosslinking method; it was found that these microcapsules showed excellent slow release, which efficiently enhanced the time of retention of avermectin and, hence, enhanced its photostability [52]. Also, sodium alginate is a conventional anionic polymeric polysaccharide that can be cross-linked with polyvalent metal cations. Sodium alginate was used to create calcium alginate hydrogels that had Lentinus edodes. Good environmental sensitivity was proven in the release from the hydrogels, and L. edodes released more often at higher pH values, temperatures, and Na^+ concentrations. This effect can increase plant resistance to most viruses and encourage plant development [53]. Synthetic organic materials as compared with natural polymers have a noticeable advantage as herbicide-assembling materials, because they have great chemical and physical stability, alkali resistance, erosion resistance, and acid resistance. Allowing for the type and quantity of the surface functional groups to be changed enables highly focused and adaptable applications [54]. The use of a star cationic polymer (SPc) to form nanoscale pesticides enhanced virulence against aphids disease. The use of an SPc nanoassembly system to release cyanobenamide was evaluated, and it showed selective toxicity against the pest western flower thrips and predators [55].

5.3. Nanoherbicides Based on Organic/Inorganic (Hybrid) Nanomaterials

Herbicides with hybrid nanomaterials, used for assembling nanoherbicides, have the ability to integrate the benefits of two or more materials, such as organic and inorganic materials, into a single structure. These versatile nanomaterials can have a wide range of characteristics, dimensions, morphologies, and chemical makeups. Additionally, hybrid nanoherbicides can support strong traceability, targetability, and stimulus responsiveness qualities [20]. Due to their biocompatibility, biodegradability, natural abundance, and ease of functionalization, biomass-based hybrids made of lignin, xylan, starch, and cellulose have been investigated for their potential to encapsulate active molecules and can be used in the targeted assembling of herbicides [56].

6. PCL Polymer as an Ecofriendly Nanocarrier for Herbicides

Suitable nanocarriers could be chosen from polysaccharides like cellulose and decomposable artificial polymers (e.g., poly ε-caprolactone) with good biocompatibility and low toxicity. A large number of bacteria and fungi are able to decompose these kinds of eco-friendly materials. PCL has attracted considerable interest in biological applications as the matrix of nanocarriers due to its good biocompatibility and biodegradability. For instance, a PCL-containing pretilachlor pre-emergent herbicide showed that the PCL nanoencapsulation decreased the toxicity of the herbicide due to a reduced effect on chromosome aberration in Allium cepa [57].

Poly ε-caprolactone (PCL) (**Figure 1**) is a synthetic aliphatic polyester and a semicrystalline polymer that is not soluble in water and is harmless to the environment. It is obtained from the polymerization of ε-caprolactone cyclic monomer, is an affordable polymer, is nearly stable in the absence of catalytic species, is a very versatile compound, and could be synthesized in different forms of micro- and nanostructures [58][59].

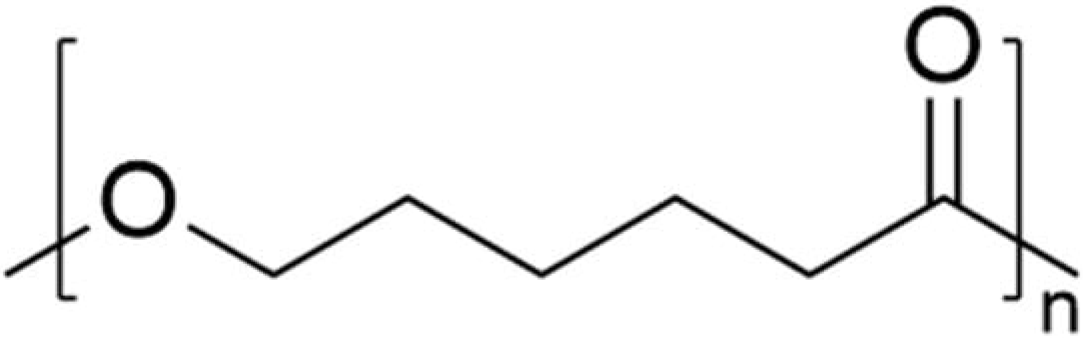

Figure 1. Chemical structure of poly ε-caprolactone (PCL).

Since the polymer is biodegradable and biocompatible, it seems to be used in agricultural applications as a sustained-release system. It takes about 2 to 3 years to complete the hydrolytic degradation of PCL polymers. The degradation process of PCL could be considered as a bulk process in two phases: a loss of molecular weight of up to 5000 Da as a result of chain scission and the onset of polymer weight loss.

7. Classical Methods for Preparation of PCL-Based Nanocapsules

Nanoprecipitation (interfacial deposition or solvent displacement) is a method developed by Fessi et al. [60] and is one of the most widely used techniques for the fabrication of nanoparticles. Compared to other methods, this method is less expensive, easy to perform, reproducible, and does not require a precursor emulsion like other methods, and both nanocapsules and nanospheres can be produced by using this method [61][62].

The commonly used polymers in this approach are biodegradable polyesters, and PCL is highlighted among them because of its biocompatibility. Another aspect of biodegradable polymers is their capability to control the release of active ingredients, which arises from their high permeability. The nature and concentration of the compartments affect the physicochemical properties of polymeric nanocapsules, and changes in the properties of nanocapsules can influence their application [62].

The emulsion–solvent diffusion technique was developed by Leroux et al. [63] (**Figure 2**). It differs from the previous processes by the extraction step of the organic solvent, where evaporation is replaced by a diffusion step in a large volume of water. This process therefore involves an organic solvent that must have a non-zero miscibility with water [61]. The subsequent addition of water after the emulsification step causes the diffusion of the organic solvent into the aqueous phase (because of its partial miscibility with water) and, finally, the formation of particles via the precipitation of the polymer. The residual organic solvent can eventually be removed from the aqueous phase via evaporation at a reduced pressure. Nevertheless, the evaporation step has no influence on the size of the particles because they are already formed as a result of the diffusion of the entire organic phase constituting the emulsion in the large volume of water [64]. Thus, this technique is particularly interesting, especially with regard to its extrapolation to an industrial scale.

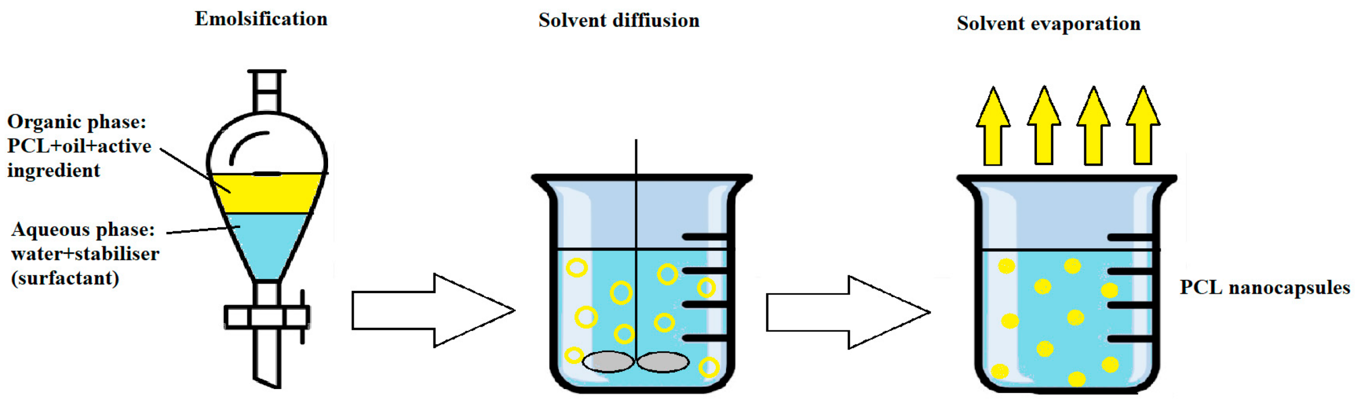

Figure 2. Diagrammatic representation of the emulsification solvent diffusion method.

8. PCL-Based Nanoherbicides

8.1. Metribuzin-PCL Nanoherbicide

Metribuzin is a pre-emergence and post-emergence herbicide used in potatoes, carrots, asparagus, lavender, and lavandin and in the seed stocks of carrots, alfalfa, wheat, etc., to control broadleaf weeds and grasses. Belonging to the same class as atrazine, metribuzin is also an inhibitor of the photosynthetic pathway, photosystem II (PSII), by binding to the QB binding site of the D1 protein. Metribuzin is released to the environment through surface runoff after spraying crops (especially within two weeks of soil application), drainpipe effluent, accidental discharge, or spray drift. It is likely to reach groundwater via leaching or to be carried into surface waters.

However, there is a lack of information about nanoherbicide behavior in environmental matrices. In a study conducted by Takeshita et al. [65], a PCL-metribuzin nanoherbicide with an encapsulation efficiency of 74.8 ± 0.5% was prepared, and its stability, its loss in different soils, and its effects on soil enzymatic activity was evaluated over time. The control effects and physiological parameters of the nanoherbicide were investigated on *Ipomoea grandifolia* plants. There were no differences in the half-life of the nanoherbicide compared to a commercial herbicide formulation. With an encapsulation efficiency of 74.8 ± 0.5%, no suppressive effects on the enzymatic activities of soil were observed. The nanoherbicide showed good pre-emergence in weed control, even at the lowest dose of 48 g a.i. ha^{-1}, indicating that the nanoherbicide had a higher efficiency than the commercial formulation in inhibiting PSII activity and reducing pigment levels.

8.2. Atrazine-PCL Nanoherbicides

Atrazine is the most widely used herbicide for encapsulation purposes in studies on PCL-based nanoherbicides. Atrazine nanoherbicides have weed control efficacy, even with lower doses of the active substance. Atrazine is an organochlorine herbicide belonging to the triazine group. It is an organic compound actively used mainly as a weedkiller for corn, as well as for other crops such as sorghum and grapes [12]. It is still in demand in many countries because of its high killing power and low cost [66]. However, its use has been banned in the European Union and Switzerland because it is a chronic water pollutant, and it has low biodegradability [66][67]. Since the ban of atrazine in several areas, weed management in corn has become complex, as the cost of alternative methods of this pillar of weed control has increased. In addition, alternative chemical herbicides, such as terbuthylazine, metolachlor, and alachlor, used to replace atrazine are not very effective, are found in high concentrations in water, and do not have better environmental profiles than atrazine [68][69]. Over 70 species, including *Lolium rigidum*, *Raphanus raphanistrum*, *Abutilon theophrastis,* and *Amaranthus palmeri*, are estimated to be resistant to triazine [12][70]. The nanoencapsulation of the herbicide may introduce alternative herbicides with reduced risks to the environment and improved efficiency.

By using the nanoprecipitation technique, PCL nanoparticles containing the herbicide atrazine were prepared by Pereira et al. [71] and characterized and evaluated for their herbicidal activity and genotoxicity. The PCL/atrazine nanoparticles had a diameter of 408.5 ± 2.5 nm and showed a high herbicide encapsulation efficiency (92.7 ± 1.2%), as well as good colloidal stability that was maintained for 90 days. In vitro monitoring showed that the encapsulated herbicide had no effect on non-target organisms (corn) in the medium but was highly effective on *Brassica* spp. compared to commercial atrazine. This confirms that encapsulation improves the bioavailability of atrazine while reducing its vertical mobility. Reducing the concentrations and amounts of atrazine applied to the treatment medium helped to reduce the toxic effects exerted on *Allium cepa* [71].

As atrazine herbicide is commonly used on maize, Oliveira et al. [72] continued their research by evaluating the side effects of PCL-atrazine nanocapsules on maize crops (as non-target plants). They studied the effect of nanocapsules of PCL-atrazine on some parameters of soil-grown maize (*Zea mays* L.), such as growth, physiological stress, and oxidative stress parameters. They observed that, 24 h after the post-emergence treatment of the maize with 1mg/mL PCL-atrazine, there was a 1.8-fold enhancement in the peroxidation of leaf lipid as compared to water-treated control plants. Moreover, the maize plants showed a 15% decrease in photosystem II (PSII) maximum quantum yield and a 21% reduction in the assimilation rate of net CO_2 in comparison to the control. Interestingly, the analyzed parameters were not affected after four or eight days.

Wu et al. [73] compared the effects of nano-PCL-atrazine and pure atrazine at different concentrations on defense mechanisms, physiological responses, and nutrient displacement in lettuce (*Lactuca sativa*) as a non-target plant. The chlorophyll pigment content, ROS production, activities of ROS scavenger enzymes (SOD, APX, CAT, POD, GST, and PPO), and macro- and micronutrient concentrations were determined in experiments with short-, medium-, and long-term exposure durations. In the short-term exposure, the growth inhibition of nano-PCL-atrazine was similar to that of atrazine, but in the long-term exposure, high concentrations of nano-PCL-atrazine had greater negative effects on the end points of ROS production, protein content, and alteration in enzyme activities than the pure atrazine.

8.3. Pretilachlor-PCL Nanoherbicide

PCL nanocapsules containing pretilachlor herbicide, with a high encapsulation efficiency of 99.5 ± 1.3%, were prepared and investigated by Diyanat et al. [74]. The nanocapsules had an irregular shape, with a particle size in the range of 70–200 nm. Studies also showed that the nanocapsules were stable in a suspension without any aggregation for 60 days. Barnyard grass was used as a target plant and rice as a non-target plant for an evaluation of herbicide activity in a pre-emergence manner. The authors reported that the nanoherbicide had no negative effect on the rice but had a significant effect on the barnyard grass. Moreover, in genotoxicity experiments (an estimation of the mitotic index using onion cells), the nanoherbicide was less toxic than a commercial formulation. Based on the obtained results, the authors recommended that nanocapsules of pretilachlor with PCL could be used effectively in agriculture as an environmentally friendly PCL–herbicide system [74].

9. Behavior of PCL-Based Nano-Enabled Herbicides in Plant Systems

Regarding the design of nanoherbicide formulations, one of the main aspects is the delivery of the active ingredient across the surface of the leaf to facilitate its reaching the action sites and improve its effectiveness. According to Takeshita et al. [37], for atrazine-loaded PCL nanoparticles, kinetic assays indicated that the release of atrazine from the nanocapsule is caused by the diffusion of the active ingredient accompanied by the relaxation of the polymer matrix, with a slower rate than conventional atrazine. Therefore, the observed rapid absorption of atrazine by mustard leaf may be due to the carriage of herbicide by PCL nanocapsules through the tissue of the plant [37]. The authors proposed that nanoherbicides stay adsorbed on the surface of the leaf, waiting for accessible pathways to become available. The size, shape, composition, surface charge (zeta potential), and loading of the nanoparticles affect their translocation. The penetration of the nanoherbicide into the leaf's barriers is a key point in designing a nanosystem.

The surface of plant cell walls is negatively charged, and PCL nanoparticles also have a negatively charged surface. Negatively charged nanoparticles have faster foliar penetration than positively charged ones because positively charged nanoparticles, due to electrostatic attraction, accumulate and aggregate on the surface of tissue. However, nanomaterials with a negative zeta potential, as a result of their poor interaction with cell walls, have a higher distribution in plant tissue [75].

According to Bombo et al. [58], although herbicide nanocapsules enter the leaf through its natural pores, stomata, and water pores, it is probable that their translocation beyond the leaf is also mediated by symplastic and apoplastic pathways. They reported that, 36 h after application, nanoparticles were observed inside cell protoplasts, and, after 48 h, they were observed inside the chloroplasts. It is proposed that the mechanism of penetration may involve endocytosis, wherein nanocapsules cross the cell wall and reach the cell membrane, resulting in the internalization of the nanoherbicide in a vesicle in the cytoplasm.

Takeshita et al. [37] reported that PCL nanocarriers loaded with atrazine had a greater mobility in leaves than atrazine's commercial formulation, as, due to the surface characteristics of the nanocarriers, they follow the water pathway in the vessels and apoplastic path more effectively than atrazine. This results in a higher distribution through the mesophyll and greater herbicide effects, which is established by measuring the inhibition of PSII activity. Due to the nanoencapsulation, atrazine showed low translocation via the phloem, but a point enhancement in the percentage of ^{14}C-atrazine was observed in other parts of the plant in addition to the treated leaf.

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