Slow-release agricultural pesticide formulations: state of the art

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Abstract

The need for a long-term sustaining of optimal concentrations of applied pesticides in the soil in agriculture resulted in the development of systems for controlled release of active substances. Such systems are based on the use of eco-friendly carrier materials that are harmless to plants, humans and environment. Inorganic substances (e.g., clays or alike substances), biodegradable polymers of natural or synthetic origin, blends of such polymers and their composites with inorganic fillers can be used as carriers. The deposited pesticides are released by diffusion or, in the case of systems based on biodegradable polymers, by degradation of the carrier. Inorganic carriers are usually impregnated with a pesticide. As for polymers, there is a wide range of methods for obtaining forms. Namely, these are the microsphere and nanoparticle formation, film casting, tablet pressing, form gelatinizing, and coprecipitation of a pesticide and a polymer from a solution. Co-extrusion of pesticides with polymers or their composites at temperatures below the degradation temperature of the components is another promising method for obtaining pesticide carriers.

Key findings

● The application of soil pesticides often requires maintaining their concentrations at optimal levels during the growing season.

● This is complicated by the gradual degradation of the active components due to chemical and biological processes.

● The use of pesticides deposited in different carriers ensures long-term maintenance of optimal bioavailable concentrations in the soil.

● Clays, biodegradable polymers, their blends and composites are widely used as carriers of active components.

1. Introduction

One of the problems related to the use of biologically active preparations (primarily various groups of pesticides) in agriculture is the need to maintain their concentrations at the required level for a long time within the growing season. Thus, the germination time of the seeds of many weeds is spread over time; a one-time application of an active but unstable herbicide in the soil may not be sufficient to suppress later seedlings. The application of increased doses of the pesticide poses a risk of an increase in the negative impact on the environment in the initial period.

The development of preparations with slow release of active ingredients into the environment can be part of the solution to the problem in relation to the use of soil-based pesticides. In recent years, this area has attracted great interest. Many research teams have been investigating the possibility of depositing pesticides of various groups in various carriers, including that of combined composition. Since herbicides comprise the largest segment of the pesticide preparations

market [1], it is this group of compounds that is most widely studied in the context of development of prolonged forms.

There are two main groups of carriers for active ingredients. The first group includes clays and clay-like materials (silicates) of natural origin, or their synthetic analogues. In the soil, the active substances are released from these materials by simple diffusion; the residual carrier material remains as a part of the soil substrate. The second important group of carriers consists of chemically or biologically degradable polymers of different nature. In this case, the active substances are released as the carrier polymer degrades in the soil, although their diffusion from the polymer matrix may also be observed as an additional release mechanism.

2. Formulations based on inorganic carriers

Usually, silicates, natural or modified clay, metal oxides or even clay soil are used as inorganic carriers. The formulations are mainly obtained by impregnation of carrier materials with pesticide solutions [2, 3], as well as by fixation of the preparation on the surface of mineral nanoparticles [4].

In the study [3], diuron and 2,4-dichlorophenoxyacetic acid (2,4-D) herbicides were encapsulated in a layered synthetic silicate magadiite. The inclusion of the herbicides was confirmed by Fourier transform infrared analysis (FTIR) and X-Ray diffraction analysis (XRDA). The maximum adsorption numbers of the herbicides were approximately 900 mmol/g for 2,4-D and 1.4 mmol/g for diuron. These values were observed in a highly acidic medium at pH 1.5. The release of herbicides into water was relatively slow and also was affected by pH. Specifically, in 42 days, 13.3% and 34.5% of absorbed 2,4-D was released at pH 4.6 and 9, respectively. The respective values for diuron were 17% and 23.5%. The maximum release (14–17% from the total amount of the released herbicides) was observed on the first day of the exposure.

In another study [5], glyphosate and 2,4-D herbicides were deposited in the interlayer regions of layered Zn/Al hydroxides. The depositing was confirmed by XRDA and scanning electron microscopy (SEM). The 48-hours release of the preparations in distilled water and in 5 and 10 mM solutions of carbonates and chlorides was determined. Half of the preparations were released into distilled water in approximately 12 hours. Carbonates accelerated the yield of the preparations, whereas chlorides slowed it down.

Clay-like carriers are often modified with ionic additives. For example, for depositing the anionic herbicide imazapyr, a montmorillonite composite obtained from an aqueous suspension with polydiallyldimethylammonium chloride (PDADMAC) was used. The latter constitutes a cation-containing polymer that provides the composite a positive charge and interacts with the herbicide as an anion [6]. FTIR showed the presence of a new peak at 2084 cm^{-1} in the herbicide-loaded composite, which confirms the formation of electrostatic interactions between the polyamine and the herbicide. The formulations with active ingredient contents of 13, 21 and 40% were obtained. In soil tests, the release of the herbicide from more loaded (40%) formulations was slower than its release from those with a minimum load. Specifically, after two waterings, 100% of pesticide in the commercial preparation, 45% of the pesticide at 13% load, and 25% at 45% load of the formulations passed through a thin layer of soil.

Similarly [7], long-term release formulations of metribuzin were designed by encapsulating the active ingredient in phosphatidylcholine (PC) vesicles and adsorbing the vesicles onto montmorillonite. The maximum active ingredient content in the long-term release formulations was 246 g/kg. Infrared spectroscopy results revealed that the hydrophobic interactions between metribuzin and the alkyl chains on PC were necessary for encapsulation. In addition, water bridges connecting the herbicide and the PC headgroup enhanced the solubility of metribuzin in PC. Experiments in a sandy soil revealed that the herbicide was not irreversibly retained in the formulation matrix. In soil column experiments, PC–clay formulations enhanced herbicide accumulation and biological activity in the top soil layer relative to a commercial formulation after six irrigations.

To impart a positive charge, the addition of trimethylammonium groups to mesoporous silicon oxide nanoparticles was performed, which made it possible to increase their efficiency as a carrier of 2,4-D [4]. As a result, the load of 2,4-D increased from 1.5% to 21.7% compared with pure silicon oxide nanoparticles. An increase in pH and temperature, and, especially, the addition of sodium chloride increased the rate of release of 2,4-D into the water. Particularly, in 100 hours approximately 12% of the active ingredient was released at pH 3, about 25% at pH 7, and about 35% at pH 10. The addition of 0.1 M sodium chloride resulted in the release of approximately 60% of the herbicide in 100 hours. In the experiment with soil columns, 15% and 30% of the herbicide were released in 30 and 60 days, respectively. However, later on the release was significantly slowed down to 40% release of the herbicide in 100 days and about 45% – in 350.

A substantial advantage of using inorganic carriers is the relatively low cost of both the materials and obtaining methods (impregnation), which is one of the most important factors favoring the use of such preparations. At the same time, diffusion is the only mechanism for the release of biologically active substances from the matrices of this kind, which limits the control of this process.

3. Formulations based on biodegradable polymers

In the case of biodegradable carriers, the rate of outflow of pesticides, along with simple diffusion, is significantly affected by the rate of degradation of the polymer matrix in the soil. In addition, the range of methods for manufacturing polymer molds is wider than when inorganic carri-

ers are used, which can be another way to control the release of active ingredients.

The most widely used approach is to obtain a variety of micro- and nanostructures, primarily polymer microspheres, microcapsules, micro- and nanoparticles. Thus, PCL nanocapsules with triazine herbicides ametrin and atrazine were obtained by the emulsion method [8]. Compared with a pure herbicide, the encapsulated formulation was less toxic to *Pseudokirchneriella subcapitata* algae in a 96-hour experiment, and more toxic to *Daphnia similis* in 24-hour and 48-hour experiments. Cytogenetic tests on human lymphocyte culture (mitotic index evaluation) showed lower toxicity of the encapsulated herbicide compared to the pure one. Study of the effect of atrazine-loaded PCL nanocapsules on biomass growth, photosystem state, gas exchange, and oxidative stress parameters of mustard showed an increase in their herbicidal activity compared to a commercial preparation [9].

Another degradable polyester, poly(lactide-co-glycolide) (PLGA), was used in combination with the "lipid-PEG" hybrid (PLGA:hybrid ratio was 75:25) for the obtaining of atrazine-loaded nanoparticles by precipitation [10]. The average particle size was 110±10 nm. The structure of the particles corresponded to the "core–shell" model. Specifically, PLGA with atrazine were arranged in the core, and "lipid-PEG" molecules – in the shell. The encapsulation efficiency was 50%. The inclusion of atrazine was confirmed by transmission electron microscopy (TEM) and FTIR, and the half-release time (T_{50}) was 72 hours. The effect of pure atrazine and the deposited formulation on potatoes led to a slowdown in the growth of stems and roots, to a decrease in the number of leaves and in the weight of raw and dry masses. In the case of the root length, the encapsulated formulation had a more significant effect than the pure one.

Biodegradable polymers, polyhydroxyalkanoates of microbial origin, in particular, are also used for depositing herbicides. In a series of papers [11, 12], microparticles based on poly-3-hydroxybutyrate (PHB) and PHB copolymers with 3-hydroxyvalerate (PHBV) loaded with atrazine and ametrin herbicides were obtained. The yield of atrazine into water from the polymer matrix was significantly reduced compared to the yield of pure herbicide. Other authors [13] also used PHBV to obtain microspheres loaded with atrazine. Specifically, it was shown that, depending on the conditions of microspheres formation, the rate of release of the herbicide into water slowed down compared to the pure herbicide. It should be noted that microspheres, due to their small size and large total surface area, are subject to fairly rapid degradation when they come in contact with the environment. Therefore, the release of deposited preparations from microparticles occurs quickly enough, which does not allow a long-term use (tens of days or more). That is why other methods of formulations obtaining are also being actively studied.

For example, poly-3-hydroxybutyrate and metribuzin herbicide formulations with a 25% load of metribuzin were obtained in the form of granules, tablets, microparticles and solution-cast films [14]. SEM, XRDA and differential scanning microscopy (DSC) showed that the formulations were stable in the sterile water for up to 49 days. The highest rate of release (approximately 50% in 5 days and 95% in 49 days) was observed for the microparticles, and the the lowest rate of release (about 40% in 49 days) was shown for the granules. In 49 days about 50% of the deposited herbicide was released out of the tablets and the films. In another paper of the same authors [15], the metribuzin release rate into the soil out of similar formulations at different loads was analyzed. The maximum value of T_{50} (60 days) was obtained for the pressed tablets, regardless of the initial content of metibuzine, and for the microgranules with a 10% load of the preparation. The lowest values (10 days) were observed for the microparticles and the films with a 50% content of the herbicide.

In addition to thermoplastic biodegradable carriers, application of materials of plant origin for this purpose is also known. Specifically, an herbal extruded mix of alfalfa and sunflower meals (1:1) with addition of glycerol and a feed supplement was used to prepare granules with insecticide avermectins against locust nymphs [16] and mosquitoes [17]. Laboratory experiments with granules containing 0.15% of avermectins fed to locust nymphs resulted in 100% death within 5 d. After the deposition in granules, resistance of the insecticide to UV radiation increased significantly, which is highly preferable in the conditions of its intended use (dry areas with a high level of solar radiation). The efficiency of avermectin-impregnated fine plant powder was also shown on mosquito larvae in water, where flotation properties of such particles can contribute to the probability of being eaten by the target pest, while non-target organisms were more resistant to the drug.

For more cost-effective obtaining of polymer preparations, it seems promising to use co-extrusion of polymer and pesticide at a temperature exceeding the melting point of both the components, but below their degradation temperature. So, a simple and low-cost method to obtain long-term release formulations by co-extrusion of a metribuzin herbicide with low-melting polyester poly-ε-caprolactone was proposed [18]. The formulations containing 10%, 20%, and 40% of herbicide were prepared. After 7 days of their water exposure, from 81% to 96% of loaded metribuzin was released; the highest release rate was observed for 40%-loaded formulations. Afterwards, biodegradation and pesticide release of the formulations were further explored. Degradation rates of the specimens increased with an increase in the pesticide content, from 9% to 20% over 14 weeks for the 10%/20%-loaded and the 40%-loaded specimens, respectively. At the same time, the release of metribuzin reached 37–38% and 55%, respectively. The content of the herbicide in the soil was lower due to its partial degradation. It reached 23–25% and 33% from

initially loaded in the polymer matrix, respectively. Release kinetics of metribuzin in water as in soil best fitted the First-order model. The used approach is promising for obtaining slow-release formulations for soil applications.

4. The use of polymer composite systems with inorganic fillers as a matrix for agrochemicals load

In many studies related to obtaining formulations with a long-term release of pesticides, polymeric composites or blends with an inorganic filler are used. In most of these studies various gelatinizing agents (alginate, chitosan, carboxymethylcellulose, gelatin) are applied as one of the composite components. Clay-like compounds and other carriers with high sorption capacity (e.g. activated carbon) are usually used as additional components.

Thus, aqueous systems with sodium alginate (gelatinizing agent) (1.4–1.5%), bentonite (0–5%) and/or activated carbon (0.5%) were used for depositing isoproturon, imidacloprid and cyromazine (0.3–1.22% in the aqueous phase). The final obtained loads in formulations with activated carbon were 9–14% for isoproturon, 6–14% for imidacloprid and 1.5–12% for cyromazine, with maximum encapsulation efficiency reaching 90-100%. As the release of isoproturon from the forms was estimated in days and tens of days, the same parameter for the more soluble imidacloprid and most of the forms was estimated in tens of hours and days. At the same time, the most severe slow-down of the pesticide release was observed for the forms with activated carbon. Particularly, for alginate forms T_{50} was approximately 4 days for isoproturone and less than 10 hours for imidacloprid, whereas for the forms with 65% of activated carbon less than 10% of the isoproturone and imidacloprid were released in 48 days and 96 hours, respectively [19].

Similar formulations based on sodium alginate with bentonite and anthracite, obtained by mixing with pesticides in an aqueous solution, were used to deposit the herbicides metribuzin and chloridazon [20]. The lowest release-rate (T_{50} 14.37 days for chloridazon-loaded and 3.31 for metribuzin-loaded formulations) was observed for anthracite-based composites.

To deposit metribuzin, carboxy methyl cellulose (CMC) and carboxy methyl cellulose – kaolinite (CMC-KAO) based formulations with a component ratio of 3.83:100 and 3.83:50:50 g/g, respectively, were used. The formulations were obtained by mixing all the components in the presence of water and aluminum phosphate with subsequent thorough mixing, drying, grinding and sieving [21]. Pesticide release study showed that the period of optimal availability of metribuzin when released into water increased from 5.03 days for the pure preparation to 15.09 days for the carboxymethylcellulose-based formulations and up to 27.13 days for the composite formulations. In the soil experiment, the corresponding values were 8.80, 17.99 and

25.16 days, respectively. The theoretically calculated T_{50} values were 3.25, 12.98 and 20.12 for water, and 4.66, 16.90 and 36.67 for soil, respectively. Further studies [22] demonstrated the greater effectiveness of the resulting composite preparation against weeds, compared with both pure herbicide and the formulations based on carboxymethylcellulose only.

Other authors [23] applied carboxymethylcellulose (CMC) in combination with bentonite to encapsulate 2,4-D herbicide. Both pure Na-bentonite and bentonite treated with aluminum, iron or cetyltrimethylammonium cations were used. The forms were obtained by successive addition of bentonite, 2,4-D and CMC in water with subsequent injecting of the resulting suspension into a 0.03 M solution of $Al_2(SO_4)_3$ and drying the resulting granules. FTIR showed the presence of complex interactions between all the components in the formulation. The greatest efficiency of pesticide encapsulation (90%) was shown for aluminum-modified bentonite-CMC with its maximum concentration of 4%. In the other cases, this value varied from 55.5% to 85.3%. The values of the rates of pesticide release into water for the formulations with bentonite were reasonably comparable and differed slightly from the pure CMC formulations. 50% release of the preparation was achieved in 15 hours for the pure CMC formulations and in 15-20 hours for the formulations with different forms of bentonite. 50% of the deposited preparation was released into the soil after five and six waterings when deposited in the pure CMC matrix and in the matrix with the addition of iron-containing bentonite, respectively.

In a similar study [24], gel granules loaded with the metolachlor herbicide were obtained from CMC with Na-bentonite and H-bentonite (the latter was obtained by treating Na-bentonite with sulfuric acid). 0.08 M iron nitrate solution was used as a cross-linking agent. The resulting changes in the IR spectrum suggest an interaction between CMC and bentonite. The dried composite granules featured lower water sorption (50–85 wt.%) compared with the granules from the pure CMC (110–120 wt.%). In this study, the addition of bentonite significantly slowed down the release of the pesticide into water, especially in the formulations with H-bentonite. T_{50} of metolachlor into water from the composites with H-bentonite was 158 hours, compared to 61.1 hours for the composites with pure CMC.

In another study [25], the herbicide imazethapyr was encapsulated in a composite hydrogel of guar gum, polyacrylate and bentonite clay for the pre-emergence application and in a nanohydrogel of guar resin and N-isopropylacrylamide for the post-emergence application. The herbicide introduced into the nanohydrogel amounted to up to 53.94 wt.% of the initial gel. The encapsulation efficiency (concentration of imazethapyr extracted from the formulation over the initial concentration of imazethapyr added to make the formulation) ranged from 68% to 99%. The amount of the pesticide introduced into

the hydrogel was 3–4 wt.%. On the first day, from 16 to 34% of the deposited herbicide was released from the hydrogel into water. After the fifth day, the release stopped. On the first day, from 14 to 57% of the herbicide was released from the nanohydrogel. Predictably, the release decreased with an increase in the content of the crosslinking agent. The effectiveness of the encapsulated forms in weed control in field experiments was higher than that of a pure preparation, although it was inferior to the treatment with a mixed "imazethapyr + pendimethalin" preparation.

One of the approaches involved obtaining a polymer matrix directly in a solution [26]. In particular, metribuzin (2–7 wt.%) was introduced in a composite consisting of bentonite (8–12 wt.%) and a mesh copolymer of acrylic acid and acrylamide. Polymerization was carried out in an aqueous solution after the introduction of bentonite and a pesticide, followed by the desiccation of the resulting formulations. An increase in the content of the clay component from 8% to 12% led to a significant slowdown in the release of metribuzin into water (between 30 and 40% in 27 days at different pesticide loads). At the same time, an increase in the content of metribuzin had little effect on the patterns of its release.

In general, such systems, possessing adequate efficiency, feature a relatively high complexity of manufacture and, consequently, a high cost, which limits their commercial availability.

5. Application of blended polymer systems

Alongside composite systems with introduced inorganic fillers (including organically modified), polymer blends are also widely used for the slow release of pesticides. Systems that differ both in composition and ratio of components, as well as in size, manufacturing methods, active substances load and methods of their deposition are widely used as controlled release systems. Such differences significantly affect the rate of release of deposited biologically active ingredients due to both different diffusion characteristics and biodegradation rates. Specifically, the applied promising polymer components include polysaccharides (starch), a number of well-known polyesters that have proven themselves as biodegradable materials (PHA, PLA, PGA, PCL), some conventional polyesters (polyethylene glycol), and wood processing products (e.g., sawdust, lignin).

Polymers of this group are also often compounded with gelatinizing agents. Thus, chitosan-alginate and chitosan-tripolyphosphate composite nanoparticles with an average size of approximately 400 nm loaded with herbicides imazapic and imazapyr were obtained [27]. The release of the herbicides was estimated in a two-chamber system with a dialysis membrane of 1000 Da. The release of free pure herbicides was 55% and 97% after 300 minutes, whereas for the chitosan-alginate deposited formulations it was by 30% and 20% lower, respectively. For the chitosan-tripolyphosphate formulations, the corresponding values were 59% and 9%, respectively. The deposited forms had a less pronounced cytotoxic effect on onion seedlings and less influence on the composition of the microbial community. In experiments with burr marigolds, deposited forms had a more significant herbicidal effect than the pure preparation.

Chitosan and alginate were also used to obtain composite nanoparticles (635±12 nm in size) loaded with paraquat herbicide [28]. DSC showed the absence of the endothermic peak characteristic for paraquat in microparticles compared to the mechanical mixture of components where it was present. The authors explained it by the interaction of the pesticide with the alginate-chitosan matrix with good mixing of the components. FTIR showed the presence of complex interactions between alginate and chitosan, as well as the absence of a number of peaks characteristic for paraquat, which was also explained by the interaction of positively charged paraquat groups with polymer chains with a change in the vibrational frequencies of herbicide molecules. A significant slowdown in the release of paraquat into water in a two-compartment membrane system was observed. The release profile was significantly altered for herbicide loaded in the nanoparticles, with near 100% release after 8 h, 2 h longer than the time required for complete release of free herbicide. Particularly, the T_{50} into water was approximately 90 hours. A decrease in its sorption in the soil when using long-term release formulations was also observed.

In another study [29], picloram herbicide in the form of microcrystals was coated with a layered composite based on an inner layer of a positively charged chitosan (CS) and an outer layer of positively charged sodium lignosulfonate (SL). FTIR showed the presence of strong electrostatic interactions between chitosan and lignosulfonate, but the absence of any changes in the characteristics of the pesticide. The coating significantly increased the photostability of the pesticide and slowed down its release into water, which depended on the number of applied coating layers. Whereas the uncoated picloram herbicide completely dissolved after 4 hours, with a 12-layers coating (6 CS layers consecutively alternating with 6 SL layers), approximately 90% of the herbicide came out after 9 hours of exposure. The T_{50} was 0.05 h, 0.43 h, 1.02 h and 2.26 h for the uncoated forms and the forms coated with 4, 8 and 12 layers of composite, respectively.

It is also possible to use such systems for depositing biopesticides. Thus, a water-insoluble polyelectrolyte complex of chitosan and polyacrylate-maleate was used to coat chitosan matrices with deposited *Trichoderma* [30]. The matrixes were coated by dipping chitosan granules with *Trichoderma* into an aqueous solution with polyacrylate-maleate and exposing them for two days at pH 4.8. No negative effect of the coating on both the growth of

Trichoderma and its ability to inhibit the pathogens of *Alternaria* and *Fusarium* genus has been observed.

Polysaccharides are not always used directly to obtain hydrogels. In the study [31], beads were obtained from a mixture of cassava starch (CS), sodium alginate (SA) and 2,4-D at a different ratio of CS and SA, and coated with natural rubber. As the CS/SA ratio increased from 0/1 to 1/1, the size of the beads increased from 0.9 mm to 1.8 mm, and the encapsulation efficiency also increased from 65% up to 100%. The three-layer rubber coating made it possible to increase the T_{50} from several hours to 700 hours. One- and two-layer coatings exhibited intermediate values.

Along with gelatinizing, thermoplastic biodegradable polymers were also used in a number of studies in the forms of pressed molds or microspheres. Thus, composite systems "poly-3-hydroxybutyrate – the second component – metribuzin" in combination with sawdust, PEG or PCL as the second component, and with a 25% load of herbicide, were obtained by cold pressing [32]. The most active release of metribuzin into water (38.7% in 35 days) was observed for a composite with PEG, and the least active release of the pesticide (16.8% in 35 days) was observed for a composite with PCL. In an experiment with model soils (field and garden), a rapid release of the preparation was shown (approximately 60% in 14 days) for a composite with PEG, and comparable values (about 20–30%, depending on the type of soil) were obtained for the remaining types of the studied forms. By the end of the experiment, from 35% to 72% of metribuzin initially introduced in the forms was found in the soil, which the authors explain by the difference in release rates as well as by its partial degradation in the soil.

In some studies, polymer mixtures were also used to obtain microspheres. For instance, microspheres loaded with malathion insecticide based on both pure PHB and PCL and their mixtures in the ratios 70/30, 80/20, 90/10, 95/5 and 97/3 were obtained by emulsion evaporation [33]. Malathion (about 30% of the total weight of the components) was added to chloroform solutions of polymers, and the resulting solution was emulsified in an aqueous solution of gelatin and Tween 80. Loading with malathion led to a reduction in the size of microspheres of the same polymer composition up to two times compared to the unloaded PHB/PCL microspheres. The surface of the microspheres made of pristine polymers was relatively smooth, while mixed particles with greater inclusion of PCL (more than 10%) demonstrated a mesh structure. The introduction of malathion, according to the DSC data, led to a shift in the melting peak of PCL that depends on the content of PCL, which indicates some interaction of the pesticide with the polymer base. The same conclusion was drawn from a slight change in peaks in the FTIR spectra, although no new peaks were observed. Release of malathion into water tests showed that the release rate was at maximum at a 30% PCL content, somewhat lower at a

20% PCL and minimal for a 5% PCL and pure PHB. However, in 5 hours of exposure, 50% of the pesticide was released from all the obtained forms. The obtained data was used for designing a mathematical model. The authors concluded that it is possible to control the release of the preparation by varying the composition of the polymer matrix.

A Spanish research team has developed and applied extrusion as a method of obtaining controlled-release forms. In one of their studies [34], preparations of the herbicide chloridazon were obtained by introducing all the components in a lignin-PEG blend at 206 °C, followed by coating the resulting mixture with ethyl cellulose (EC) or EC with the addition of dibutylsebacinate (DBS) plasticizer. The greatest delay in the release of the herbicide into water (approximately 50% in 65 hours) was observed for the forms coated with EC with DBS. In another study by the same authors [35], metribuzin preparations were obtained in a similar way by melting the active substance with a lignin-PEG blend at 126 °C, followed by covering the resulting mixture with EC or EC-DBS. Based on DSC and FTIR results, the authors assumed the dispersion of pesticide molecules into the polymer matrix and the formation of hydrogen bonds between lignin and PEG. In this case, the greatest delay in the release of the preparation into water (about 50% in 20 hours) was observed for EC-coated forms. A similar approach with the same components was used to deposit imidacloprid [36]. The maximum T_{50} for deposited imidacloprid was 168.6 hours. TG-DSC showed a significant mass loss for EC-coated samples at temperatures below 360 °C at the first stage of heating compared to the uncoated samples. According to results of FTIR, the formation of new hydrogen bonds between the ester groups of PEG and lignin was observed.

Similarly, formulations of metribuzin and chloridazon were obtained by co-melting of a pesticide, lignin and PEG (at a 65:20:15 ratio) at melting temperatures of the pesticides (126 °C and 206 °C, respectively), followed by covering the forms with a mixture of EC or EC-DBS (90:10) [37]. Compared to the uncoated forms, an increase in T_{50} was achieved from 1.74 h to 65.39 h for the forms with chloridazon and from 1.01 h to 20.44 h for the forms with metribuzin. The release into the soil also slowed down. Particularly, from 70 to 90% of free pure pesticides were washed out by three waterings in soil columns, whereas only 50–60% of metribuzin from the uncoated matrices, 20–40% from the coated forms on sandy-clay soil and 10–30% on sandy soils, depending on the thickness and composition of the coating, were washed out. For chloridazon, the corresponding values were 40% for sandy-clay soils for the uncoated forms and 5–18% for the coated ones. On sandy soils, the release of chloridazone was much slower. However, in this case, the application of coated forms slowed it down. After ten waterings, more than 90% of free pure metribuzin, 70% of metribuzin from the uncoated forms, and 60–65% of metribuzin from the coated

forms were washed out on sandy-clay soils. On sandy soils, similar values were more than 90%, 70% and 50–60%, respectively. As for chloridazon, these indicators were more than 90%, 70%, 50–60% for sandy-clay soils and 85–95%, 70% and 32–58% for sandy soils. The efficiency of the use of such forms, along with their relatively low cost, allows suggesting further studies and the expansion of the practical applications.

6. Conclusions

Considering the prospects for the development and application of long-term release pesticide formulations, a large number of various possible and sufficiently effective solutions must be noted. However, the commercialization of such solutions requires a cost-cutting of both carrier materials and preparation manufacturing technologies. Either natural materials of wide availability (clay, chitosan, alginate) or synthetic polymers (e.g., PCL) can be considered promising carriers. Extrusion can be noted as a promising technology for obtaining preparation carriers. Although its use limits the range of materials possible for application, it does not require any solvents or other reagents at the processing stage and is a relatively easy and cheap process itself.

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