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Weed management with the use of nano-encapsulated herbicide formulations: A review

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Abstract
The overall yield loss in different crops due to weed infestation is estimated at around 36.5% in India. The use of herbicides is the only viable on-farm technology today to control weeds. More than 90% of herbicides are misused, and as a result, they are lost in the environment, do not reach the target site, and do not effectively reduce weeds in crops. Nanoencapsulation of herbicides is a delivery method in which an active ingredient is covered with various materials of different sizes in the nano range and released in a controlled way for achieving season long weed free conditions. Nanoencapsulation can protect active ingredients from premature degradation (*e.g.*, photolysis, hydrolysis, biodegradation, *etc*.) and unnecessary losses by leaching and volatilization. Studies have shown that nanoencapsulation of herbicides can produce more targeted and less toxic formulations for agricultural applications. Due to the enhanced herbicidal activity in comparison with a commercial formulation, the use of nanoencapsulated herbicide would permit the application of lower dosages of the herbicide. The use of lower doses of herbicides is desirable as it reduces the long-term effects of residues of these herbicides in agricultural areas and their toxicity to the environment, maintaining the sustainability of agricultural production. The target specific release of nanoencapsulated herbicide is also helpful in killing the weeds without even interacting with the crop plants, which ultimately results in higher crop yield.

Keywords: Weed management, nanotechnology, nanoencapsulation, nanoherbicides

Introduction

In the current scenario, approximately 4 million tons of pesticides are used annually worldwide for food production, of which 40% are herbicides, 30% are insecticides, and 20% are fungicides (Rojas *et al.*, 2022) [42]. A weed is a plant that grows where it is not desired. Weeds are a menace in agriculture. On an average 320 man hours are required to remove weeds from one hectare of land (Chinnamuthu and Viji, 2018) [9]. Use of herbicides is the only viable on-farm technology today to control weeds. Since 2/3 of Indian agriculture is rainfed farming where usage of herbicide is very limited, weeds have the potential to jeopardize the total harvest in the delicate agro-ecosystems. Herbicides are chemical substances that are utilized to specifically, partially or totally control or kill plants. An effective herbicide should control weeds with reasonable doses selectively non-toxic to crops, remain in the area where applied, persist throughout the growing season taking care of frequently germinating weeds and leaving no residue at the end of the season permitting subsequent crops in the sequence. It is well recognized that the over dependence on herbicides has caused severe damage to our ecosystem that are manifested into their movement to non-target areas, contamination of soil and water bodies, and development of herbicide-resistant weeds.

Nanotechnology is a technology having the potential ability to study, design, create, synthesis, manipulation of functional materials, devices, and systems to fabricate structures with atomic precision by controlling the size of the matter at the scale 1-100 nanometers (Chinnamuthu and Viji, 2018) [9]. The main aim of nanotechnology in agriculture is to maximize output (crop yields), minimize the input (fertilizers, pesticides and herbicides) and monitoring environmental factors (sensors) and applying targeted action. Nanotechnology has many applications in all stages of production, processing, storing, packaging and transport of agricultural products. Nanopesticides were named as one of ten chemical innovations that will change the world in a sustainable way by the IUPAC and nanopesticides were ranked first for their potential low impact on the environment and human health (Gomollón-Bel, 2019) [17]. Since 2016, every year October 9 is a day to celebrate and raise awareness on how nanotechnology has enriched lives. This date, 10/9, pays homage to the nanometer scale, 10^{-9} meters.

Products database available at Statistic Bank (StatNano, 2022) [49], there are 10,087 nanotechnology-based products commercialized, only 231 nano-products launched for agriculture application. Most of these products are nano-fertilizers (43%), and nanoformulations aimed at improving plant survival against weeds, disease, pest and other stress represent 28% of these products.

Why do we need nanotechnology applications in weed management?

Only a small portion of herbicide is absorbed by the plants. The rest is lost through one or more of the following ways *viz*., volatilization, adsorption, leaching, photo decomposition, chemical degradation and microbial breakdown. Continuous use of herbicides results in development of resistance in weeds towards that particular herbicide (Jasieniuk *et al.*, 1996) [22]. International survey of herbicide resistant weeds recorded 495 unique cases of herbicide resistant weeds globally, with 255 species (148 dicots and 107 monocots) in 2018. Weeds have evolved resistance to 23 of the 26 known herbicide sites of action and to 163 different herbicides. Herbicide resistant weeds have been reported in 92 crops in 70 countries. The maximum number of herbicide-resistant weed species reported in different crops are in the order of: wheat > maize > rice > soybean > spring barley > canola > cotton (Heap, 2019) [20]. Science of nanotechnology can be used as a tool to fabricate the slow release nanoencapsulated pre-emergence herbicide for achieving season long weed free condition without hampering the environment. Nanoherbicides are being developed to address the problems in perennial weed management and exhausting weed seed bank. Encapsulation by nanomaterials can protect active ingredients from premature degradation and unnecessary losses.

What is nanoencapsulated herbicide?

Nanoencapsulation of herbicides is a delivery method in which an active ingredient is covered with various materials of different sizes in nano range and released in a controlled way for achieving season long weed free condition. Substances being coated or encapsulated material are commonly known as core material, filler or internal phase, for example herbicide. Materials used for encapsulation are referred to as coating, external phase, membrane or shell, for instance nano capsules. In general, nano-encapsulated herbicides have two typical release behaviors: (i) sustained (slow) release and (ii) stimuli-responsive release. Rate of release of herbicidal suspension through diffusion is a membrane controlled system. Likewise, there are several systems developed for the controlled release of active ingredients after encapsulation of herbicide according to their properties *viz*., specific release, moisture release, heat-release, pH release, ultrasound release, magnetic release, *etc*.

Methods of nanoparticle production

The nanomaterials prepared through two basic methods (according to Royal Society and Royal Academy of Engineering, UK):

1. Top-down depending on size reduction from bulk materials
2. Bottom- up system where materials are synthesis from atomic level

Also, there are some other methods for producing nanomaterials like attrition and pyrolysis, and biological synthesis of nanoparticles.

Development of new nanoencapsulated herbicide

Encapsulation of active ingredient (a.i.) is done by Kumar and Chinnamuthu (2014) [29]:

1. Indirect method of nanoencapsulation (IDM)
2. Direct method of nanoencapsulation (DM)
3. Solvent evaporation method (SEM)
4. Nano spray method (NSM)

Materials used in herbicide encapsulation

Wilkins (1990) [53] first classified the materials used in encapsulation according to their degree of biodegradation:

1. Starch and systems based on amylose
2. Other polysaccharides (cellulose and derivatives, chitin, chitosan, dextran, alginate)
3. Proteins (casein, albumin, gelatin)
4. Lipophilic materials (rubbers and waxes)
5. Synthetic polymers (polyvinyl alcohol, polylactato, polyglycolato, other polyesthers, polyamines, polyamide-type acids, polyacrylamide)
6. Miscellaneous (polyhydroxybutirato, tannins, lignins, resins, biopolymers)

Types of nano-enabled herbicides

There are three types of nano-enabled herbicides

1. Organic nano-enabled herbicides: Organic nanomaterials are outstanding materials for assembling nanoherbicides, and they can be based on polymers, lipids, lignocellulosic materials, proteins, complex macromolecules as dendrimers, *etc*. Overall, polymers are widely used in nano-enabled herbicide formulations due to their biodegradability and biocompatibility. Examples of some organic nano-enabled herbicides are given in Table 1.
2. Inorganic nano-enabled herbicides: Inorganic nano-enabled herbicides can be based on silica, metal, mesoporous silica nanoparticles, *etc*. Some of these nanoherbicides can release ions, while others can encapsulate organic molecules and release them in a controlled manner. Examples of some inorganic nano-enabled herbicides are provided in Table 2.
3. Hybrid nano-enabled herbicides: Hybrid materials have the potential to combine the advantages of two or more materials, such as organic and inorganic, into a single structure. These multifunctional nanomaterials can have a variety of properties, sizes, morphologies, and chemical compositions. Also, hybrid nanoherbicides can promote good targetability, traceability and stimuli-responsiveness properties. Examples of some hybrid nano-enabled herbicides are furnished in Table 3.

Table 1: Examples of some organic nano-enabled herbicides

Nanoherbicides	Plants	References
PCL(poly(ε-caprolactone)_ATZ NPs; PCL_Ametryn NPs; PCL_Simazine NPs	*Allium cepa* L.	Grillo *et al.* (2012) [18]
Nanoemulsion containing glyphosate	*Eleusine indica* L.	Jiang *et al.* (2012) [23]
CS(chitosan)/TPP(tripolyphosphate)_PQ(paraquat) NPs	*Allium cepa* L.; *Zea mays* L.; *Brassica* sp. L	Grillo *et al.* (2014) [19]
PCL_ATZ (Atrazine) NPs	*Brassica* sp.; *Zea mays* L.;	Pereira *et al.* (2014) [39]
Biochar_2,4-D	*Brassica* sp.; *Zea mays* L.	Abigail *et al.* (2016) [1]
Pectin NPs_ metsulfuron methyl	*Chenopodium album* L.	Kumar *et al.* (2017) [30]
Poly(lactic-co-glycolic acid)_ATZ NPs	*Solanum tuberosum* L.	Schnoor *et al.* (2018) [43]
Nanoemulsion_palm oil; *Parthenium hysterophorus* L. crude extract	*Diodia ocymifolia*	Zainuddin *et al.* (2019) [55]
NCs (nano/cellulose)_savory (*Satureja ortensis* L.) essential oil	*Lycopersicon esculentum; Amaranthus retroflexus* L.	Taban *et al.* (2020) [50]
Nano-hydrogel_ glyphosate	Weeds; *Oryza sativa* L.	Zhang *et al.* (2020) [56]
Carbon nanotubes_Glyphospate	*Arabidopsis thaliana*	Ke *et al.* (2021) [26]
CS/TPP_PQ NPs	*Spinacia oleracea* L.	Pontes *et al.* (2021) [41]
PCL_Metribuzin NPs	*Ipomoea grandifolia*	Takeshita *et al.* (2022) [51]

Table 2: Examples of some inorganic nano-enabled herbicides

Nanoherbicides	Plants	References
Mesoporous silica NPs_Trimethylammonium_2,4-D	*Cucumis sativus* L.; *Triticum aestivum* L.	Cao *et al.* (2018) [4]
Layered double hydroxide Imazamox	*Brassica nigra* L.	Khatem *et al.* (2019) [27]
Clay-imazaquin	*Brassica oleracea* var. *botrytis* L.	López-Cabeza *et al.* (2019) [33]
Mg-Al-layered double hydroxide_2,4-D	*Arabidopsis thaliana* L.	Nadiminti *et al.* (2019) [35]
Diquat dibromide@mesoporous silica nanoparticles-SO_3	*Datura stramonium* L.	Shen *et al.* (2019) [45]
Zinc hydroxide nitrate-Sodium dodecylsulphate-Bispyribac	*Oryza sativa* L.	Sharif *et al.* (2020) [44]
Nanoformulation-sepiolite_Mesotrione	*Zea mays* L.; *Helianthus annuus* L.	Galán-Jiménez *et al.* (2020) [14]
Herbicide@Hydrotalcites	*Amaranthus retroflexus*	Gao *et al.* (2021) [15]
Tribenuron-methyl zein-based nanoparticles	*Convolvulus arvensis* L.	Heydari *et al.* (2021) [21]

Table 3: Examples of some hybrid nano-enabled herbicides

Nanoherbicides	Plants	References
AgNPs_CS(chitosan)_PQ(paraquat)	*Eichhornia crassipes*	Namasivayam *et al.* (2014) [36]
Wheat gluten_organically modified montmorillonite_ethofumesate	*Lepidium sativum L.*	Chevillard *et al.* (2014) [6]
GSNO (nitrosoglutathione)-containing alginate/chitosan nanoparticles	*Zea mays* L.; *Glycine sp.*	Pereira *et al.* (2015) [40]
pH-responsively controlled-release nanopesticide@ Fe_3O_4 NPs_CS	*Cynodon dactylon* L.	Xiang *et al.* (2017) [54]
Attapulgite-NH_4CO_3-Gly – Amino silicol oil – poly(vinyl alcohol)	*Zoysia matrella* L.	Chi *et al.* (2017) [8]
Light-responsively controlled-release herbicide particle	*Imperata cylindrica* L.	Chen *et al.* (2018) [5]
Near-infrared light-responsively controlled-release herbicide particles	*Cynodon dactylon* L.	Liu *et al.* (2019) [32]
Magnetic-responsive controlled-release herbicide	*Cynodon dactylon* L.	Chi *et al.* (2021) [7]
MOF(Metal–organic frameworks) @DiS-O-acetil	*Echinochloa crus-galli* L.; *Amaranthus viridis* L.	Mejías *et al.* (2021) [34]

Positive aspects for nanotechnology application in weed management

- Innovative technology that develops precision to meet the intense demand for food.
- Minimizing crop loss, reducing costs, enhancing yield and input use efficiency.
- Nanomaterials synthesized from biopolymers (cellulose and starch) are safe and environmentally friendly.
- The higher solubility of nanoparticles in suspension.
- Higher surface area and improved targeted activity.
- Suppressing toxic residue deposition and altering the efficacy of microorganisms.
- Avoiding the resistances build up in weeds.
- Lower eco harm with safe and relaxed transport.
- Recycling of the magnetic nanocarrier materials (Xiang *et al.*, 2017) [54].

Negative aspects for nanotechnology application in weed management

- Improper use of this technology can pose a greater threat to living organisms.
- Accumulation of nanomaterials in food products.
- Ability to pierce the healthy human skin.
- Air-borne nanoparticles pose an extreme level of threat to human and animal health.
- Unwanted and undesirable effect on non-target plants and plant-associated organisms.
- Nano-herbicides may block the vascular bundle in plants and may reduce pollination.
- Phytotoxicity, cytotoxicity, and genotoxicity.
- It may cause cell death or DNA mutation.
- Negative impact of nanomaterials on certain soil microbial communities and algae.

Challenges for nanotechnology application in weed management

- The major challenge in adopting this technology on a large scale is overcoming the risk issue. And as we know that 'technology-yes but safety-must', before the adoption of this technology, it is very important to assess the possible risks and consequences of using nanoparticles.
- The agricultural sector is still comparably marginal and has not yet been able to make progress in the market to any greater extent relative to other fields of nanotech application. Nanotechnology remains insignificant and has not yet taken the market because of its poor cargo loading capacity.
- Nanoparticles behave in an unpredictable manner, which may be harmful to life.
- Limited research on nanotechnology-based on its risky elements and toxicity.
- Nanomaterials are still being explored for applications in agrochemicals.
- Production cost, evaluation standards, registration policies and public concern issues must be addressed.

Effect of nanoencapsulated herbicide formulations

Application rate of herbicide

Nanoencapsulation potentiated the activity of the herbicide in relation to commercial herbicide formulation, allowing maintenance of its activity even when applied at a reduced dosage. So, the nanoencapsulated herbicide presented a low environmental risk, with increased weed control. It may be due to improved site of action by nanoencapsulation, which maintained the product's efficacy even with a reduction in the applied dose. Namasivayam *et al.* (2014) [36] observed that all the tested concentration of silver nanoparticles-chitosan encapsulated paraquat induced necrotic lesions on *Eichhornia crassipes* with the diameter of 1.0, 1.2 and 1.5 cm at 05, 10 and 25 µg/ml. Free paraquat recorded 0.8 and 1.0 cm of necrotic lesions at 10 and 25 µg/ml concentration. Sousa *et al.* (2018) [48] found that the use of 10-fold diluted atrazine-loaded PCL nanocapsules (200 g a.i./ha) resulted in the same inhibitory effect in root and shoot growth of weeds as the commercial formulation at the standard atrazine dose (2,000 g a.i./ha). Sousa *et al.* (2020) [47] revealed that at standard dosage (2,000 g a.i./ha) and at half-dosage (1,000 g a.i./ha), nanoatrazine was equally or more efficient in affecting most of the evaluated parameters than conventional atrazine at full dosage. It might be associated with the modified release of atrazine by the nanocapsules, with a better adhesion of the nanoformulation to the leaves or with the uptake of the nanocapsules by the leaf stomates, thereby preventing atrazine loss into the environment and improving the delivery of the herbicide to the target organism. Longer term presence of the nanoencapsulated herbicide in plant metabolism, surpassing the tolerance mechanisms of the weed. Similar findings reported by Sousa *et al*. (2022) [46] and Takeshita *et al*. (2022) [51].

Effect of herbicide on weed growth

Slow release and improved delivery of nanoencapsulated herbicides to the target organism leads to lower weed growth. Sousa *et al.* (2018) [48] found that the growth of *Amaranthus viridis* plants was equally reduced by nanoatrazine and commercial formulation. In the case of *Bidens pilosa*, atrazine-loaded nanocapsules decreased more effectively the root and shoot growth than the commercial formulation, leading to a loss of plant biomass. Vimalrajiv *et al.* (2019) [52] recorded lower weed density and weed dry weight with application of pendimethalin + hand weeding at 35 DAS, which was at par with the application of H_2O_2 *fb* pendimethalin + Ag Nps. This might be due to the strong oxidizing capacity of H_2O_2 that results in oxidative stress that causes cellular damage and death of seeds. The applied nanoparticles might have entered into the weed system and degraded the phenol and starch present in the tubers. Further combined application of silver nanoparticles with pendimethalin might have reduced the emergence in addition to killing of emerged weeds resulting in lower weed population and dry weight of weeds. Bommayasamy and Chinnamuthu (2021) [3] recorded the lowest weed density and weed dry matter production with the application of oxadiargyl loaded with zeolite at 20 DAT. It might be due to zeolite and biochar entrapped herbicides have increased sorption and decreased the dissipation of herbicide in soil which helps to release herbicide slowly through the entire season which destroys food reserves of weed seeds and causes lesser regeneration of weeds. Takeshita *et al*. (2022) [51] observed that plants treated with nanoMTZ and MTZ for the highest dose (480 g a.i./ha), and nanoMTZ for the lowest dose (48 g a.i./ha) induced similar reductions in shoot and root dry masses of *Ipomoea grandifolia* compared to the control samples. These results indicated that the nanoencapsulation potentiated the activity of the herbicide in relation to commercial formulation.

Effect of herbicide on plant physiological parameters

Both commercial atrazine and PCL nanocapsules containing atrazine did not lead to any side effects on maximum quantum yield of PSII, net photosynthesis or leaf lipid peroxidation of the maize plants, as compared to the control (Oliveira *et al*., 2015b) [38]. Negative effects of atrazine were transient, probably due to the ability of maize plants to detoxify the herbicide. Sousa *et al.* (2020) [47] revealed that at standard dosage (2,000 g a.i./ha), nanoatrazine induced higher and faster reductions of maximum PSII activity of *Digitaria insularis* at two expanded leaves than conventional atrazine. Sousa *et al.* (2022) [46] recorded that plants treated with nanoatrazine (at 200 g a.i./ha) induced significantly higher inhibition of the maximum quantum efficiency of photosystem II than conventional atrazine at the same concentration, 24 and 96 hours after application. The enhanced inhibition of PSII activity by nanoatrazine might be due to greater uptake of the nanoherbicide by stomata and hydathodes of leaves. Takeshita *et al*. (2022) [51] reported the maximum inhibition of PSII activity and decrease in pigment levels of *Ipomoea grandifolia* under nanoencapsulated metribuzin and commercial metribuzin with the highest dose (480 g a.i./ha) was observed. It might be due to improved site of action by nanoencapsulation. Although the findings provided clear evidence of the ability of PCL nanocapsules to increase the activity of atrazine towards a target species, the mechanisms involved remain unclear.

Effect of herbicide on crop yield

Crop growing in an environment with minimum disturbance due to weeds reflected on crop yield by enhancing the growth and seed yield. This might be due to reduced competition between crop and weed for different resources. Kumar and Chinnamuthu (2017) [28] indicated that 6 percent starch encapsulated pendimethalin by solvent evaporation method resulted in higher growth and yield of blackgram. Vimalrajiv *et al.* (2019) [52] concluded that among the herbicide treatments, the pre-emergence application of pendimethalin + HW on 35 DAS recorded the highest seed yield and haulm yield. The next best treatment was application of H_2O_2 *fb* pendimethalin + Ag Nps. Bommayasamy and Chinnamuthu (2021) [3] recorded higher grain yield of rice with the application of butachlor at 1.25 kg/ha *fb* hand weeding on 40 DAT followed by oxadiargyl loaded with zeolite. This might be due to better control of weeds over a longer period of time, thus providing a favourable environment for better growth and development of crop, leading to enhanced crop yield.

Effect of herbicide on nutrient uptake

Slow release of nanoencapsulated herbicides significantly reduced weed dry matter production which led to synthesizing more food materials through effective photosynthesis and higher nutrient uptake by crop. Bommayasamy and Chinnamuthu (2021) [3] recorded the higher N, P and K uptake by rice with the application of butachlor at 1.25 kg/ha *fb* hand weeding on 40 DAT, which was comparable with oxadiargyl loaded with zeolite and oxadiargyl loaded with biochar. It might be due to zeolite and biochar entrapped herbicides have increased sorption and decreased the dissipation of herbicide in soil which helps to release herbicide slowly through the entire season which destroys food reserves of weed seeds and causes lesser regeneration of weeds. Further application of zeolite which acted as a soil conditioner; increased fertilizer use efficiency by controlled release of nutrient in match with the requirement of plants during different physiological growth stages.

Effect of herbicide on weed control

Slow release of entrapped herbicide reduced the herbicide movement within the soil column and kept the sizable portion of the active ingredient in the upper soil layer over a long period. This may lead to improved weed control efficiency and reduce the frequencies of herbicide application. Oliveira *et al.* (2015a) [37] reported that atrazine-containing PCL nanocapsules provided very effective post-emergence herbicidal activity and the use of nanoencapsulated atrazine enabled the application of lower dosages of the herbicide, without any loss of efficiency. Kumar and Chinnamuthu (2017) [28] indicated that 6 percent starch encapsulated pendimethalin by solvent evaporation method, released the nanoencapsulated pendimethalin slowly with sufficient quantity to control the weed seed germination. Diyanat and Saeidian (2019) [12] recorded the lowest percentage of purslane emergence under the PCL nanoencapsulated metribuzin treatment, which was significantly lower than the commercial metribuzin treatment. Vimalrajiv *et al.* (2019) [52] recorded higher weed control efficiency using H_2O_2 *fb* pendimethalin + Ag Nps. They also noted lower weed index with the application of pendimethalin + hand weeding at 35 DAS, which was followed by treatment H_2O_2 *fb* pendimethalin + Ag Nps. This improved weed control might be due to the strong oxidizing capacity of H_2O_2 that results in oxidative stress that causes cellular damage and death of seeds. Further combined application of silver nanoparticles with pendimethalin might have reduced the emergence in addition to killing of emerged weeds resulting in lower weed population and dry weight of weeds. Kurniadie *et al*. (2022) [31] found that a mixture of paraquat (280 g a.i./ha) and chitosan significantly increased the herbicidal efficacy against *Ageratum conyzoides*, *Paspalum conjugatum* and *Borreria alata* under the rainfall conditions. The chemical structure of chitosan might have contributed to the penetration of paraquat into plant tissues.

Effect of nanoencapsulation on stability of herbicide

Encapsulation controls the active ingredients' release rate and protects susceptible materials from undesirable environmental conditions. Daneshvari *et al*. (2021) [11] observed that unlike the EC formulation, the amount of active ingredient in the encapsulated formulation was not significantly decreased following 8 and 16 h of exposure to natural sunlight. They also found that with increasing UV exposure, the active ingredient in the EC formulation decreased linearly and reached 43% after 8 h. In comparison, only 0.9% of the initial herbicide level in the encapsulation was lost during the same time. Results indicated that an effective herbicide such as trifluralin can be protected from volatilization and photodegradation by developing an encapsulated formulation.

Effect of nanoencapsulation on availability of herbicide

Nanoencapsulation of herbicide decreases its absorption by the soil colloids and increases its availability for the target plant. Diyanat *et al*. (2019) [13] observed that polycaprolactone nanocapsules containing pretilachlor were distributed in the layers of 0–5 and 5–10 cm and not found at the depth of 10–15 cm. Most of the encapsulated pretilachlor remained in the top layers (0–10 cm), which is desirable in weed control.

Effect of herbicide on soil microbial population

Microorganisms are influenced by several factors including the application of herbicides. Among the different soil microbes, more sensitive microbes to herbicides are bacteria (Ghinea *et al*., 1998) [16]. Sulfentrazone applied to sugarcane crop at lower doses of 720 and 840 g a.i./ha did not affect the microflora but in case of higher doses of 1320 and 2400 g a.i./ha initial reduction of microflora was observed and recovered 30 days after application (Kalaiyarasi, 2012) [24]. This might be due to carbon released from degraded herbicide which leads to an increase of the soil microflora population (Bera and Ghosh, 2013) [2]. Kannamreddy *et al.* (2020) [25] reported that all the tested commercial and nanoencapsulated herbicides showed reduction in bacterial, fungal and actinomycetes population at 25 DAS compared to initial population. But at 50 DAS there was a great increase in microbial population compared to 25 DAS in all herbicide applied treatments. There was no significant difference among all the treatments at 50 DAS in the microbial population. They also found that pendimethalin @ 1 kg a.i./ha and encapsulated sulfentrazone @ 0.3 kg a.i./ha recorded higher nodule count and nodule dry weight of blackgram at 30 DAS. But at 60 DAS there was no significant difference among the treatments except with unweeded control. It might be due to herbicidal degradation by microbes, there was gradual increase in soil microbiome and nodulation ability at 60 DAS.

Phytotoxic effect of herbicide

Modified release and improved target delivery of the nanoencapsulated herbicides reduce side effects/ phytotoxic effects on non-target plants and plant-associated organisms.

Namasivayam *et al.* (2014) [36] observed that silver nanoparticles-chitosan encapsulated paraquat induced necrotic lesions on *Eichhornia crassipes*. Whereas, necrotic lesions were not recorded on paddy and wheat leaves. So, there was no phytotoxicity of nanoencapsulated paraquat against paddy and wheat leaves. Oliveira *et al.* (2015b) [38] suggested that the use of PCL nanocapsules containing atrazine did not lead to persistent side effects in maize plants, and that the technique could offer a safe tool for weed control without affecting crop growth. Diyanat and Saeidian (2019) [12] also indicated that PCL nanoencapsulated metribuzin had no side effect on soybean.

Toxicity of herbicide

Studies have shown that nanoencapsulation of herbicides can produce more targeted and less toxic formulations for agricultural applications. Clemente *et al.* (2013) [10] reported that poly(ε-caprolactone) (PCL) nanocapsules containing ametryn and atrazine resulted in lower toxicity to the human and alga (*Pseudokirchneriella subcapitata*) and higher toxicity to the microcrustacean (*Daphnia similis*) as compared to the herbicides alone. These findings indicated that encapsulation of the herbicides acted to reduce the damage caused to the cells, which can be explained by the slower release and consequently smaller quantities of the herbicides available to promote cellular toxicity. Grillo *et al.* (2014) [19] noted that chitosan and tripolyphosphate encapsulated nanoherbicides are environmentally safer alternatives for weed control. Takeshita *et al.* (2022) [51] also verified that nanoencapsulated metribuzin in polymeric nanoparticles presented a low environmental risk, with increased weed control.

Conclusion

The use of herbicides is fundamental to maintaining crop yields and expanding the extent of the production area. Herbicides have eased the problem of weed control, but there are still problems, such as herbicide persistence in soil, that have been lowering the quality of soil. Apart from that, the trends among the weeds of developing resistance to the herbicides have been a serious issue. Nanotechnology, with its unique way of releasing herbicides, can give promising results. Studies have shown that nanoencapsulation of herbicides can produce more targeted and less toxic formulations for agricultural applications. Due to the enhanced herbicidal activity in comparison with a commercial formulation, the use of nanoencapsulated herbicide would permit the application of lower dosages of the herbicide. The use of lower doses of herbicides is desirable as it reduces the long-term effects of residues of these herbicides in agricultural areas and their toxicity to the environment. Encapsulated herbicides can aid in the easy delivery of herbicides to weed plants, reducing residual accumulation in soil. The target specific release is also helpful in killing the weeds without even interacting with the crop plants and ultimately results in a higher crop yield. Nanotechnology is thus a boon that can be further developed with regard to the target site inhibition of the biochemical reactions of weed.

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