Use of Nano Technology in Weed Management

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European Commission (EC) recommendation, a nanomaterial is defined as "natural, incidental, or industrial material with particles, in an unbound state or in the form of aggregate or agglomerate where 50% or more of the particles in the number and size distribution, one or more than one dimensions lies in the range of 1–100 nm" (Neme *et al.*, 2021).

Nanoparticle synthesis

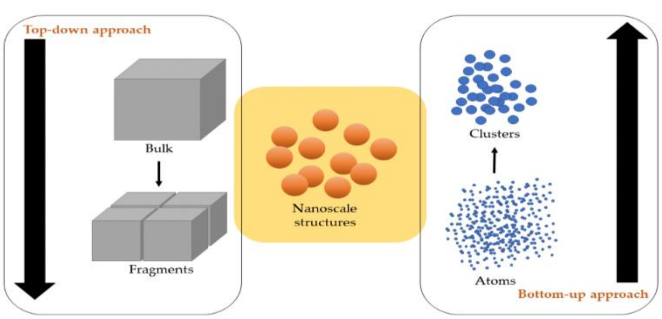
A variety of methods are being used for the synthesis of nanoparticles, which are generally categorized into two categories (Royal Society and Royal Academy of Engineering).

(a) Top-down approach (which focus on reducing the size of bulk materials)

(b) Bottom-up approach (where materials are synthesized from the atomic level)

Top-down: In top-down approach, mechanical physical procedures such as grinding, milling, and crushing are used to manipulate a small number of atoms or molecules to construct exquisite patterns. This approach makes substantial use of nano composites and nano-grained bulk materials such as metallic and ceramic nanomaterials (10 - 1000 nm).

Bottom-up: In a 'Bottom-up' approach, several molecules self-assemble in parallel steps based on their molecular recognition characteristics. From atoms or molecules, this processing yields increasingly complex structures. This approach is mostly used to produce nanomaterials with consistent sizes, morphologies, and size ranges (1 - 100 nm).



Nano Formulations

(Susha *et al.*, 2022) suggested that the nano formulations as,

- Nano capsulations
- Nano carriers
- Nano emulsion
- Nano adjuvants
- Nano biosensor

Nano-encapsulation:

Nano-encapsulation is the process of encapsulating solid, liquid, or gas nanoparticles (also known as the core or active) in a secondary substance (also known as the matrix or shell) to generate nano capsules. Nanoencapsulation could allow for the simultaneous application of many substances while inhibiting interactions until they are released (Korres *et al.*, 2019).

The utilization of atrazine-containing PCL nano capsules potentiated the post-emergence control of *Amaranthus viri* and *B. pilosa* by the herbicide (Sousa *et al.*, 2018) indicating the potentiality of nano formulation as an efficient alternative for weed control.

(Sousa *et al.*, 2018) conducted the experiment on post-emergence herbicidal activity of nano atrazine against *Alternanthera tenella* plants compared to other weed species. The encapsulation of atrazine into poly(epsilon-caprolactone) nano capsules has been shown to improve the efficiency of the herbicide and decrease its environmental impacts. The response of *A. tenella* plants to nano atrazine, a second experiment was carried out in a greenhouse with four-leaf stage plants treated with nano and conventional atrazine at 200, 500, 1000, and 2000 g a. i. ha^{-1}. Nano atrazine showed higher efficiency (up to 33%) than commercial atrazine in inhibiting photosystem II activity at all doses until 48 h after application.

Nano-carrier

Herbicide nanocarrier research is primarily focused on decreasing the environmental impact of herbicides, specifically reducing herbicide non-target toxicity. Some of the nanocarrier materials include: chitosan, tri-polyphosphate, alginate, poly -å caprolactone, starch and rice husk.

Chitosan with paraquat herbicide were less hazardous to crops (Grillo *et al.*, 2014). 2,4-D rice husk biochar (DrBC) reducing herbicide leaching and providing long-term release (Abigail *et al.*, 2016). Calcium carbonate with prometryn recorded 20 % greater efficacy in suppressing *Cynodon dactylon* (Xiang *et al.*, 2018).

(Khan *et al.*, 2022) conducted the experiment on synthesis, characterization, and evaluation of nanoparticles of clodinofop propargyl and fenoxaprop-p-ethyl on weed control, growth, and yield of wheat (*Triticum aestivum L.).* The targeted weeds, where the nano herbicides were sprayed at the third to fourth leaf stage.

Six different doses were applied. The mortality and visual injury caused by both chitosan based nano herbicides reached 100% at the recommended dose of standard herbicide. The size of both herbicides was found to be 35–65nm. The simplicity of making chitosan-loaded herbicide complexes leads to their improved release characteristics, which can significantly change how herbicides are applied.

(Abigail *et al.*, 2016) conducted the experiment on Biochar-based nanocarriers. Biochar prepared from rice husk (rBC) was used as a nano sorbent for the sustained delivery of 2,4-dichlorophenoxyacetic acid (2,4-D) and for its potential use as an eco-friendly nano herbicide formulation. For the biochar-based 2,4-D nano formulation (DrBC), the loading efficiency of the herbicide onto the rBC nanocarrier was checked at various weight ratios, where a weight ratio of 1:0.25 (rBC:2,4-D) was found optimum. The sustained release of 2,4-D from the DrBC nano formulation was detected for about 26 days.

Nano emulsions

Nano emulsions are emulsions that are nanoscale in size and are used to improve the delivery of active herbicidal substances. These are thermodynamically stable isotropic systems in which an emulsifying agent, such as surfactant and co surfactant, is used to combine two immiscible liquids into a single phase. Nano-emulsion droplets are typically 20-200 nm in size.

The nano emulsion of pretilachlor microemulsion (ME) and monolithic dispersion (MD) was found to be much superior in managing *Echinochloa crus-galli* compared to the commercially available formulation (Kumar *et al.*, 2016). At 1000 ìL/L, a nano emulsion of *Satureja hortensis L.* essential oil totally reduced all growth characteristics of *Amaranthus retroflexus* (Hazrati *et al.*, 2017).

(Somala *et al.*, 2022) conducted an experiment in Citronella essential oil-based nano emulsion as a post-emergence natural herbicide. A natural herbicide nano emulsion was fabricated from citronella (*Cymbopogon nardus L.)* essential oil (CEO) and a nonionic surfactant Tween 60 mixed with Span 60 at hydrophilic-lipophilic balance 14 using a micro fluidization method. The smallest droplet size was obtained from the micro fluidization condition at 20,000 psi and 7 cycles. The current report confirms that the CEO nano emulsion may act as a post-emergence herbicide.

Nano-adjuvants

There are commercially available herbicide adjuvants that claim to contain nanoparticles. (Chandana *et al.*, 2021) used a surfactant derived from nano-technology with a basis of soybean micelles to sensitize the crops resistant to glyphosate.

Nano-biosensors

Nano-biosensors can be used as a tool for detection of enzyme-inhibiting herbicides. The herbicide Metsulfuron-methyl (an acetolactate synthase inhibitor) was detected in the soil using a novel nano-biosensor based on atomic force microscopy (Da Silva *et al.*, 2013). Precision agriculture employs nanotechnology-based sensors to ensure the proper release of herbicide spray mixtures and precise control of herbicide applications. Herbicides could be used more effectively and efficiently with nano biosensors while being environmentally friendly (Duhan *et al.*, 2017).

Benefits of Nano Technology

1. **Weed seed bank and perennial weeds perennating organs exhaustion**: The use of H_2O_2 at 300 ml/m^2 followed by pendimethalin at 0.75 kg/ha + ZnO nanoparticles at 500 ppm/m^2 resulted in a significant reduction in weed emergence patterns due to the disruption in the seeds before and during their emergence, and resulted in increase in black gram yield (Vimalrajiv *et al.*, 2018).
2. **Germination promotion by germination inhibitor degradation:** Maximum degradation of the phenolic compound vanillic acid was reported with iron oxide (Fe_2O_3) nanoparticles at 25 mg i.e., 60.6% degradation relative to control (Viji and Chinnamuthu, 2019).
3. **Perennial weeds management through exhaustion of food reserves**: The food reserves in the tubers of *C. rotundus* are depleted by silver nanoparticles. The degradation of starch into reducing sugars is brought by the interaction of á amylase with silver nano-particles (Viji *et al.*, 2016).
4. **Faster foliar penetration, movement and impact in the plant system of nano-herbicides:** Depending on the entry point, several tissues (epidermis, endodermis) and barriers (Casparian strip, cuticle) must be traversed by herbicides before reaching the vascular tissues (roots or leaves). Nanomaterials can move up and down the plant using the apo plastic and/or symplastic pathways, as well as radial movement to switch from one to the other. Endocytosis, pore formation mediated by carrier proteins, and plasmodesmata has all been postulated

as methods for the internalization of nanoparticles within cells (Perez-de-luque, 2017).

5. **Enhanced herbicide efficacy in rainfed ecosystem by smart delivery of nano formulations:** To achieve controlled release of the herbicide active ingredient, these hollow-shell particles were loaded with pendimethalin using a passive method. Even at 230ºC, the formulation remained intact and without any microbial degradation (Kanimozhi and Chinnamuthu, 2012).
6. **Slow-release nano formulations for season long weed control:** Nanoencapsulation can also improve herbicide application, providing better penetration through cuticles and tissues and allowing slow and constant release of the active substances (Pradeesh and Chinnamuthu, 2020).
7. **Detoxification of herbicide residues:** The use of poly (epsilon-caprolactone) (PCL) as an atrazine carrier after encapsulation had no influence on the herbicide's long-term residual action on soybean as the mobility of atrazine was reduced, it resulted in a spectacular reduction in the phytotoxic accumulation of atrazine in soil, as well as increased herbicide activity (Pereira *et al.,* 2014).

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