Review Article

A Review on Smart Herbicides: The Future of Weed Management

ABSTRACT

Weeds pose significant challenges to global agricultural productivity, with India alone experiencing annual losses of $11 billion due to weed infestations, despite the extensive use of herbicides. Doubts persist regarding the effectiveness of these herbicides, prompting the exploration of more efficient control methods. Nanotechnology emerges as a promising avenue for herbicide development, offering 'Smart herbicides' with heightened effectiveness and reduced application volumes. Nanoherbicides employ innovative mechanisms, effectively depleting weed seed banks, degrading germination inhibitors, and facilitating gradual herbicide release. Techniques like damaging weed pollen grains and utilising carbon nanotubes demonstrate inventive approaches to seed bank depletion. Controlled release formulations ensure prolonged and efficient weed suppression while minimising environmental impact. Moreover, incorporating metal ions accelerates herbicide residue degradation, mitigating environmental persistence. Enhanced plant growth with nano herbicide application emphasizes their potential as sustainable weed control solutions. However, further research is essential to ensure their safety and efficacy before widespread adoption in commercial agriculture, addressing potential risks associated with their application. Introducingnano herbicides signifies a significant advancement in sustainable weed management practices, promising a future where agricultural productivity can be safeguarded against weed infestations.

Keywords:*nanoherbicides, nano-encapsulation, slow release, smart delivery, targeted weed management, weed seed bank*

1. INTRODUCTION

'Weed' refers to any plant displaying aggressive growth or invasiveness outside its native habitat. Economically, weeds threaten crop productivity. The changing agricultural environment and continuous progress in intensive farming are anticipated to persist depending on herbicides as a fundamental method for weed control [1]. Annual weeds regenerate from seeds dispersed in the soil or environment during previous seasons, while perennial weeds regenerate from existing plants, dormant buds, roots, stolons, rhizomes, and tubers[2]. Naturally adapted to endure high levels of stress and competition, weeds are often called 'pioneer' plants, establishing themselves first, even in harsh conditions [3]. The weed nutrient removal is higher [4]and their seeds possess adaptations that enable survival through various stressors, rendering them more adept at establishment in an area than crops [5].

India annually loses agricultural produce worth $11 billion to weeds, exceeding the budgetallocation for agriculture in 2017-18. The potential yield losses due to weeds, particularly in rice ($4,420 million), wheat ($3,376 million), and soybean ($1,559 million), necessitate urgent attention to the issue[6]. Therefore, it is evident that novel and more effective measures are imperative for controlling the weed menace in agriculture[7]. Chemical weed control with herbicides, offer easier method especially in rice where grain yield obtained was 159.9% higher in herbicide treated plots (5.46 t/ha) compared to weedy check with a higher B: C ratio of 1.83 [8]. Efficiency of post-emergence herbicide depends on plant traits, spray characteristics and environmental conditions during spray application [9].Selective herbicides target specific weed species while minimising harm to desired crops, whereas non-selective herbicides clear vegetation indiscriminately. Factors considered in herbicide selection include persistence, uptake method, and mechanism of action [10]. Also, weeds show dynamic spatial variations both within and across fields, along with temporal fluctuations throughout and between seasons [11]. However, continuous use of a single herbicide is not effective in eliminating the weed menace in context of emerging weed shifts [12].

2. HERBICIDES: THE REAL FACE

In the developing countries of the Asia-Pacific region, herbicides are predominantly available in forms such as wettable powder, emulsifiable concentrate, and solution. These formulations are commonly called 'conventional' due to their requirement for increased dosage or repeated applications to achieve the desired effectiveness. Furthermore, the drawbacks of conventional herbicide formulations contribute to their suboptimal performance. Rotating herbicides and use of appropriate mixtures are two key approaches to suppress the weed floral shift and resistance development to herbicide in weeds [13]. Wettable powders (WP) necessitate constant and thorough agitation in the spray tank, causing abrasion to pumps and nozzles, potentially visible residues on plant and soil surfaces, and inhalation hazards for applicators during handling (pouring and mixing) of the powder. Emulsifiable concentrates have higher phytotoxicity compared to other formulations, are more readily absorbed through the skin of humans or animals, and contain solvents that may cause deterioration of rubber or plastic hoses and pump parts. Soluble liquids contain the salt form of a herbicide, potentially resulting in higher overall salt concentrations in the spray tank than other formulations. Emulsions in water contain a few active substances due to the specific solubility properties required. Herbicides face numerous limitations, including difficulty in penetrating seed coats due to incompatibility issues and small-sized pores, inability to induce dormant resting weed seeds or vegetative parts to germinate and be killed by the herbicide, rapid release, high residue, herbicide persistence in soil, groundwater contamination, and potential health issues. These limitations of currently used herbicides have prompted scientists to seek better alternatives for effective weed management while minimising flaws in existing methods, thus paving the way for the development of ‘nano herbicides’.

3. NANO (SMART) HERBICIDE

There is a need for herbicides that offer novel and highly effective weed control mechanisms, devoid of the shortcomings of current formulations. Considering these criteria, herbicides produced through nanotechnology emerge as a promising solution. They are engineered and administered primarily with suitable carriers, ensuring their active site of action operates at the nanoscale level, one billionth of a meter (nanometer, 10^{-9} m). The primary advantages include heightened effectiveness and reduced application volume, making them capable of intelligent weed management and known as 'Smart herbicides'.

The term "nano" originates from Greek, meaning "dwarf" [14], and in technical terminology, it refers to one billionth of something. Nanotechnology harnesses matter properties, processes, and phenomena at the nanometer scale, typically ranging from 1 to 100 nm. Synthesising nanoparticles of various sizes, shapes, and compositions is necessary to create new materials with distinct properties [15], achieved through either 'top-down' or 'bottom-up' approaches in nanoparticle synthesis [16]. Nanotechnology focuses on producing and stabilising various types of nanoparticles offering a promising platform for delivering active materials to targeted sites without compromising their activity [17]. Nano-formulations are generally designed to enhance the apparent solubility of poorly soluble active ingredients and release them slowly or in a targeted manner. Although nanotechnology principles are already employed in agriculture for various purposes such as seed germination, insect management, disease management, and packaging, their application in herbicides remains limited due to challenges such as distinguishing between crops and weeds at the nano level and the unconventional properties exhibited by substances at this scale.

3.1 Nano herbicidal approach for weed control

A nanoherbicide comprises tiny particles containing active herbicidal ingredients or intricately engineered structures to transport herbicidal molecules. Herbicides are incorporated into nanomaterials (NMs) to enhance their bioavailability, thereby improving weed management. A precise match between the nanostructure and herbicide molecules must be achieved to produce an NM capable of effectively delivering a significant amount of herbicide to weeds[18]. The active ingredient is either adsorbed, attached, encapsulated, or entrapped onto or into the nano-matrix. The controlled release of the active ingredient is facilitated by the slow-release properties of NMs, bonding between the ingredients and the material, and environmental conditions [19]. Nanoherbicides also provide a large specific surface area, enhancing their affinity for the target.

Delivery techniques for nano herbicides include nanoemulsions, nanocapsules, nanocontainers, and nanocages, offering capabilities such as slow release, precise action, and increased reactive area for active molecules [20]. Constraints associated with droplet size can be overcome by using NM-encapsulated or nanosized herbicides, leading to more efficient spraying and reduced losses from drift and splash. Nanoherbicides in the size range of 1–100 nm can interact with soil particles to eliminate weed seeds and roots. Most herbicides available in the market primarily target the above-ground parts of weed plants, neglecting viable underground plant parts like rhizomes or tubers, which serve as sources for new weeds in subsequent seasons. Encapsulating herbicides can improve their efficiency in reaching plants. The characteristics of nanoparticles influence their uptake and movement within the plant and the application method. Nanomaterials can follow apoplastic and symplastic pathways for movement within the plant and radial movement to transition between pathways [21].

3.2 Smart delivery mechanism

The development of target-specific herbicide molecules encapsulated within nanoparticles aims to target specific receptors in weeds, penetrating them for effective action. For instance, nanoherbicides designed to inhibit glycolysis in the food reserves of root system can lead to the starvation of specific weed plants, resulting in their death. Numerous mechanisms like this can be exploited using nanoherbicides. The choice of carrier molecules varies depending on factors such as mode, duration of use, and the targeted weed type. Critical components required for synthesising nanoherbicides include suitable nanomaterials and effective herbicides. These nanoparticles are typically 2000 to 50,000 times smaller than the particles used in conventional herbicides, increasing surface area for improved plant uptake, enhanced solubility in spray tanks, and reduced risk of settling and separation [22]. Carrier systems in formulating nano herbicides encompass chitosan, tripolyphosphate, alginate, poly epsilon-caprolactone, starch, rice husk, and silica dioxide nanoparticles [23]. Among the various nano-herbicide formulations studied, nano-encapsulated herbicides are the most suitable [24].

3.3 Nano encapsulation and types

Nanoencapsulation refers to encapsulating substances with various coating materials at the nanoscale range. Encapsulation involves the creation of a continuous thin coating around solid particles, liquid droplets, or gas cells to fully enclose them within the capsule wall. Various nanoencapsulation methods include the indirect method, direct method, solvent extraction, and spray dry process [25]. These methods primarily differ in their application under field conditions. In the indirect method, the fabrication of nanoherbicides involves several steps. Initially, uniform spherical $MnCO_3$ cores are synthesised followed by coating the cores with bilayers of polymers using the Layer by Layer (LbL) assembly method. The core-shell is then treated with HCl to etch out the core and form a hollow shell. This hollow shell is subsequently loaded with active ingredients either actively (energy-dependent) or passively utilising the permeability of the polymer layer in the presence of the solvent used for dissolving the herbicide.

In the direct method, the synthesis of the core is conducted, and the herbicide is directly added to the core material followed by the addition of bilayers of polymers using the LbL assembly method[26]. In the solvent evaporation method, herbicide deposition occurs in a preformed polymer, where the organic phase (polymer + herbicide) is combined with the aqueous one (polysorbate surfactant) while stirring using a magnetic stirrer at room temperature [27]. The suspension is shaken for 10 minutes at room temperature, and acetone (solvent) is then removed under reduced pressure using a rotary evaporator [28]. In the spray dry method, the prepared organic and aqueous phases are added to the nanospray drier, yielding a uniform nanoencapsulation formulation[29]. This method ensures enhanced properties such as crystallinity, orientation, solubility, plasticiser level, and cross-linking [30], while enhancing capsule properties like size, wall thickness, configuration, conformity, and coating layers [31].

3.4 Targeted mode of action

Nanoherbicides represent a revolutionary approach to weed control, surpassing conventional methods in effectiveness. Through diverse mechanisms of action, they achieve superior outcomes. Firstly, nanoherbicides excel in depleting weed seed banks, effectively reducing the future emergence of undesirable plants. Additionally, they demonstrate proficiency in breaking down germination inhibitors, facilitating the removal of barriers to weed growth [32]. Moreover, nano herbicides efficiently deplete weed food reserves, depriving them of essential nutrients crucial for proliferation. Their unique formulation enables the slow release of herbicides, ensuring prolonged efficacy against target weeds. Furthermore, nanoherbicides accelerate the degradation of herbicide residues, minimising environmental impact while maximising efficiency [32].

3.4.1 Exhausting weed seedbank

Reducing weed incidence can be achieved most effectively by depleting the weed seed bank, the primary source of weeds across generations. However, the stale seedbed technique, a cultural weed management method involving fallow periods often practised during summer to diminish the weed seed bank, proves ineffective when considering costs [33]. This technique entails frequent tilling and irrigation, thereby increasing weed management expenses. Weed seeds possess specialised mechanisms to withstand both biotic and abiotic stresses and so priority should be given to minimising the expansion of the weed seed bank and depleting it.

Damaging the pollen grains of weed flowers is one method while inducing sterility by dehydrating pollen grains with a nanoparticle (Ag/Na) spray proves effective thereby preventing seed production [34].Carbon nanotubes (CNTs) can render seeds non-viable instead of effectively targeting seedlings[35]. CNTs can penetrate cracks and openings in the seed coat, acting as conduits for water and chemicals [36], ultimately leading to seed coat permeation, breaking dormancy, and accelerating germination [37]. Nanoencapsulationof atrazine significantly increased mortality rates of *B. pilosa* seedlings, even at a tenfold dilution, with encapsulation reducing the long-term residual effect of the herbicide, likely due to decreased atrazine mobility in soil, leading to higher herbicide availability for seedlings [38]. The nanoformulation exhibited enhanced herbicidal effects against the target plant *Brassica sp*., causing 100% mortality and increased activity.

3.4.2 Degrading germinationinhibitor

Germination inhibitors contribute to prolonged dormancy in weeds, extending their longevity in soil. Breaking down these inhibitors promotes weed germination and enhances the efficacy of herbicides. For example, the tubers of purple nutsedge (*Cyperus rotundus*) one of the world's most problematic weeds contain numerous buds but only a few sprouts, while others remain dormant due to phenolic compounds[39];[40]. Nanoparticles have been employed to disrupt dormancy and induce germination in purple nutsedge tubers by disintegrating phenolic compounds [41]. In addition to promoting tuber sprouting, treated tubers (with nanoparticles) exhibited increased sprouts per tuber, dry matter, root and shoot length [42], rendering them susceptible to herbicide action. *Cyperus rotundus* contains more than 23 phenolic compounds, including caffeic acid, ferulic acid, chlorogenic acid, vanillic acid, and hydroxybenzoic acid [43]; [40];[44].

Abiotic stress elevates the quantity of germination inhibitors to inhibit germination (dormancy), while their degradation promotes germination [41]. Iron oxide nanoparticles at a concentration of 3.0 g kg per tubers significantly enhanced phenol degradation (89%), underscoring their role in catalysing hydroxyl radical generation in advanced oxidation processes (AOPs), potentially aiding in weed management by increasing germination percentage in treated *Cyperus rotundus* tubers [45]. ZnO treatment at 1500 mg kg^{-1} reduced starch and phenol content while significantly enhancing germination (80%) compared to the control, indicating its efficacy in promoting tuber growth through electron donor properties. However, further research is needed to understand its impact on tuber viability [41].

3.4.3 Exhausting foodreserve

The duration of dormancy in weeds is determined by the amount of stored food material they possess. Once this food material is depleted, weeds have no alternative means of sustenance and are compelled to perish [46]. Nanoparticles (NPs) exhibit a stimulatory effect on starch degradation. Silver nanoparticles were bio-conjugated with α-amylase and used to degrade starchpresent in tubers [45]. Silver nanoparticles facilitate the hydrolysis of starch in tubers of *Cyperus rotundus*, depleting starch and the energy required for weed survival [47]. In the case of *Bidens pilosa* and *Amaranthus viridis*, nanoencapsulated (NC)+ atrazine (ATZ) significantly reduced the relative growth rate, demonstrating high efficacy. Although NC+ATZ at 1/10 was less effective in inhibiting root and shoot growth than NC+ATZ, it still outperformed all other treatments, underscoring the effectiveness of nanoherbicides [48].

3.4.4 Slow release herbicide

The primary limitation of conventional herbicides lies in their ineffectiveness, with uncontrolled release and wastage of herbicides being the major contributing factor. Utilising carrier substances and nanoformulations can circumvent this issue by forming zwitterions or charged clusters during synthesis [49]. To mitigate environmental impacts associated with herbicide use, controlled release formulations of pendimethalin copper-chitosan nanoparticles were developed, with pH 5.5 exhibiting the highest release rate, indicating improved solubility and stability of the nano-formulation under acidic conditions [22]. Encapsulation of paraquat within nanoparticle polymeric matrices results in delayed release compared to its free form, with only 70% releasedunder laboratory conditions versus 92% for the free herbicide and further hindrance under field conditions due to factors such as low humidity and interaction with soil organic matter [50].

Evaluation of 2,4-D leaching in soil columns demonstrated higher concentrations in top segments due to rice husk carriers and colloids. This indicated increased herbicide persistence and bioavailability to target plants, with the lowest residual concentration observed in the most profound segment [51]. Nanoencapsulated alachlor with specific polymers reduces volatilisation, particularly when incorporated into soil, as shown by studies utilising technical alachlor, Lasso 4EC, and polymeric formulations (cellulose acetate butyrate ethyl cellulose) under controlled conditions for 32 to 39 days, with evolved alachlor collected in ethylene glycol and analysed by reverse-phase high-performance thin-layer chromatography with densitometry [52]. Metolachlor nanoparticles (MNPs) exhibitedmore significant inhibition on rice and *Digitaria sanguinalis* seedlings compared to large MNPs (L-MNPs) and metolachlor microparticles (MMPs) at low concentrations, with controlled release maintaining their persistence effectiveness, attributed to high activity due to absorption into plants [53].Controlled-release formulations utilising mesoporous silica nanoparticles reducedthe leaching of 2,4-D sodium salt by 48.4% compared to the free system, confirmed by soil column leaching tests [54].

3.4.5 Degradation of herbicide residues

Excessive herbicide usage leads to soil residue accumulation and subsequent damage to succeeding crops. Studies have demonstrated that when combined with nanoparticles and compatible carriers, metallic ions aid in rapidly degrading herbicide residues like Ag with magnetite nanoparticlesstabilised with carboxymethyl cellulose [55]. Iron nanoparticles with positive charges effectively interact with the lone pairs on nitrogen in atrazine herbicide, facilitating rapid removal with 90–98% efficiency [56]. Atrazine levels in soil decreased irrespective of formulation, with higher levels in NC+ATZ than ATZ but no difference between NC+ATZ 1/10 and ATZ 1/10, suggesting that nanoencapsulation may reduce residual effects by lowering herbicide dosage [38].

Nanoparticles containing paraquat resulted in a slight reduction in cellular viability in Chinese hamster ovary cells, though it remained close to 100%, indicating their potential to alleviate herbicide toxicity [50]. The association of herbicide with nanoparticles reduced DNA damage in onions compared to free paraquat, suggesting nanoparticle-provided protection against its toxic effects, with free paraquat causing more significant damage [50]. Nanoencapsulation of pendimethalin using the solvent evaporation technique resulted in prolonged herbicide release over 40 days, showing no significant impact on earthworm survival, indicating its safety and effectiveness [57]. Studies conducted to remove atrazine revealed that Ag modified Fe_3O_4-carboxymethyl cellulose nanoparticles demonstrated 82-88% degradation of atrazine and proved effective for degrading atrazine in soil samples[58];[59].

3.4.6 Enhanced Efficacy

Nanoherbicides containing H_2O_2, pendimethalin, and ZnO NPs contributed to increased plant height in black gram by establishing a weed-free environment, enhancing enzyme activity, optimising auxin metabolism, and facilitating improved Zn absorption, thereby fostering crop growth [60]. The nanoemulsion formulation of pretilachlor at 600 g/ha demonstrated superior weed control at 30 and 60 days after treatment compared to commercial formulations due to its smaller particle size, as evidenced by [61]. Solid lipid nanoparticles (SLN) incorporating herbicides demonstrated heightened efficacy in inhibiting plant growth compared to commercial formulations, suggesting their potential for agricultural applications even at lowerconcentrations [62].

4. CONCLUSION

Nanoherbicides can act as intelligent herbicides, presenting a promising and safe approach for sustainable and efficient weed control. They offer enhanced stability compared to existing methods and formulations. However, thorough research is necessary to comprehensively grasp the science behind nanoherbicides before they can be widely implemented in commercial agriculture.

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