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3 **A Review on Nano Herbicides: The Future of Weed**
4 **Management**

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6
7 **ABSTRACT**

8
9 Weeds pose significant challenges to global agricultural productivity, with India alone
10 experiencing annual losses of \$11 billion due to weed infestations, despite the extensive use of
11 herbicides. The drawbacks of conventional herbicide formulations contribute to their suboptimal
12 performance. Rotating herbicides and use of appropriate mixtures are two key approaches to suppress
13 the weed floral shift and resistance development to herbicide in weeds. Doubts persist regarding the
14 effectiveness of these herbicides, prompting the exploration of more efficient control methods. Using lower
15 amounts of herbicides is preferred because it decreases the lasting impact of herbicide residues in
16 agricultural regions and their environmental toxicity. Nanoherbicides can facilitate the efficient transport of
17 herbicides to weed plants, thereby minimizing the buildup of residues in the soil. Nanotechnology
18 emerges as a promising avenue for herbicide development, offering 'Smart herbicides' with heightened
19 effectiveness and reduced application volumes. Nanoherbicides employ innovative mechanisms,
20 effectively depleting weed seed banks, degrading germination inhibitors, and facilitating gradual herbicide
21 release. Techniques like damaging weed pollen grains and utilising carbon nanotubes demonstrate
22 inventive approaches to seed bank depletion. Controlled release formulations ensure prolonged and
23 efficient weed suppression while minimising environmental impact. Moreover, incorporating metal ions
24 accelerates herbicide residue degradation, mitigating environmental persistence. Enhanced plant growth
25 with nano herbicide application emphasizes their potential as sustainable weed control solutions.
26 However, further research is essential to ensure their safety and efficacy before widespread adoption in
27 commercial agriculture, addressing potential risks associated with their application. Introducing nano
28 herbicides signifies a significant advancement in sustainable weed management practices, promising a
29 future where agricultural productivity can be safeguarded against weed infestations.

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

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36 **1. INTRODUCTION**

37
38 'Weed' refers to any plant displaying aggressive growth or invasiveness outside its native habitat.
39 Economically, weeds threaten crop productivity. The changing agricultural environment and continuous
40 progress in intensive farming are anticipated to persist depending on herbicides as a fundamental method
41 for weed control [1]. Annual weeds regenerate from seeds dispersed in the soil or environment during

42 previous seasons, while perennial weeds regenerate from existing plants, dormant buds, roots, stolons,
43 rhizomes, and tubers[2]. Naturally adapted to endure high levels of stress and competition, weeds are
44 often called 'pioneer' plants, establishing themselves first, even in harsh conditions [3]. The weed nutrient
45 removal is higher [4]and their seeds possess adaptations that enable survival through various stressors,
46 rendering them more adept at establishment in an area than crops [5].

47 India annually loses agricultural produce worth \$11 billion to weeds, exceeding the
48 budgetallocation for agriculture in 2017-18. The potential yield losses due to weeds, particularly in rice
49 (\$4,420 million), wheat (\$3,376 million), and soybean (\$1,559 million), necessitate urgent attention to the
50 issue[6]. Therefore, it is evident that novel and more effective measures are imperative for controlling the
51 weed menace in agriculture[7].Manual and mechanical removals were the most prominent methods of
52 weed management in India. But these were not very efficient, especially in unfavourable weather and soil
53 conditions. Hand weeding is highly labourintensive process and requires a lot of efforts. The prevailing
54 trend in weed management is the adoption of modern agricultural practices, leveraging chemicals,
55 machinery, and other modern technologies [8]. Chemical weed control with herbicides, offer easier
56 method especially in rice where grain yield obtained was 159.9% higher in herbicide treated plots (5.46
57 t/ha) compared to weedy check with a higher B: C ratio of 1.83 [9]. Efficiency of post-emergence
58 herbicide depends on plant traits, spray characteristics and environmental conditions during spray
59 application [10].Selective herbicides target specific weed species while minimising harm to desired crops,
60 whereas non-selective herbicides clear vegetation indiscriminately. Factors considered in herbicide
61 selection include persistence, uptake method, and mechanism of action [11]. Also, weeds show dynamic
62 spatial variations both within and across fields, along with temporal fluctuations throughout and between
63 seasons [12]. However, continuous use of a single herbicide is not effective in eliminating the weed
64 menace in context of emerging weed shifts [13].

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66 **2. HERBICIDES: THE REAL FACE**

67 In the developing countries of the Asia-Pacific region, herbicides are predominantly available in forms
68 such as wettable powder, emulsifiable concentrate, and solution. These formulations are commonly
69 called 'conventional' due to their requirement for increased dosage or repeated applications to achieve
70 the desired effectiveness. Furthermore, the drawbacks of conventional herbicide formulations contribute
71 to their suboptimal performance. Rotating herbicides and use of appropriate mixtures are two key
72 approaches to suppress the weed floral shift and resistance development to herbicide in weeds [14].
73 Wettable powders (WP) necessitate constant and thorough agitation in the spray tank, causing abrasion
74 to pumps and nozzles, potentially visible residues on plant and soil surfaces, and inhalation hazards for
75 applicators during handling (pouring and mixing) of the powder. Emulsifiable concentrates have higher
76 phytotoxicity compared to other formulations, are more readily absorbed through the skin of humans or
77 animals, and contain solvents that may cause deterioration of rubber or plastic hoses and pump parts.
78 Soluble liquids contain the salt form of aherbicide, potentially resulting in higher overall salt

79 concentrations in the spray tank than other formulations. Emulsions in water contain a few active
80 substances due to the specific solubility properties required. Herbicides face numerous limitations,
81 including difficulty in penetrating seed coats due to incompatibility issues and small-sized pores, inability
82 to induce dormant resting weed seeds or vegetative parts to germinate and be killed by the herbicide,
83 rapid release, high residue, herbicide persistence in soil, groundwater contamination, and potential health
84 issues. These limitations of currently used herbicides have prompted scientists to seek better alternatives
85 for effective weed management while minimising flaws in existing methods, thus paving the way for the
86 development of 'nano herbicides'.

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88 **3. NANO (SMART) HERBICIDE**

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

96 The term "nano" originates from Greek, meaning "dwarf" [15], and in technical terminology, it refers
97 to one billionth of something. Nanotechnology harnesses matter properties, processes, and phenomena
98 at the nanometer scale, typically ranging from 1 to 100 nm. Synthesising nanoparticles of various sizes,
99 shapes, and compositions is necessary to create new materials with distinct properties [16], achieved
100 through either 'top-down' or 'bottom-up' approaches in nanoparticle synthesis [17]. Nanotechnology
101 focuses on producing and stabilising various types of nanoparticles offering a promising platform for
102 delivering active materials to targeted sites without compromising their activity [18]. Nano-formulations are
103 generally designed to enhance the apparent solubility of poorly soluble active ingredients and release
104 them slowly or in a targeted manner. Although nanotechnology principles are already employed in
105 agriculture for various purposes such as seed germination, insect management, disease management,
106 and packaging, their application in herbicides remains limited due to challenges such as distinguishing
107 between crops and weeds at the nano level and the unconventional properties exhibited by substances at
108 this scale.

109

110 **3.1 Nano herbicidal approach for weed control**

111 A nanoherbicide comprises tiny particles containing active herbicidal ingredients or intricately
112 engineered structures to transport herbicidal molecules. Herbicides are incorporated into nanomaterials
113 (NMs) to enhance their bioavailability, thereby improving weed management. A precise match between
114 the nanostructure and herbicide molecules must be achieved to produce an NM capable of effectively
115 delivering a significant amount of herbicide to weeds[19]. The active ingredient is either adsorbed,

116 attached, encapsulated, or entrapped onto or into the nano-matrix. The controlled release of the active
117 ingredient is facilitated by the slow-release properties of NMs, bonding between the ingredients and the
118 material, and environmental conditions [20]. Nanoherbicides also provide a large specific surface area,
119 enhancing their affinity for the target.

120 Delivery techniques for nano herbicides include nanoemulsions, nanocapsules, nanocontainers,
121 and nanocages, offering capabilities such as slow release, precise action, and increased reactive area for
122 active molecules [21]. Constraints associated with droplet size can be overcome by using NM-
123 encapsulated or nanosized herbicides, leading to more efficient spraying and reduced losses from drift
124 and splash. Nano herbicides in the size range of 1–100 nm can interact with soil particles to eliminate
125 weed seeds and roots. Most herbicides available in the market primarily target the above-ground parts of
126 weed plants, neglecting viable underground plant parts like rhizomes or tubers, which serve as sources
127 for new weeds in subsequent seasons. Encapsulating herbicides can improve their efficiency in reaching
128 plants. The characteristics of nanoparticles influence their uptake and movement within the plant and the
129 application method. Nanomaterials can follow apoplastic and symplastic pathways for movement within the
130 plant and radial movement to transition between pathways [22].

131

132 **3.2 Smart delivery mechanism**

133 The development of target-specific herbicide molecules encapsulated within nanoparticles aims to
134 target specific receptors in weeds, penetrating them for effective action. For instance, nanoherbicides
135 designed to inhibit glycolysis in the food reserves of root system can lead to the starvation of specific
136 weed plants, resulting in their death. Numerous mechanisms like this can be exploited using
137 nanoherbicides. The choice of carrier molecules varies depending on factors such as mode, duration of
138 use, and the targeted weed type. Critical components required for synthesising nanoherbicides include
139 suitable nanomaterials and effective herbicides. These nanoparticles are typically 2000 to 50,000 times
140 smaller than the particles used in conventional herbicides, increasing surface area for improved plant
141 uptake, enhanced solubility in spray tanks, and reduced risk of settling and separation [23]. Carrier
142 systems in formulating nano herbicides encompass chitosan, tripolyphosphate, alginate, poly epsilon-
143 caprolactone, starch, rice husk, and silica dioxide nanoparticles [24]. Among the various nano-herbicide
144 formulations studied, nano-encapsulated herbicides are the most suitable [25].

145

146 **3.3 Nano encapsulation and types**

147 Nanoencapsulation refers to encapsulating substances with various coating materials at the
148 nanoscale range. Encapsulation involves the creation of a continuous thin coating around solid particles,
149 liquid droplets, or gas cells to fully enclose them within the capsule wall. Various nanoencapsulation
150 methods include the indirect method, direct method, solvent extraction, and spray dry process [26]. These
151 methods primarily differ in their application under field conditions. In the indirect method, the fabrication of
152 nanoherbicides involves several steps. Initially, uniform spherical $MnCO_3$ cores are synthesised followed

153 by coating the cores with bilayers of polymers using the Layer by Layer (LbL) assembly method. The
154 core-shell is then treated with HCl to etch out the core and form a hollow shell. This hollow shell is
155 subsequently loaded with active ingredients either actively (energy-dependent) or passively utilising the
156 permeability of the polymer layer in the presence of the solvent used for dissolving the herbicide.

157 In the direct method, the synthesis of the core is conducted, and the herbicide is directly added to
158 the core material followed by the addition of bilayers of polymers using the LbL assembly method[27]. In
159 the solvent evaporation method, herbicide deposition occurs in a preformed polymer, where the organic
160 phase (polymer + herbicide) is combined with the aqueous one (polysorbate surfactant) while stirring
161 using a magnetic stirrer at room temperature [28]. The suspension is shaken for 10 minutes at room
162 temperature, and acetone (solvent) is then removed under reduced pressure using a rotary evaporator
163 [29]. In the spray dry method, the prepared organic and aqueous phases are added to the nanospray
164 drier, yielding a uniform nanoencapsulation formulation[30]. This method ensures enhanced properties
165 such as crystallinity, orientation, solubility, plasticiser level, and cross-linking [31], while enhancing
166 capsule properties like size, wall thickness, configuration, conformity, and coating layers [32].

167

168 **3.4 Targeted mode of action**

169 Nanoherbicides represent a revolutionary approach to weed control, surpassing conventional
170 methods in effectiveness. Through diverse mechanisms of action, they achieve superior outcomes.
171 Firstly, nanoherbicides excel in depleting weed seed banks, effectively reducing the future emergence of
172 undesirable plants. Additionally, they demonstrate proficiency in breaking down germination inhibitors,
173 facilitating the removal of barriers to weed growth [33]. Moreover, nano herbicides efficiently deplete
174 weed food reserves, depriving them of essential nutrients crucial for proliferation. Their unique formulation
175 enables the slow release of herbicides, ensuring prolonged efficacy against target weeds. Furthermore,
176 nanoherbicides accelerate the degradation of herbicide residues, minimising environmental impact while
177 maximising efficiency [33].

178

179 **3.4.1 Exhausting weed seedbank**

180 Reducing weed incidence can be achieved most effectively by depleting the weed seed
181 bank, the primary source of weeds across generations. However, the stale seedbed technique, a cultural
182 weed management method involving fallow periods often practised during summer to diminish the weed
183 seed bank, proves ineffective when considering costs [34]. This technique entails frequent tilling and
184 irrigation, thereby increasing weed management expenses. Weed seeds possess specialised
185 mechanisms to withstand both biotic and abiotic stresses and so priority should be given to minimising
186 the expansion of the weed seed bank and depleting it.

187 Damaging the pollen grains of weed flowers is one method while inducing sterility by
188 dehydrating pollen grains with a nanoparticle (Ag/Na) spray proves effective thereby preventing seed
189 production [35]. Carbon nanotubes (CNTs) can render seeds non-viable instead of effectively targeting

190 seedlings[36]. CNTs can penetrate cracks and openings in the seed coat, acting as conduits for water
191 and chemicals [37], ultimately leading to seed coat permeation, breaking dormancy, and accelerating
192 germination [38]. Nanoencapsulation of atrazine significantly increased mortality rates of *B.*
193 *pilos* seedlings, even at a tenfold dilution, with encapsulation reducing the long-term residual effect of the
194 herbicide, likely due to decreased atrazine mobility in soil, leading to higher herbicide availability for
195 seedlings [39]. The nanoformulation exhibited enhanced herbicidal effects against the target plant
196 *Brassica sp.*, causing 100% mortality and increased activity.

197

198 **3.4.2 Degrading germination inhibitor**

199 Germination inhibitors contribute to prolonged dormancy in weeds, extending their longevity
200 in soil. Breaking down these inhibitors promotes weed germination and enhances the efficacy of
201 herbicides. For example, the tubers of purple nutsedge (*Cyperus rotundus*) one of the world's most
202 problematic weeds contain numerous buds but only a few sprouts, while others remain dormant due to
203 phenolic compounds[40];[41]. Nanoparticles have been employed to disrupt dormancy and induce
204 germination in purple nutsedge tubers by disintegrating phenolic compounds [42]. In addition to promoting
205 tuber sprouting, treated tubers (with nanoparticles) exhibited increased sprouts per tuber, dry matter, root
206 and shoot length [43], rendering them susceptible to herbicide action. *Cyperus rotundus* contains more
207 than 23 phenolic compounds, including caffeic acid, ferulic acid, chlorogenic acid, vanillic acid, and
208 hydroxybenzoic acid [44]; [41];[45].

209 Abiotic stress elevates the quantity of germination inhibitors to inhibit germination
210 (dormancy), while their degradation promotes germination [42]. Iron oxide nanoparticles at a
211 concentration of 3.0 g kg per tubers significantly enhanced phenol degradation (89%), underscoring their
212 role in catalysing hydroxyl radical generation in advanced oxidation processes (AOPs), potentially aiding
213 in weed management by increasing germination percentage in treated *Cyperus rotundus* tubers [46]. ZnO
214 treatment at 1500 mg kg⁻¹ reduced starch and phenol content while significantly enhancing germination
215 (80%) compared to the control, indicating its efficacy in promoting tuber growth through electron donor
216 properties. However, further research is needed to understand its impact on tuber viability [42].

217

218 **3.4.3 Exhausting food reserve**

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

227 still outperformed all other treatments, underscoring the effectiveness of nanoherbicides [49].

228

229 **3.4.4 Slow release herbicide**

230 The primary limitation of conventional herbicides lies in their ineffectiveness, with
231 uncontrolled release and wastage of herbicides being the major contributing factor. Utilising carrier
232 substances and nanoformulations can circumvent this issue by forming zwitterions or charged clusters
233 during synthesis [50]. To mitigate environmental impacts associated with herbicide use, controlled release
234 formulations of pendimethalin copper-chitosan nanoparticles were developed, with pH 5.5 exhibiting the
235 highest release rate, indicating improved solubility and stability of the nano-formulation under acidic
236 conditions [23]. Encapsulation of paraquat within nanoparticle polymeric matrices results in delayed
237 release compared to its free form, with only 70% released under laboratory conditions versus 92% for the
238 free herbicide and further hindrance under field conditions due to factors such as low humidity and
239 interaction with soil organic matter [51].

240 Evaluation of 2,4-D leaching in soil columns demonstrated higher concentrations in top
241 segments due to rice husk carriers and colloids. This indicated increased herbicide persistence and
242 bioavailability to target plants, with the lowest residual concentration observed in the most profound
243 segment [52]. Nanoencapsulated alachlor with specific polymers reduces volatilisation, particularly when
244 incorporated into soil, as shown by studies utilising technical alachlor, Lasso 4EC, and polymeric
245 formulations (cellulose acetate butyrate ethyl cellulose) under controlled conditions for 32 to 39 days, with
246 evolved alachlor collected in ethylene glycol and analysed by reverse-phase high-performance thin-layer
247 chromatography with densitometry [53]. Metolachlor nanoparticles (MNPs) exhibited more significant
248 inhibition on rice and *Digitaria sanguinalis* seedlings compared to large MNPs (L-MNPs) and metolachlor
249 microparticles (MMPs) at low concentrations, with controlled release maintaining their persistence
250 effectiveness, attributed to high activity due to absorption into plants [54]. Controlled-release formulations
251 utilising mesoporous silica nanoparticles reduced the leaching of 2,4-D sodium salt by 48.4% compared to
252 the free system, confirmed by soil column leaching tests [55].

253

254 **3.4.5 Degradation of herbicide residues**

255 Excessive herbicide usage leads to soil residue accumulation and subsequent damage to
256 succeeding crops. Studies have demonstrated that when combined with nanoparticles and compatible
257 carriers, metallic ions aid in rapidly degrading herbicide residues like Ag with magnetite
258 nanoparticles stabilised with carboxymethyl cellulose [56]. Iron nanoparticles with positive charges
259 effectively interact with the lone pairs on nitrogen in atrazine herbicide, facilitating rapid removal with 90–
260 98% efficiency [57]. Atrazine levels in soil decreased irrespective of formulation, with higher levels in
261 NC+ATZ than ATZ but no difference between NC+ATZ 1/10 and ATZ 1/10, suggesting that
262 nanoencapsulation may reduce residual effects by lowering herbicide dosage [39].

263 Nanoparticles containing paraquat resulted in a slight reduction in cellular viability in Chinese

264 hamster ovary cells, though it remained close to 100%, indicating their potential to alleviate herbicide
265 toxicity [51]. The association of herbicide with nanoparticles reduced DNA damage in onions compared to
266 free paraquat, suggesting nanoparticle-provided protection against its toxic effects, with free paraquat
267 causing more significant damage [52]. Nanoencapsulation of pendimethalin using the solvent evaporation
268 technique resulted in prolonged herbicide release over 40 days, showing no significant impact on
269 earthworm survival, indicating its safety and effectiveness [58]. Studies conducted to remove atrazine
270 revealed that Ag modified Fe₃O₄-carboxymethyl cellulose nanoparticles demonstrated 82-88%
271 degradation of atrazine and proved effective for degrading atrazine in soil samples[59];[60].

272

273 **3.4.6 Enhanced Efficacy**

274 Nanoherbicides containing H₂O₂, pendimethalin, and ZnO NPs contributed to increased plant
275 height in black gram by establishing a weed-free environment, enhancing enzyme activity, optimising
276 auxin metabolism, and facilitating improved Zn absorption, thereby fostering crop growth [61]. The
277 nanoemulsion formulation of pretilachlor at 600 g/ha demonstrated superior weed control at 30 and 60
278 days after treatment compared to commercial formulations due to its smaller particle size, as evidenced
279 by [62]. Solid lipid nanoparticles (SLN) incorporating herbicides demonstrated heightened efficacy in
280 inhibiting plant growth compared to commercial formulations, suggesting their potential for agricultural
281 applications even at lower concentrations [63].

282

283 **3.5 Side effects of Nano herbicides**

284 Misuse of this technology carries significant risks to living organisms. This includes the potential
285 accumulation of nanomaterials in food products and their ability to penetrate healthy human skin.
286 Airborne nanoparticles represent a particularly severe threat to both human and animal health.
287 Additionally, there are concerns regarding unintended effects on non-target plants and organisms
288 associated with plants. Nano-herbicides, for instance, may obstruct plant vascular bundles and hinder
289 pollination. Issues such as phytotoxicity, cytotoxicity, and genotoxicity could also manifest, potentially
290 resulting in cell death or DNA mutations. Furthermore, nanomaterials may have adverse effects on
291 specific soil microbial communities and algae [64].

292

293 **4. CONCLUSION**

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

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299 **COMPETING INTERESTS**

300 Authors have declared that no competing interests exist

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