

Review Article

Novel Nanotechnological Tools for Weed Management – A Review

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Nanotechnology is emerging out as the greatest imperative tools in recent agriculture and predictable to become a driving economic force in the near future. It is science of manipulating materials at nano-scale. Among the latest technological advancements, nanotechnology occupies a central position. It has many applications in all stages of production, processing, storing, packaging and transport of agricultural products. At the same time Nanotechnology employs different chemical agents and novel delivery systems to implement crop productivity and potentials to decrease use of bulk agrochemicals, Nanotechnology may afford keener solutions for the current problems in the field of agriculture. The reduced use of herbicides and pesticides with increased efficiency, controlled release and targeted delivery will lead to precision farming. Improvement of crops in agriculture is a continuous process. Nano-herbicides are being developed to address the problems in perennial weed management and exhausting weed seed bank. Remediation of environmental contamination of the industrial waste and agricultural chemicals like pesticides and herbicide residues are possible through metal nanoparticles. Details of possibilities and concepts of application of nanotechnology in the weed management and results obtained already in these areas are reviewed in this paper.

Keywords: Nanotechnology, nano-herbicides, nano-polymer, Nano Application, Smart Packing

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Introduction

“Nanotechnology is the art and science of manipulating matter at the nanoscale” the design, characterization, production, and application of structure, device, and system by controlling shape and size at nanoscale [1]. Nanotechnology is developing as the sixth revolutionary technology in the current era. This technology is emerging out as the greatest imperative tools in recent agriculture and predictable to become a driving economic force in the near future. At the same time Nanotechnology employs different chemical agents and novel delivery systems to implement crop productivity and potentials to decrease use of bulk agrochemicals, Nanotechnology may afford keener solutions for the current problems in the field of agriculture. Agriculture is considered the backbone of most developing countries, with more than 60% of the population dependent on it for their livelihood. In the same times there are many challenges facing agriculture sector, especially in weed management. It is considered as an emerging field of science widely subjugated in many scientific fields and supposed playing the main role in the field of agriculture and food science in next era, but till now there is lack in scientific studies about its application in agriculture in the worldwide [2].

Direct applications of nanotechnology in agriculture include delivery of agrochemicals and pesticides, nano-scale carriers, smart packing, nanosensors, veterinary care, fisheries and aquaculture, Agriculture is always most potentiated and stable sector because it produces and provides raw materials for food and feed industries. Due to the increasing world population, increase the total food grain production, shrinking arable lands, restricted water availability, deteriorating soil organic matter, climate change and so many other reasons; it is necessary to use the advance technologies such as nanotechnology in agricultural sciences. Nanotechnology has many applications in all stages of production, processing, storing, packaging and transport of agricultural products and other marketing facilities. The purpose of nano materials in agriculture is to reduce the amount of spread chemicals, minimize herbicide and pesticide losses in agriculture and increased yield through weed management. The significant interests of using nanotechnology in agriculture includes specific applications like nanoherbicide and nanopesticides to trail products and herbicide levels to increase the productivity without decontamination of soil, water and protection against various biotic and abiotic stresses.

The agricultural practices associated with Green Revolution have greatly increased global food supply, but excessive and inappropriate use of farm-inputs (especially herbicides) increased toxins in soils, groundwater and surface waters threatening to life and life supporting systems [3-6]. Nano-herbicides are being developed to address the problems in perennial weed management and exhausting seed bank of weed. Levels of environment pollution can be evaluated quickly and effectively by gas sensors and nano smart dust [7]. The situation might be reversed by mimicking nature [8] for which nanotechnology could be a possible viable conduit [6, 9], especially if we are able to substantially reduce herbicide use by synergizing concepts of allelopathy with nanotechnology so as to clean up environment without loss of productivity. Present paper is an attempt towards it.

What is Nano-technology?

The term “Nano” is derived from the Greek word “nanos” meaning ‘DWARF’ (Small). “Nano-technology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom/one molecule or ions.”

Nanotechnology is defined by the US Environmental Protection Agency (2007) as a science of understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible. [10-11] to define nanoparticles from the view point of agriculture include “particulate between 10 and 1000 nm in size dimensions that are simultaneously colloidal particulate”. Nanotechnology is the science and technology of tiny things, the materials that are less than 100 nm in size. One nanometer is 10^{-9} meters; Nanotechnology combines solid state physics, chemistry, chemical engineering, biochemistry, biophysics, and materials science. Nanotechnology is a new scientific approach that includes the use of materials and equipment capable of using physical and chemical properties of a substance at molecular levels to explore the biological and material worlds in nanometer-scale and use it in various carriers from medicine to agriculture [12].

What are nanoparticles (NPs)?

Nanoparticle is defined as the natural or manufactured origin, possess in the range of 1–100 nm in at least one dimension (**Figure 1**). Generally, nanometer is one billionth of a meter e.g. Nano emulsion, carbon nanotubes, quantum dots, nanorods, micro and nano-encapsulation etc. [13] or ranges from 1 nm to 1 mm in diameter [14] also, the physical properties of nanoparticles are different from the properties of the bulk material [15]. Nanoparticles, whether of Morphology-aspect ratio or size, hydrophobicity, solubility-release of toxic species, surface area or roughness, surface species contaminations or adsorption, during synthesis or history, reactive oxygen species (ROS) O_2/H_2O , capacity to produce ROS, structure, composition, competitive binding sites with receptor and dispersion and aggregation are the important characteristics of nanoparticles

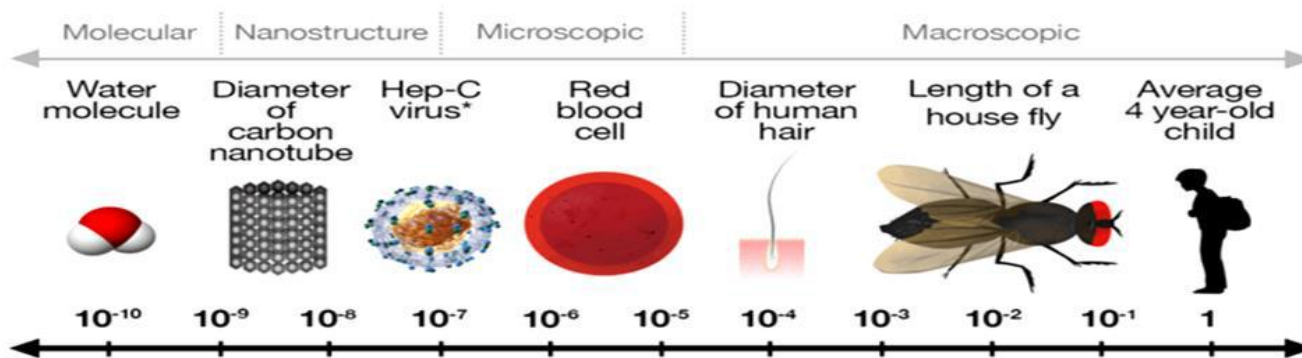


Figure 1 Scale of nanoparticles [16]

Methods of Nanoparticle Production

The Nano materials prepared through two basic methods (Top-down depending on size reduction from bulk materials) and Bottom-up system where materials are synthesis from atomic level (according to Royal Society and Royal Academy of Engineering).

“Top-down” systems: where tiny manipulations of little number of atoms or molecules fashion elegant patterns, through mechanical- physical methods like grinding, milling and crushing for producing nanoparticles, this method use for producing Nano composites and Nano-grained bulk materials like metallic and ceramic nano materials in extensive size distribution (10 - 1000 nm) as shown in **Figure 2**.

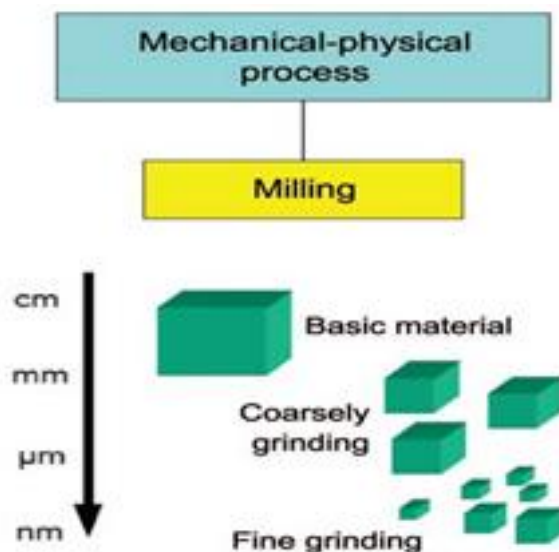


Figure 2 Schematic diagram for preparing nanoparticles by mechanical process (Laboratory for Micro and Nanotechnology).

Bottom-up system: in ‘Bottom-up’ building up, numerous molecules self-assemble in parallel steps, as a function of their molecular recognition characters, this processing produces more complex structures from atoms or molecules, also, this method produce a uniform controlling sizes, shapes and size ranges of nano materials (**Figure 3**).

Usually this method used for preparing most of the nano-scale materials (1 - 100 nm), it is plays an essential role in the production of nanostructures and nano materials. Also, there are some other methods for produce nano materials like attrition and pyrolysis, and biological synthesis of nanoparticles.

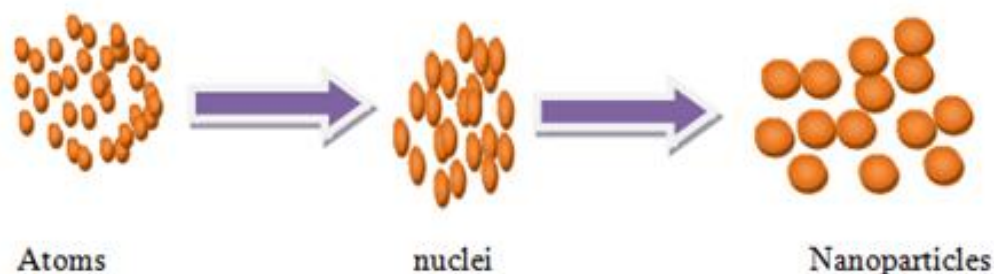


Figure 3 Structures of Nano particles are fabricated by chemical procedures [17]

Some unique features of nanoparticles

In nano-world, materials less than 100-nanometer size behave completely different, the rules that manage the behaviour of the elements of our known world start to give way to the rules of quantum mechanics, and everything changes. There are various advantages that nanotechnologies offer due to the unique functional properties of nanoparticles and materials like.

- Higher charge density and higher reactivity of nanoparticles due to small size [18].
- As the surface area increases in comparison to volume, the activity of the atoms on the surface of the particles becomes more than the inside the particles.
- As a result of large surface to volume ratio, the nanoparticles had more strength, increased heat resistance, decreased melting point and different magnetic properties of Nano-clusters
- Differences in the exposed surfaces of different nanoparticles lead to variances in atomic distribution across the nanoparticles, this, in turn, affect the electron transfer rate kinetics between metal nanoparticles and corresponding adsorbed species.
- Nanoparticles have higher catalytic activity when they are present in tetrahedral structure followed by cubic and spherical structure, recognized for the improvement of chemical reactivity at the sharp edges and corner of the former [19].

Nano materials use in agriculture

Nano materials often have chemical, physical, or biological properties that are different from those of their larger counterparts and due to their different properties, nanomaterial may pose different safety issues than their larger counterparts. There has been main attention in using nanotechnology in agriculture and the food system due to great potential as it can improve the quality of different products, also, with the rapid advancement of nanotechnology since the last decade of last century, controlled preparation of Nanomaterial's with desired morphology and size, and newly established concepts and methodology have underpinned the solid bases to solve the unsolved questions in nutrient uptake. Direct applications of nanotechnology in agricultural production and products generally embrace delivery of various agrochemicals, the study of plant disease mechanisms and genomes improvement [20].

There are various positive effects of nano materials in agriculture

In nano-world, materials less than 100-nanometer size behave completely different. There are various advantages that nanotechnologies offer due to the unique functional properties of nanoparticles and materials like:

1. The higher solubility of nanoparticles in suspension.
2. The higher surface area and particle size of the nanoparticles, which facilitates penetration of seed coats and subsequently emerging roots.
3. Better bioavailability of molecules to the seed radicals [21]
4. Providing actual concentration and controlled release of pesticides in response to certain conditions (TiO₂ Nano particles used as plant fertilizer for mung bean to enhance crop production) [22]
5. Improved targeted activity [23]
6. Lower Eco harmful with safe and relaxed transport.
7. Nano-fertilizer for balance crop nutrition [24]
8. Crop improvement (Zinc Nano fertilizer used to enhance crop production of *Pennisetum americanum*)
9. Plant protection ingredients (pesticides, fungicides, weedicides)
10. Weed management.
11. Nano pesticides
12. Nano sensors
13. Post-Harvest Technology [25]
14. Bioprocessing (bio synthesized) nanoparticles for agricultural use
15. Bio sensors for Aqua culture
16. Nano biotechnology (Analysis of gene expression and Regulation) [26]
17. Monitoring the identity and quality of agricultural produce
18. Precision agriculture: Precision agricultural techniques might be used to promote increase crop yields but not damage soil and water, decrease nutrients loss due to leaching and emissions, in addition to enhance nutrients long-term incorporation by soil microorganisms
19. Seed technology.
20. Water management
21. Plant growth regulators
22. Soil management [27]
23. Agricultural engineering aspects
24. Food technology

Disadvantages of Nanotechnology

The Catchy term 'Nanotechnology' also poses some risks and problem towards the health and also towards environment. When considering risk and safety in term of the same will be relevant to only certain area. The initial studies performed for nano materials have caused serious health hazards and also showed toxic effects, also when entered into human body caused tissue damage reaching all the vital organs. Another emerging technique is utilizing silver nano particles for the delivery of fertilizers to plants because of their antimicrobial properties, but studies have considered that it poses serious threat to ecosystem causing membrane damage, reducing the annual growth of grass, depletion photosynthesis in alga (*Chlamydomonas reinhardtii*). Silver nano particles are usually difficult to recover; some plant species tends to use this nano particle maximum and accumulates in its tissue exceeding the limit. Soybean is a cash crop in most of the country was produced using manufactured nano materials with fossil fuel

equipment that will allow NNM to locally deposit on the crop. With routine waste water treatment plants, Results were impacts on plant - microbe interaction affecting N₂ fixing symbiosis for which some metals are sensitive.

Weed management

In agriculture, weed management is a very big problem due to inefficacy of herbicides for multi weed species removal and emergence of herbicide resistance weeds due to continuous exposure of single herbicide. This enables the crop loss of more than 40 % as compared to other environmental factors such as pests, diseases, soil related factors and crop related conditions etc., Mostly, herbicides are applied through foliar spray, which does not kill them completely particularly perennial weeds such as *Cynodan dactylon*, *Cyperus sp.* and *Solanum elaeagnifolium*, but these herbicides destructs the structure and function of the plant-specific chloroplast, inhibits lipid biosynthesis, interference with cell-division by disrupting the mitotic sequence or inhibiting the plants [28]. Hence, application of encapsulated herbicide molecule via root absorption is a simple process as compared to foliar absorption because roots do not have cuticles like leaves. Even though there is some barriers for herbicide absorption through roots, but lipophilic based herbicide molecules can be easily absorbed since it's having lipophilic structure. [29] reported that target specific herbicide molecule encapsulated with nanoparticle aims for specific receptor in the roots of target weeds, which enter into system and translocated to parts that inhibit glycolysis of food reserve in the root system and it makes the specific weed plant to starve for food and gets killed. In rainfed farming, nano encapsulated herbicide will get the dispersment after it receives the sufficient moisture level. So that the weed seeds with the receipt of rain will get killed by the immediate release of new herbicides molecule.

Present scenario of herbicide use

Weeds accounts for several loss of total cost of production, which includes 10-15% loss of food production in the field. Use of herbicides is the only viable on-farm technology today to control weeds. Out of the total annual consumption of 2 million tons of pesticides, herbicides share 47.5 per cent. 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.

Detoxification of herbicide residues

Excessive use of herbicides leave residue in the soil and cause damage to the succeeding crops. Continuous use of single herbicide leads to evolution of herbicide resistant weed species and shift in weed flora. Atrazine, an s-triazine-ring herbicide, is used globally for the control of pre-and post-emergence broadleaf and grassy weeds, which has high persistence (half-life-125 days) and mobility in some types of soils. Residual problems due to the application of atrazine herbicide pose a threat towards widespread use of herbicide and limit the choice of crops in rotation. Recent finding from TNAU, India raises hope to remediate the atrazine residue from soil within a short span of time. Application of silver modified with nanoparticles of magnetite stabilized with Carboxy Methyl Cellulose (CMC) nanoparticles recorded 88% degradation of herbicide atrazine residue under controlled environment [30].

Combating herbicide induced ecosystem damage

Herbicides are known to damage entire ecosystem and food-web. Although, efforts were made to reduce herbicide use by developing controlled release and targeted delivery herbicides that are simultaneously safe to handlers and environment, these technologies are not being implemented to field. Herbicide resistance due to uninterrupted exposure of plant community having mild vulnerability to an herbicide in one season and different herbicide in another season has also become a serious issue [31-32]. Herbicides performance in tropical environments can sometimes be erratic and inefficient. This is especially true for soil-applied herbicides where high temperatures, intense rainfall, low soil organic matter and microbial activity results in rapid breakdown and loss through leaching, degradation by photolysis, hydrolysis and by microbial degradation. Another problem of weed control is that herbicides are premeditated to control or kill the germinating or growing above ground part of the weed plants, leaving viable underground propagating parts like rhizomes or tubers intact.

Amidst this situation, the new science, nanotechnology throws rays of hope for the development of nano-herbicides with highly specific, controlled release and increased efficiency to evade the weed competition under different ecosystem of crop production. The properties and effects of nano scale particles and materials differ significantly from larger particles of the identical chemical composition. By controlling structure precisely at nano scale dimensions, it is possible to control and tailor properties of nanostructures, such as nano capsules, in a very

precise manner for slow release herbicide to achieve season long weed control in an eco-friendly way, without leaving any toxic remains in soil and environment [33]. With “smart delivery system” in combination with active ingredients, lesser than conventional amounts of herbicide will be effective. It is discerned that having size in nano dimensions, nano-herbicides will blend with soil particles and prevent the growth of weed species that have become resistant to conventional herbicides.

Smart delivery mechanism

Developing a target specific herbicide molecule encapsulated with nanoparticle are aimed for specific receptor in the roots of target weeds, which enter into system and translocate to parts that inhibit glycolysis of food reserve in the root system (**Figure 4**). This will make the specific weed plant to starve for food and gets killed [29]. In rainfed areas, application of herbicides with insufficient soil moisture may lead to loss as vapour. Still we are unable to predict the rainfall very precisely; herbicides cannot be applied in advance anticipating rainfall. The controlled release of encapsulated herbicides is expected to take care of the competing weeds with crops.

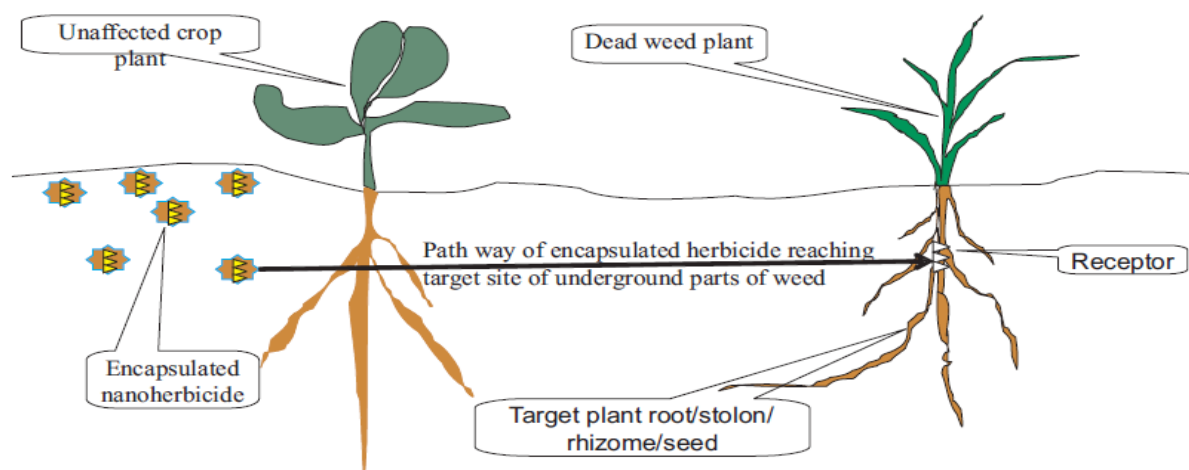


Figure 4 Smart delivery of nano encapsulated herbicide in the crop-weed environment [16]

Nano-herbicides for smart weed control

Nanotechnology applications have just begun for use in crop protection after being explored in medicine and pharmacology. Encapsulation and controlled release technologies have revolutionized the utilization of herbicides. The easiest way to eliminate weeds is to destroy their seed banks in the soil and prevent them from germinating when weather and soil conditions become favourable for their growth. Weeds cause significant economic losses in crop yields, posing a serious problem in agriculture. However, despite the benefits of the herbicide use, there are very harmful consequences for humans, animals and the environment. Herbicides are mixed with groundwater and atmosphere because of seepage and evaporation, and cause harm to the environment, outside the areas of application. It is possible to get rid of weeds by an environmentally friendly and low-cost approach thanks to the nano-herbicides, which is one of the products of the ground breaking nanotechnology revolution all over the world [33]. The amount of herbicides used will be lower when the active ingredient to be employed for controlling weeds is modified by a “smart” carrier system. Thanks to the high surface to volume ratio provided by the nano scale dimensions, they will have a higher interaction with soil particles in the applied area. Although the conventional herbicides are effective on the weeds’ parts above-ground, they are not effective on the parts below ground (tubers etc.). In this case, the remaining parts of the plant below-ground become a source for the weeds in the next season. The specific receptors of weeds under the ground are targeted by modifying a herbicide molecule with encapsulated nanoparticles. In this way, fewer weeds will require a control in the next season. [34] Obtained chitosan/tripolyphosphate nanoparticles as carrier systems to paraquat herbicides. The data obtained showed that the nanoparticles were able to decrease the herbicide toxicity [34-35].

The control of parasitic weeds with nano capsulated herbicides reducing the phytotoxicity of herbicides was reported by [36]. Various types of herbicide formulations, with emphasis on controlled release formulations, microencapsulation and systemic application are discerned to increase the possibilities of their various modes of action including in conjunction with nanoparticle carrier against parasitic weed. Properly well-designed nano capsules provide enhanced penetration through cuticle and allow slow and controlled release of active ingredients on reaching

the target weed. Lower doses of herbicides would be required for the reason that they will not be degraded by the crop, and they will accumulate preferentially in the parasitic weed due to the sink effect [33]. [37] reported development of organic–inorganic nano hybrid material for controlled release of 2,4-dichlorophenoxyacetate. He used zinc–aluminium layered double hydroxide to host the herbicide active ingredient by self-assembly technique.

Developing a target specific herbicide molecule encapsulated with nanoparticles is aimed at specific receptor in the roots of target weeds, which enter into roots system and translocate to parts that inhibit glycolysis or other pathways of food reserve in the root system. This will make the specific weed plant to starve for food and gets killed [29].

In rain fed areas, application of herbicides with insufficient soil moisture may lead to loss as photodecomposition. The controlled release action of encapsulated herbicides is expected to take care of the competing weeds with crops. Adjuvants for herbicide application are also available that including nano materials. One nano surfactant based on soybean micelles has been reported to create glyphosate-resistant crops susceptible to glyphosate when it is applied with the ‘nanotechnology-derived surfactant’.

[38] has introduced alginate nanoparticles for herbicide paraquat. The nanoparticles are used for evaluation of Ph. size, zeta potential and polydispersion.

[39] studied that those weeds which are not affected by herbicides can be controlled by nanoherbicides and diminish the usage of chemicals and other such kind of things. Nanoparticles which are used in agriculture are most important for the destruction of herbicides.

[40] found that the Nano-formulations (nano dispersions / nano emulsions) of herbicide are designed to attack the seed coating of weeds and prevent weed germination. Up to 88 per cent detoxification of atrazine by Carboxy Methyl Cellulose (CMC) by nano-particles was observed by

[41] studied that weed decreased the crop production so various methods are used to destroy them. For eradication of weeds, nano herbicides are used which destroy the weeds and do not pollute soil and environment. If we mix any other efficient material with herbicides, then herbicides will be less used.

[42] studied that the atrazine is the widely used herbicide in order to kill the weeds and unwanted grass growing near the crops, continuous use of herbicides makes soil lose all the nutrients and make them resistant to the plants, therefore application of modified silver with nano particles and carboxy methyl cellulose makes degradation of herbicide easier.

[40] studied that the continuous use of same herbicide for persistent period of time leads to evolution of weed resistance against that particular herbicide. Up to 88% detoxification of a herbicide ‘‘atrazine’’ by Carboxy Methyl Cellulose (CMC) nano particles has been reported.

[43] reported that the Foliar applied herbicide in perennial weeds such as *Cynodan dactylon*, *Cyperus spp.*, and *Solanum elaeagnifolium* fail to kill them completely due to Molecular characterization of underground plant parts for a new target domain and developing a receptor based herbicide molecule having specific binding property with nano-herbicide molecules like carbon nanotubes capable of killing the viable and dormant underground propagules of weed seeds

Conclusion

In the present agricultural scenario, there are extensive use of agrochemicals to boost agricultural production has polluted not only the top soil, groundwater and food. Increasing agricultural productivity is necessary, but keeping the in mind the damage to the ecosystem new approaches need to be considered. Nanotechnology is becoming increasingly important for the agricultural sector. The adoption of new technology in different fields of agriculture by the proper monitoring systems, smart systems of chemicals and gene delivery in the crops, nano-herbicides, encapsulation, nano-formulations and many other applications will revolutionize the agriculture. It will increase the productivity and reduction in agricultural wastes will occur that will indirectly reduce the pollution from the environment. It is the need of time to incorporate nano-technology in the agriculture system with further research studies and practical application in the fields.

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