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A Review on Nanotechnology in Weed Management

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Abstract

To meet the needs of ever growing population, there is a rising demand for food production. Weeds interact with crops and reduce productivity. Weeds are managed with the aid of herbicides. To control weeds, herbicides must be used repeatedly. This repeated application of herbicides leads to increase in environmental hazard and harms non-target organisms and neighboring crops due to chemical drift. Some herbicides have long and extended periods of residual effects which restrict the choice of the following crop in the rotation. In this case, nanotechnology has demonstrated the capacity to deliver chemical and biological pesticides using nanoparticulates based formulations with high efficacy. In order to improve bioavailability and weed eradication, herbicides are been coated on nanomaterials. Additionally, nanoherbicides can improve formulation's wettability and dispersion with less or no probability of the spread to adjacent locations. It is due to their increased specific surface area and chemical reactivity; nanoherbicides have a stronger affinity for their intended targets in plant system. When creating nanoherbicides, a variety of carrier systems, including chitosan, alginate and poly epsilon caprolactone are been used. The slow release-season-long weed control, food reserve exhaustion and rapid herbicide residue degradation are all significant functions of nano herbicides.

Keywords : Weed management, Weed seed bank, Nanotechnology, Nano herbicides

To feed the ever increasing population in India and the world, the food production needs to be increased. The main causes of decreased yields during the process of production is weed competition, an increase in insect and disease incidence and decline in soil fertility. Weeds have the most negative impact on agricultural output apart from the all abiotic and biotic factors. To eradicate weeds and increase crop yield, herbicides are used. Herbicide residue levels in natural water sources, land and food have increased due to the excessive usage of herbicides (Shezad *et al*., 2011). One of the most serious environmental pollutants in recent years is herbicide contamination. Herbicide dissipation from the applied soil surface to the water bodies, where it finally reaches non-target organisms and humans in particular, is primarily caused by conventional herbicide application methods. The biological activity of the active substances is increased when nanoparticles are used as carriers in agriculture, which also reduces the amount of herbicide needed and the risk of water contamination due to leaching (Cea *et al*., 2010). Nanotechnology, the term used to describe the processes of generation, manipulation and use of nanomaterials, has emerged as a promising field that could help in alleviating problems associated with agrochemicals. Nanoherbicides are being developed to address the problems in perennial weed management and exhausting seed bank of weed.

What is Nanotechnology ?

The term 'Nano' is derived from the Greek word 'nano' meaning 'DWARF' (Small). 'Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom / one molecule or ions'. According to the US

Environmental Protection Agency (2007) nanotechnology is a science of understanding and control of matter at dimensions of roughly 1-100 nm, where unique physical properties make novel applications possible (Nakache *et al.,* 1999 and USDA, 2002). 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 (Fakruddin, 2012).

What are Nanoparticles (NPs)?

Nanoparticles, whether of natural or manufactured origin, having size ranges from 1-100 nm in at least one dimension. Generally, nano meter is one billionth of a meter *e.g.,* Nano emulsion, carbon nanotubes, quantum dots, nanorods, micro and nanoencapsulation etc. (Somasundaran *et al.,* 2010.). Nanoparticles are not simple molecules but are composed of three layers namely, (a) The surface layer which may be functionsalised with a variety of small molecules, (b) The shell layer, which is chemically different from the core in all aspects and (c) The core which is the central portion of the nano particle and refers to the nanoparticle itself (Khan *et al.,* 2019). Based on their properties, shapes or sizes nanoparticles can be classified. They possess unique physical and chemical properties due to their small size, high surface area and ability to absorb and scatter light in the visible and near infra-red range Buffle (2006).

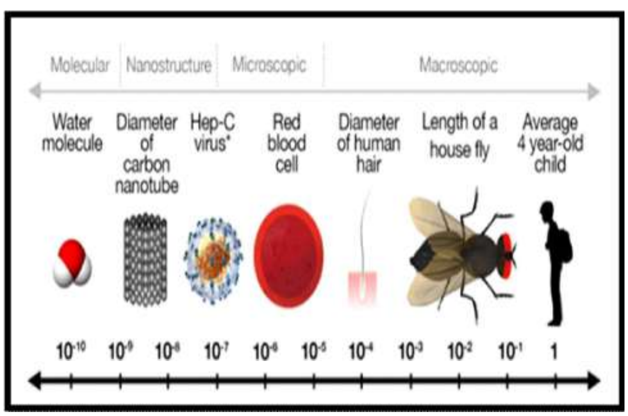

Fig. 1: Scale of nanoparticles (Joshi *et al*, 2019)

Methods of Nanoparticle Production

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

Top-down System

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 is used for producing Nano composites and Nano-grained bulk materials like metallic and ceramic nanomaterials in extensive size distribution (10 - 1000 nm) as shown in Fig. 2.

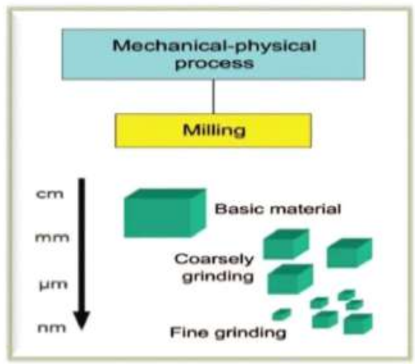

Fig. 2 : Schematic diagram for preparing nanoparticles by mechanical process

Bottom-up System

In 'Bottom-up' building up, numerous molecules self-assemble in parallel steps as a function of their molecular recognition characters, this process produces more complex structures from atoms or molecules and this method also produce an uniform controlling sizes, shapes and size ranges of nano materials (Fig. 3).

Existing Management Options of Weeds

Manual Method

Traditionally physical power of human being has been utilized to remove weeds. It has been estimated that on an average 320 man hours are required to remove weeds from one hectare of land. Further manual method of weed management is laborious, time consuming and inefficient due to adverse soil conditions.

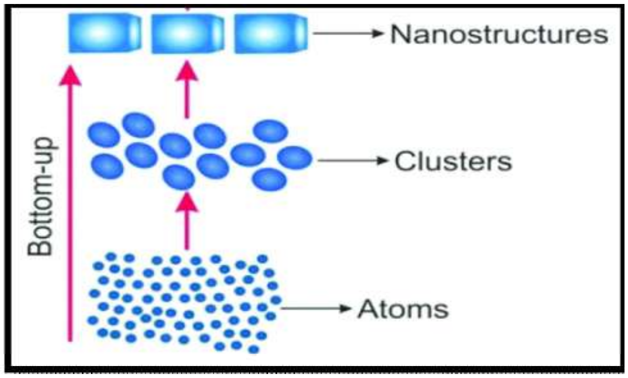

Fig. 3 : Structures of Nano particles fabricated by chemical procedures. Abobatta (2018)

Mechanical Method

Introduction of mechanical methods relieved from drudgery to some extent. Ploughing with help of animal power or mechanical implements has been one of the most widely used practices to prepare land for planting. Although effective for clearing fields of existing vegetation and preparing a seedbed, tillage also predisposes many weed species to germination. Tillage causes a breakup of *Cyperus rotundus* tubers bringing them close to the soil surface where they are subjected to carbohydrate starvation, desiccation and cold injury (Glaze, 1987). Inter cultivation in the wide row spaced crops is effective only between rows and the weeds untouched within rows. In some instances, tillage worsens the weed problem. Commonly known silver night shade *Solanum elaeagnifolium* spread by rhizomes or root fragments. Frequent tilling of soil leads to multiplication of this weed through root fragments.

Chemical Method

Present weed management technologies aim to control only the emerging weeds or emerged weeds. Mostly they target only the above ground growing part of the weeds. None of the available herbicides are inhibiting activity of viable underground plant parts like rhizome or tubers which act as a source for new plants in the current season. Due to the unavailability of such kind of molecules, one must wait either germination of weed seeds or appearance of weeds for foliar application of herbicides. Especially in *Cyperus* species, the foliar applied herbicides mainly destroy the plants above ground parts, but do not affects the root system and the tubers.

At present, thousands of herbicide formulations are available in the market to combat weed plants under diverse situations. Although, herbicides will continue to be the dominant technology in weed management programs, several problems have arisen including herbicide movement to non-target areas, environmental contamination and development of herbicide resistant weeds. Continuous use of same herbicides or herbicides belonging to a similar group is believed to be the chief reason for development of herbicide resistance in weeds and may cause weed shift problem.

Herbicide Resistance

- Herbicide resistance may be defined as the condition, whereby, a plant withstands the normal field dose of an herbicide, as a result of selection and genetic response to repeated exposure to herbicides with a similar mode of action
- 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
- In India, extensive use of Isoproturon for over 20 years in rice-wheat ecosystem led to evelopment of resistance in *Phalaris minor*, a grass weed resembles wheat crop

Nano Encapsulation of Herbicides

Nano encapsulation is a membrane controlled system in which herbicides are coated with any semi permeable membrane that may be organic, inorganic polymer so that they are dissolved in water.

The active ingredients are released as a result of,

- Diffusion
- Osmotic pressure
- Ion exchange
- Degradation of matrices

Encapsulating herbicides with nanoparticles boost the efficiency of herbicides by aiming at the specific receptor of the specific weed after entering into the root system and inhibiting glycolysis thus starving them to death.

Nanoencapsulation of herbicides is done with the purpose of its slow-release, so that the active ingredients are released and available in concentration and with a duration that is just right to get an intended response from the weeds without getting any negative response from the crop plants. The carrier systems employed in formulating nanoherbicides are presented in Table 1.

Present Scenario of Herbicide Use

Weeds are responsible for numerous reductions in production costs, including a reduction of 10-15 per cent in agricultural food production. The only effective weed control method now used on farms is the use of herbicides. Herbicides account for 47.5 per cent of the 2 million tonnes of pesticides used worldwide annually. It is widely acknowledged that an excessive reliance on herbicides has seriously harmed our ecology, as seen by the spread of these chemicals to regions that weren't intended for them, the contaminating of soil and water sources and the emergence of plants that are resistant to them.

Smart Delivery Mechanism

Developing a target specific herbicide molecule encapsulated with nanoparticles are aimed for specific receptor in the roots of target weeds, which enter into system and translocate to parts that inhibit glycosis of food reserve in the root system (Fig. 4). This will make the specific weed plant to starve for food and gets killed (Chinnamuthu *et al*., 2007). In rainfed areas, application of herbicides with insufficient soil moisture may lead to losses as through the process of vapourization. Still we are unable to predict the rainfall very preciously; 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.

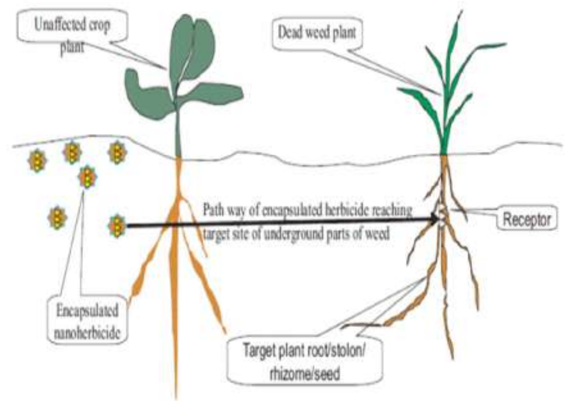

Fig. 4: Smart delivery of nano encapsulated herbicide in the crop-weed environment (Joshi *et al*, 2019)

Applications of Nanotechnology in Weed Management

- Exhausting weed seed bank
- Nano herbicides to control perennial weeds

TABLE 1

Carrier systems employed in formulating nanoherbicides

Carrier system	Title	Reference
Chitosan and tripolyphosphate	Chitosan/tripolyphosphate nanoparticles loaded with paraquat herbicide: An environmentally safer alternative for weed control	Grillo *et al*. (2014)
Chitosan	Chitosan nanoparticles loaded the herbicide paraquat: The influence of the aquatic humic substances on the colloidal stability and toxicity.	Grillo *et al*. (2015)
Chitosan and Starch	Alginate reinforced chitosan and starch beads in Slow Release Formulation of Imazaquin Herbicide- Preparation and charaterization	Nnamonu *et al*. (2012)
Alginate	Development and evaluation of a controlled release system of TBH herbicide using alginate microparticles	Faria *et al*. (2017)
Chitosan	Nanoparticles based on chitosan as carriers for the combined herbicides Imazapic and Imazapyr	Maruyama *et al*. (2016)

- Slow release season long weed control
- Detoxification of herbicide residues
- Nano herbicides for rainfed agriculture
- Decrease the dose of herbicide
- Reduce the leaching losses, volatilization etc.

Exhausting Weed Seed Bank

Chinnamuthu and Kokiladevi (2007) reported that smart delivery of herbicide will be highly useful to exhaust the weed seed bank and is a great accomplishment for the farming community.

An experiment was conducted by Brindha and Chinnamuthu (2012) and the results revealed that that the ZnO nanoparticles were effectively degraded the phenolic compounds. The tubers treated with ZnO nanoparticles at 1500 mg kg^{-1} under dry method (powder form) and 2250 mg/kg under wet method (liquid form), respectively, influenced the tuber germination by means of phenol degradation and biochemical components significantly. Degrading the phenols found in the tubers may stimulate the emergence of dormant buds. Reduced tuber multiplication may result from depleting the tubers' food reserves.

Degrading the phenol breaks the dormancy and induces the germination of all buds present in the tubers at once. As the tubers are germinate, they can be controlled by using herbicides or cultural methods which results in reduced weed seed bank size. Advanced oxidation processes (AOPs) have been realized as efficient technologies for phenol degradation (Bach *et al*., 2010).

Viji and Chinnamuthu (2015) reported that iron oxide nanoparticles at the concentration of 3.0 g kg $tubers^{-1}$ recorded higher percentage of phenol degradation (89 per cent) over control, which was on par with 2.5 g kg $tubers^{-1}$ (87.1 per cent) over control. Advanced oxidation processes (AOP) are widely used for the removal of recalcitrant organic constituents such as phenols. These procedures are based on generating highly oxidative HO radicals in the reaction medium. In the case of the AOPS, the generation of hydroxyl radicals takes place through a catalytic mechanism in which the iron oxide nanoparticles play a very important role in phenol degradation. As a result the dormancy of tubers is broken and all the buds germinate at once which provides an opportunity to eradicate all the germinated buds by using chemicals and reduce the weed seed bank.

An experiment was conducted to study the effect of herbicides in combination with nanoparticles and hydrogen peroxide on weed emergence and weed seed bank besides growth and nodulation of black gram variety. The results revealed that Application of H_2O_2 at 300 ml/m^2 *fb* pendimethalin at 0.75 kg/ha + ZnO nanoparticles at 500 ppm / m^2 registered significant reduction in the emergence pattern of weeds due death of weed seeds before emergence as well killing of emerged weeds and increased yield of crop (Vimalrajiv *et al*., 2018).

Nano-Herbicides to Control the Perennial Weeds

The use of nanoherbicide, which is in the 1-100 nm range, will try to blend with the soil particle and eliminate the entire weeds from their roots without damaging other food crops. Due to extremely small particle sizes of nano-scale herbicides, they can easily blend with soil and reach seeds that are buried below the reach of tillers. This method will eliminate weeds even if their seeds are hidden in the ground and prevent them from sprouting under most favorable conditions.

Viji and Chinnamuthu (2019) conducted an experiment on nanoparticle effect on degradation of vanillic acid, a germination inhibiting dormancy factor present in *Cyperus rotundus*. Due to its highest free radical scavenging potential, vanillic acid is expected to protect plant roots from the adverse effects produced by free radicals. Maximum degradation of vanillic acid was observed with iron oxide nanoparticles at 25 mg *i.e.,* 60.6 per cent degradation compared to control. By degrading the germination inhibitor, the buds present in each tuber burst open and thus the entire network of tuber germinate at a time. Once the weed appear above ground can be managed effectively with the different means of control measures.

Slow Release Season Long Weed Control

Maruyama *et al*. (2016) reported that the release percentages of 55 and 97 per cent were obtained for free Imazapic and Imazapyr, respectively, after 300 min, while in the presence of the nanoparticles, the values decreased to 30 per cent (Imazapic) and 20 per cent (Imazapyr) after 300 min. It showed that encapsulation of the combined herbicides resulted in slower release, compared to the free compounds.

An experiment was conducted to study the effect of entrapped slow release pre-emergence herbicide oxadiargyl on weed control duration and yield of transplanted rice. The herbicide molecule was entrapped with zeolite, biochar and starch and water soluble polymer. When oxadiargyl loaded with zeolite was applied on 3 DAT, total weed dry weight was dramatically reduced at all phases of crop growth in comparison to commercial formulations. (Bommayasamy *et al*., 2018).

For the slow release formulations of agrochemicals, it has been discovered that synthetic cationic surfactants, organic polymers and natural plant components like lignin and starch materials have the adsorbing property. This results in the efficient release to the crop-based cultivation system. Using ethylcellulose (EC), micro-encapsulated alachlor formulations were effective in decreasing herbicide losses from volatilization (Dailey, 2004).

Grillo *et al*. (2014) conducted an experiment on kinetics of soil sorption of paraquat, unloaded (PQ) or associated with the Chitosan/Tripolyphosphate nanoparticles (NP: PQ), at 25 °C. They observed that the sorption process was fast, with an equilibrium reached in ~30 min. It indicates that use of the nanoparticles could help to mitigate the problem of soil sorption of paraquat, leaving more of the herbicide available to target the plan.

Detoxification of Herbicide Residues

Susha and Chinnamuthu (2012) discovered based on the *in vitro* study that silver modified ferric oxide (Fe_3O_4) - CMC nanoparticles were superior in destroying atrazine. They discovered that within 24 hours of treatment, 82–88 per cent of the atrazine was degrading. In order to standardize the synthesis of iron-based metal nanoparticles and nanocomposite materials for greater surface reactivity, stabilizing with the right capping agent is necessary in order to sustain the reaction under various agro-ecosystems.

Research conducted on the photo-catalytic behaviour of nanoparticles to destroy 2,4-D residues. The sol-gel process was used to synthesize titanium dioxide (TiO_2) nanoparticles that were doped with platinum (Pt) particles. By effectively separating the photogenerated electrons and holes, the electrons produced on the TiO_2 surface by UV light illumination quickly move to the Pt particle, significantly increasing the photo catalytic activity. Pt plays a positive role as electron acceptor, which results in the provision of more acceptor centres with increasing Pt-doping, the rate of 2,4-D degradation rises as Pt concentration is increased. (Abdennouri *et al*., 2015).

Decrease the Dose of Herbicide

Jhones *et al*. (2014) demonstrated that when compared to the commercial formulation, solid lipid nanoparticles (SLN) containing herbicides had a greater impact on both the aerial parts and roots of plants. This demonstrated the efficiency and agricultural potential of SLN-containing herbicides because all formulations inhibited growth when applied at the recommended concentrations, but at 10 times lower concentrations, the impact of the commercial formulation was diminished, while SLN containing herbicides remained effective which results in the lower doses of herbicide application.

According to Vimalraj *et al*. (2018), the application of a nanoparticle herbicide combination had a substantial impact on the black gram plant's height. At all three stages, the weed-free plot generated taller plants. Application of H_2O_2 *fb* pendimethalin together with ZnO NPs generated plants with heights that were comparable to weed-free plots. The absence of weeds caused an increase in plant height because it sped up plant metabolism of auxin and enzyme activity, which in turn helped the crop growth. It can also be attributed due to improved absorption of ZnO nanoparticles influenced the plant growth.

Nano Herbicides Reduce the Leaching Losses, Volatilization Losses etc.

Oliver *et al*. (2004) conducted the experiment for 32 days in which all formulations were incorporated in the soil, evolved alachlor from the alachlor and Lasso 4EC formulations substantially exceeded that from the polymeric formulations only through the first 4 days could indicate increased degradation of the microcapsules with passage of time. This suggest that microencapsulation of alachlor with selected polymers can reduce volatilization, particularly when the formulation is incorporated in the soil.

For the DnRH formulation and the control, the leaching of 2,4-D was assessed at different depths of the soil column (0-4, 4-8, 8-12 and 12-16 cm) (2,4-D technical). The top segment had the highest concentration of 2,4-D, which was observed to be lowered in the succeeding bottom parts. The presence of colloids in the soil may be the cause of the higher retention of 2,4-D on the topmost segment. The results indicate the bioavailability of the DnRH formulation in field situations where higher herbicide persistence may have improved the active herbicide's bioavailability to the target plants for an extended period of time. However, the residual herbicide concentration was found in practically all four segments of the control column that contained technical grade 2,4-D, which illustrates the possibility for ground water contamination. The lowest 12–16 cm column segment had the lowest residual 2,4-D levels (Abigail *et al*., 2016).

According to Cao *et al*. (2018), the total amount of 2,4-D sodium salt that leached was much less in the CRFS (48.4 %) than in the free system (97.3 per cent). The controlled release of 2,4-D sodium salt from formulations based on MSN-TA nanoparticles was confirmed by the soil column leaching test. As a result, the herbicide's vertical movement through the soil was retarded and its potential for leaching was reduced.

Bommayasamy and Chinnamuthu (2020) conducted an experiment on effect of encapsulated/loaded herbicide oxadiargyl on total weed density, weed dry weight in rice. Among the weed control treatments, application of oxadiargyl loaded with zeolite recorded mean lower weed density, which was at par with 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 entire season which destroy food reserve of weed seeds and caused lesser regeneration of weeds.

Nano Biosensors for Herbicide Residue Detection

To prevent any hazardous effects on humans and animals upon ingestion, inhalation or contact, herbicide residues and its metabolites left in the field as well as in the produce must be detected. Analytical procedures have limitations in terms of precision levels and need a lot of time to detect and quantify residues. Hence alternate methods being evaluated using sensors for the quick detection and quantification residues to parts per billion levels. Compared to a standard sensors biosensor are further highly precised in detection and quantification. A biosensor is composed of a biological component, such as a cell, enzyme or antibody, linked to a tiny transducer, a device powered by one system which supplies power to a second system. The biosensors detect changes in cells and molecules that are then used to measure and identify the test substance, even if there is a very low concentration of the tested material. When the substance binds with the biological component, the transducer produces a signal proportional to the quantity of the substance.

Trifluralin herbicide residue was detected using an electrochemical sensor consisting of a carbon electrode modified with copper nanowires (Mirab-Semnakolaii *et al*., 2011). The presence of copper nanowires improved the conductivity, resulting in increased of rate of electron transfer. This sensor showed a linear response in concentration range from 100 to 0.2 nmol./L with 0.008 nmol./L of detection limit and quantitation limit of 0.15 nmol./L for trifluralin and the supporting electrolyte phosphate buffer solution of 0.05 mol./L and pH 4.0.

The advantages of using nano herbicides over conventional herbicides are explained in Table 2.

Negative Effects of Nano Materials in Plants

- Nano particles on biological systems and the environment such as toxicity generated by free radicles leading to lipid peroxidation and DNA damage.

TABLE 2

Advantages of using nano-herbicides over conventional herbicides

Carrier system	Advantages	Reference
Controlled release formulations	Nano-based formulation may allow herbicides to intelligently control the release speed of its active ingredient	Itodo *et al.* (2017)
Herbicide uptake efficiency	Nano-based formulation may increase herbicide efficiency and also save herbicide resource.	Kah *et al.* (2013)
Mode of controlled release	Both the release rate and release pattern of herbicides can be controlled through its encapsulation using a semi-permeable membrane coating	Prasad *et al.* (2014)
Duration of *a.i.* release	Nano-based formulation of herbicides can extend effective duration of the herbicide active ingredient in soil	Rana *et al.* (2015)
Rate of herbicide loss to the environment	Nano-based formulation of herbicides can reduce its rate of loss into soil by runoff or leaching.	Jampílek *et al.* (2015)

- High concentration of nano silica silver produced some chemical injuries on the tested plants (cucumber leaves and pansy flowers)
- Large surface can make them too reactive and explosive in some situations
- Health issues-Nanoparticles easily enter into body through skin
- Environmental issues-Nanoparticles could accumulate in soil, water and plants
- On plant growth - Use of some nano particles like Ag, TiO_2 will reduce germination of seed, shoot and root growth of wheat, barley, onion etc.

Weeds are the pioneer plants which compete with crops for nutrients, light and water. Herbicides are used intensively to control the weeds. The half life of herbicides is very short ranging from few hours to couple of weeks. The intensive use of herbicides cause several problems like soil, ground water and food contamination. Nano-herbicides helps to reduce this problems. They are required in low amount with high bioavailability to the problematic weeds and also reduce the phytotoxcitiy to the non target organisms. Nano herbicides persist in soil where they are applied through out the entire growing season and take of the germinating weeds and leaves no residue at the end of the growing season allowing for taking up the next crop. Even the one tenth of the recommended dose of nanoherbicide can control the weeds effectively than the complete recommended dose of commercial formulation.

Future Line of Work

Nanotechnology is thus a boon that can further be developed with regard to the target site inhibition of the bio-chemical reactions of weed. The science of nanotechnology is still in its nascent phase. Therefore, development of systems that would improve the release profile of herbicides without altering their characteristics and novel carriers with enriched activity without significant environmental damage is the focus areas that require further investigations. The potential hazards associated with the continuous use of these tiny particles are still unknown completely. Hence, sound research and development is still required to sharp out this technology and make the best use of it.

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