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Nanotechnology in Weed Management - A Review

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ABSTRACT

Modern agriculture is the need of the hour, because conventional agriculture will not be able to feed an ever increasing population with changing climate, depleting resources and shrinking landscape. But at the same time application of nano-materials in agri-food sector has to be evaluated for public acceptance. The field of nanotechnology opens up prospective potential applications for agriculture. Among the latest technological advancements, nanotechnology occupies a prime position. Nanotechnology applications are already being explored and used in medicine and pharmacology, but interest for use in agriculture is just starting. The development of nano devices as smart delivery systems to target specific sites and nanocarriers for controlled chemical release is vital. The reduced use of herbicides, pesticides and fertilizers with increased efficiency, controlled release and targeted delivery will lead to precision farming. Nanotechnology has been in use in improved pest management and crop protection and through it has improved existing crop management techniques in the short to medium term but its usage in weed control is at nascent stage. One such technology is Nanoencapsulation, which can also improve herbicide application, providing better penetration through cuticles and tissues, and allowing slow and constant release of the active substances.

Keywords: Nanodevices, Nanocarriers, Nanocapsules, Nanoparticles, Weed Management

AGRICULTURE today, is facing numerous challenges such as climate change, reduction in cultivable land and low productivity of agricultural crops that leads to poverty and malnutrition. Among these challenges, lower crop productivity is one of the major setback. Many factors are involved in lower productivity of agricultural crops of which declining soil fertility and mismanagement of applications of inputs particularly, plant protection measures (herbicides and pesticides) are considered as an important yield limiting factors. These inputs could not reach the plant timely, which causes not only large economic and resource losses but also very serious environmental pollution. Therefore, to increase the input use efficiency of applied inputs and to enhance crop productivity from stagnant level, alternate advanced technology is the need of the hour. One such avenue is Nanotechnology.

Definition of Nanotechnology

Royal Society and Royal Academy of Engineering (2004) defined that 'Nanotechnology is the Design, Fabrication and Utilization of materials, structures, devices and systems through control of matter on the nanometre length scale and exploitation of novel phenomena and properties (physical, chemical, and biological) at that length scale in at least one Dimension'. National Nanotechnology Initiative, 2007, emphasised that 'Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometres, where unique phenomena enable novel applications'. Nanotechnology employs nanoparticles (NPs) having one or more dimensions in the order of 100 nm or less.

Applications of nanotechnology in agriculture is in the nascent stage and theoretical, but it has the power to change the whole agriculture and food systems in the coming years. This novel scientific approach has the potential to advance agricultural productivity through crop improvement, crop management and crop protection. In this background, the review has been prepared to focus on potential applications of nanotechnology in major agricultural divisions like crop improvement, crop management, crop protection and food science (Fig. 1).

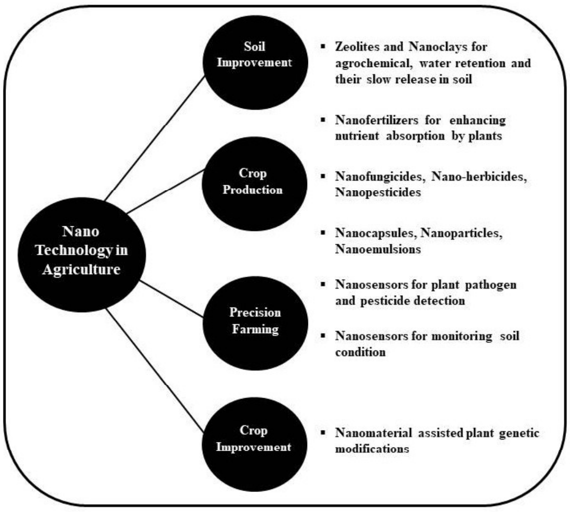

Fig. 1: Applications of Nanotechnology in Agriculture

Current Status of Weed Management

Manual and mechanical removals were the most prominent methods of weed management in India. However, these were not very effective, particularly under adverse soil and weather conditions. Manual weeding is highly labour-intensive, involves a lot of drudgery. Modernization of agriculture involving the use of chemicals, machinery and other modern technologies is the trend when it comes to weed management. More and more farmers are opting for herbicides mainly due to increased labour cost and their unavailability. Farmers in India are now demanding and using herbicides for weed control than ever before. However, the non- availability of right herbicides and adoption of faulty application techniques due to lack of awareness are often noticed, leading to poor efficacy of the product.

Globally, herbicides are the leading group of pesticides with 45 per cent of the total consumption compared to a mere 18 per cent in India. The herbicide share in India is expected to rise faster in the years to come. In fact, non-selective herbicides are now being used on the highway, railways, public amenity areas and in irrigation canals and drainage ditches for clearance of unwanted vegetation. Herbicide application is more common in crops like wheat, rice, soybean, maize and plantation crops like tea. Their use in other crops including pulses, oil seeds, vegetables and spices is on the rise. Growing weed infestation is becoming a major concern of various stakeholders including the farmers. In fact, some cropped situations managing weed menace is more difficult than nutrient or water management. Farmers are in dire need of suitable cost-effective weed management technologies, driving them towards farm mechanization and chemical weed control.

Unlike other pesticides, herbicides by and have lower toxicity (higher LD_{50} value) and reported to leave no or very low levels of residues in the soil, crop produce and ground water. There are however, concerns of residual effect of herbicides on susceptible intercrops or succeeding crops and development of herbicides resistance in weeds. It is well documented that integrated weed management approach involving different methods specifically the cultural methods is more sustainable. However, it is not being adopted by majority of the farmers for a variety of reasons. Weed management has traditionally been a part of agronomy. Weed problems are dynamics in nature and likely to be more serious in the coming decades due to the,

1. Adoption of high-yielding varieties and hybrids
2. High- input agriculture
3. Altered agronomy- discontinuation of intercropping, mulching and adoption of zero tillage, organic farming systems
4. Monocropping and mixed cropping systems, causing shift in weed flora; development of herbicide resistance in weeds
5. Growing infestation of weedy rice, parasitic and other obnoxious weeds.
6. Globalization and invasion of alien weeds
7. Implication of climate change; and lack of quality human resource in weed science, Sharma, *et al.* (2018)

Hence for better management of weeds, need of new technology is vital, like application of Nanotechnology to control weeds.

Nano-Herbicides for Effective Weed Control

Weeds are the biggest threat in agriculture and decline the yield of crop to a greater quantity by using the nutrients which otherwise were available to the crop plants. Eradicating weeds by conventional means are time consuming. There are a number of herbicides available commercially. They kill the weeds in the field, but also damages crop plants if applied in unscientific method.

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 per cent 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 (Wakabayashi and Boger, 2004). 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 are some barriers for herbicide absorption through roots, but liphophilic based herbicide molecules can be easily absorbed since it's having liphophilic structure. Chinnamuthu and Kokiladevi (2007) 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 glycosis 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 dispersement on receiving sufficient moisture level. So that the weed seeds with the receipt of rain will get killed by the immediate release of new herbicides molecule. Gruere *et al.,* 2011 claimed that nano surfactant based on soybean micelles make glyphosate resistant crops into susceptible.

Nanoherbicides can play a very important role in removing weeds from crops in an eco-friendly way, without leaving any harmful residues in soil and environment Pérez de luque and Rubiales (2009). Encapsulation of herbicide in polymeric nanoparticles also results in environmental safety, (Kumar *et al.*, 2015). Disproportionate use of herbicides for longer period of times leaves residues in soil, which cause damage to succeeding crops (Chinnamuthu and Boopathi, 2009). Target speciûc nanoparticles loaded with herbicide has been developed for delivery in roots of weeds. These molecules enter into the roots system of the weeds, translocate to cells and inhibit metabolic pathways such as glycolysis. This ultimately leads to death of plants (Nair *et al.,*2010 and Ali *et al.*, 2014). Toxicity of poly (ε-caprolactone) nanocapsules containing ametryn and atrazine against alga *Pseudokirchneriella subcapitata* and the micro-crustacean *Daphnia similis* has been tested. Herbicides encapsulated in the poly (ε-caprolactone) nanocapsules resulted in lower toxicity to the alga (*Pseudokirchneriella subcapitata*) and higher toxicity to the microcrustacean (*Daphnia similis*) as compared to the herbicides alone, Clemente *et al.* (2014).

Polymeric Nanoparticles

Among the various types of nanoparticles used for formulating nanoherbicides, polymeric nanoparticle prepared either in the form of nanospheres or nanocapsules, is the most attractive form. Poly (epsilon caprolactone) is one polymer repeatedly used for the encapsulation of atrazine herbicide. Poly (epsilon caprolactone) possesses good physico chemical properties along with enhanced bioavailability and biocompatibility. The polymeric nanoparticles containing atrazine herbicide was prepared and were characterized for size, polydispersity index, pH and encapsulation efficiency. The stability of the nanoparticles was found to be for a period of three months. The nanoparticle formulations reduced the mobility of the herbicide in soil but enhanced its herbicidal activity in comparison with free atrazine (Pereira *et al.,* 2014). When tested against target plant, *Brassica* sp., the polymeric nanoparticles encapsulated with atrazine were proven effective. In another study, Grillo *et al.* (2012) used the polymer for encapsulated three triazine herbicides such as atrazine, ametryn and simazine to reduce the environmental impact caused by them. The encapsulated polymeric nanoparticles of triazines possessed better association efficiency over 84 per cent. The nanoparticles were found to have stability of size, zeta potential, pH and polydispersity for nearly 270 days. In vitro release experiments by using the triazine herbicide formulations revealed that the nanocapsules release the triazine *via* controlled release by relaxing the polymeric chains. The polymeric herbicide nanoparticles showed relatively less genotoxicity in *Allium cepa* chromosome aberration assay.

Alginate/Chitosan (Ag/Cs) nanoparticles were chosen for the encapsulation of paraquat herbicide. This polymeric complex has simple preparation methods adding further to their alternative use in agricultural applications. The Ag/Cs nanoparticle carrier system showed significant difference in the release profiles of free paraquat and the herbicide nano particles. The herbicide nanocarrier has altered the interaction of the herbicide in soil and indicated the effective means of averting the negative impacts of the herbicide induced by paraquat herbicide. The enhanced interaction of paraquat released from Ag/Cs system in comparison with free paraquat revealed the effective polymeric nanoparticles as an excellent choice for eliminating the herbicide usage–associated ill effects. In a different study, the paraquat herbicide was encapsulated into chitosan/tripolyphosphate nanoparticle and was proved efficient with this polymeric nanoparticle system as well. The herbicidal efficiency of paraquat was not found reduced even after encapsulated with very less toxicity. Cell culture viability tests and *Allium cepa* chromosomal aberration tests testified to the increased safety of the polymeric herbicide systems against nontarget organisms (Grillo *et al.,* 2014). Few works reported till date on polymeric nanoparticles encapsulated with herbicide provides a safe basis for using herbicides by reducing the adverse environmental impacts caused by them on human health as well as on the environment.

Inorganic nanoparticles

Silica dioxide nanoparticles (SiNP) were explored as inorganic herbicide carriers in the recent past for active substances which are pH sensitive. These SiNPs maintain optimal herbicide concentrations with accompanied reduction in frequency of herbicide consumption rate. These systems protect and stabilize the herbicide and reduce their wastage with easy deposit on the plant leaves. Rani *et al*. (2014) stated the possible use of silica nanoparticles as herbicide carriers via a dynamic adsorption mechanism and sustained release.

Potential uses in controlling parasitic weeds

The first steps for applying nanoencapsulation in agriculture have been taken. Many avenues are now open, and many possibilities remain still unexplored. In the case of controlling parasitic plants, nanoencapsulation could be used to solve problems regarding phytotoxicity on the crop of the herbicides used against the parasite (Goldwasser *et al.,* 2003). For example, it is known that broomrape (*Orobanche* spp.) tubercles act as strong sinks for nutrients and water, and also for systemic herbicides (Joel 2000). If nanoencapsulated herbicides are applied, they will extend systemically in the crop, avoiding phytotoxicity problems and / or detoxification. As soon as the nanocapsules reach the parasitic weed, the herbicide will be released. This means that lower doses of herbicides such as glyphosate or imidazolinones would be needed, because (i) they will not be degraded by the crop and (ii) they will accumulate in the parasitic weed owing to the sink effect. The release of the herbicide could be activated under certain conditions within the parasitic weed or just some time after application.

Encapsulation of other herbicides could also provide improvements in their application. Sulfonylurea herbicides are applied through the soil to control *Orobanche* spp., but several applications are needed to achieve effective control. If the herbicide were encapsulated and slowly released into the soil during the crop season, a better control could be achieved with just one application and with lower herbicide rates.

It might also be possible, applying encapsulated herbicides as seed coatings, to obviate the multiple treatments needed with non-encapsulated herbicides (Jurado exposito *et al.*, 2007).

In addition, nanocapsules could be designed for improving penetration through leaves and cuticles. Liposomes and lipid vesicles can cross through the plant cuticle easily owing to their amphiphilic composition (Wiesman *et al.,* 2007). Polymeric nanocapsules can be functionalised with different substances and this can be used to modify the surface characteristics as required. For example, adjuvants such a soil concentrates or surfactants could be directly bonded to the nanocapsule shell, allowing better penetration through the cuticle. It is also possible to link different molecules, some of them useful for movement through non-polar substances (cuticle waxes, cell membranes) and others for movement through polar substances (water).

It might also be possible to develop an agrochemical containing different substances for different functions (plant protection, fertilisation, hormones, etc.) and encapsulated separately to avoid interactions between them and degradation. In this way, several substances could be applied with the same treatment to the crop, and the nanocapsules could be regulated to release their load according to the characteristic of every loaded substance. Different active substances (for example, different herbicides) with a synergistic effect could be applied separately with the same treatment and released inside the parasite tubercles, so acting more effectively without harming the crop. For example, glyphosate, imidazolinones and sulfonylureas might be encapsulated separately within a polymeric shell. The shell would be functionalised with surfactants to improve the penetration through the cuticle, and applied systemically through the leaves. Thus, three herbicides with two different modes of action might be used with the same treatment. In addition, a residual effect in the soil would be avoided. Nanoencapsulation might also make it possible to combat parasitic weeds with herbicides that usually cannot be applied systemically (for example, contact herbicides), improving the efficacy of every single treatment and reducing the lethal amount to be delivered, (Alejandrop and Diego, 2009).

The Bad News

One of the most important issues to be addressed before the extensive utilisation of nanoparticles and nanocapsules is their possible toxicity. Several cytotoxicity studies are being developed, mainly focused on animal and human cell damage (Lewinski, *et al*., 2008). Some results have been published concerning plant cells and magnetic nanoparticles, suggesting possible development of chromosomal aberrations and interactions with photosynthetic system II. Ultra high concentrations (2000 mg L^{-1}) of different nanoparticles can affect root growth of some plants. Many questions are still unresolved, because the putative toxicity of nanoparticles depends on many factors such as the materials used, the size and the enhancements added (drugs, ligands, coatings, etc.) and also on the cell type. Cytotoxicity does not imply phytotoxicity: it is possible that low concentrations of certain nanoparticles could affect plant cells locally, but this does not mean that the plant as a whole organism would be damaged. Additional studies should be conducted to determine what happens with nanodevices inside the plants, where they accumulate (fruits, leaves, etc.) and / or if they are destroyed / excreted after some time. If they are incorporated into the food chain, what happens to animals / humans consuming such plants? Are plant viruses or viral capsids a risk to animals but acceptable for plants, and vice versa? It is also important to note that not all nanostructures pose the same toxicity risks. For example, liposomes and nanocapsules based on natural organic compounds such as lipids and chitin are potentially less hazardous than those based on heavy metals such as nanoparticles.

What may be the Future of Nanoagrochemicals?

Two potential scenarios that the development of nanoagrochemicals in the first, developments continues along the current path and nanoagrochemicals are likely to become or at least be perceived as, the next emerging category of contaminants associated with agricultural practices. Alternatively, nanotechnology could become a potential source of emerging solutions to mitigate contamination by herbicides, pesticides and fertilizers. This second scenario can only be achieved by rapid changes by industry, researchers and regulatory agencies, following for instance, some of the directions suggested below.

a) Available analyses of nanoagrochemicals typically consider all products discussed in literature, many of which represent an unacceptable risk, without being relevant for agricultural applications (*e.g.,* ingredients that are extremely persistent or whose efficacy is marginal). Increasing collaborations between disciplines that are involved at all stages of the development and evaluation of agro-chemicals (*e.g.,* formulation, plant, material, and environmental scientists) will support the develop-ment of products fitting within the multiple constraints of the agro chemical sector and that are likely to bring an added value relative to existing products.

b) The requirements of the latest EU directive regarding a better evaluation of formulations are typically viewed as additional constraints. Current approaches to chemical regulatory assessment often consist of applying incremental safety factors to account for the increasing level of uncertainty. Alternatively, new science-based tools should be developed to assess and fully exploit what the science of formulation has to offer, based on the risks and benefits over the entire life cycle of the products.

c) With increasing regulatory pressure and risk of stigmatization, incentives are needed to promote innovation that may lead to the development of more intelligent solutions for plant protection and nutrition. Promotion of more collaboration across sectors (*e.g.,* research, industry, and regulators) and integration of social science and law will ensure consumer acceptance and the development of suitable legal frameworks.

Nano encapsulation appears to be the most promising technique for short-term applications in the field. The development of nanocapsules for controlled release and systemic application of herbicides will greatly increase the possibilities of their utilisation against parasitic plants, for example by allowing the use of herbicides with different modes of action such as contact herbicides. It is likely that the cost of the ûrst generations of such nanoencapsulated herbicides will not allow their use in low-input crops (sorghum or legumes), but with time the prices should lower and the cost should become affordable. Nanocapsules and viral capsids have emerged as powerful tools in the biotechnological field. Their potential use in the laboratory for genetic and molecular work, including transformation is huge. They can be used for delivering nucleic acids in a controlled way, and for activating or silencing specific genes, opening new avenues for the development of resistant plants (against parasitic weeds or herbicides).

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