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Nanotechnology and allelopathy: synergism in action

N. K. DHILLON AND [1]S. S. MUKHOPADHYAY

Director (Seeds), [1]Department of Soil Science
Punjab Agricultural University, Ludhiana – 141004, Punjab

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ABSTRACT

From seed drilling-to-dinner table, weeds account for S! loss of total cost of production. Efforts to control them resulted limited success, and often accompanied with degrading environmental quality and threat to life support system. Nanotechnology is less than a decade old initiative in agriculture, but success stories have started emerging. For example, the application of Carboxy Methyl Cellulose (CMC) nanoparticle successfully detoxificated up to 88 per cent of atrazine, and encapsulation of nano-herbicide to reduce phytotoxicity appears to be promising. Other areas, where it may be explored are: (i) controlled release of herbicide, which may respond to environmental triggers like temperature, humidity, light and so on, (ii) design of advance nano-adjuvant, which may eventually replace active ingredients, (iii) regimenting nano-adjuvant and nano-active- ingredients with smart delivery system, (iv) designing nanoparticles that would be translocated to weed roots, and kill them by inhibiting glycolysis of their food reserves (marketed herbicides kill only above ground part of weeds), and (v) designing nano-formulations (nano-dispersants / nano-emulsions) of herbicides that sterile weed seeds by damaging seed coating. The advantages of nanotechnology applications in weed control would be improved efficiency and reduced amount of herbicides, avoidance of phytotoxity of crops, and rejuvenation of ecosystem damaged by herbicides. Nanotechnology interface in agriculture has to imitate nature and thereby would be benefitted by the advances made in the allelopathy.

Keywords : Mimicking nature; nano-adjuvant; nano-herbicide, weed control

Nanotechnology is likely to take all forms of agriculture by storm – from seed to seeds; tillage to silage, food to feed, and packaging to parceling. 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 (Bhalla and Mukhopadhyay, 2010; Mukhopadhyay, 2011; Sharma and Mukhopadhyay, 2013; Mukhopadhyay, 2014). The situation might be reversed by mimicking nature (Mukhopadhyay and Brar, 2006; Naik and Stone, 2005) for which nanotechnology could be a possible viable conduit (Khot *et al.,* 2012, Kuzma and VerHage, 2006; Mukhopadhyay, 2014), 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.

Defining nanotechnology

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. This definition is slightly rigid on the size dimensions, while greater stress could have been placed on inherent problem-solving capability of the materials. Other attempts (Nakache *et al.,* 1999 and USDA, 2002) to define nanoparticles from the view point of agriculture include "particulate between 10 and 1000 nm in size dimensions that are simultaneously colloidal particulate". More appropriately, nanotechnology could be described as the science of designing and building machines in which every atom and chemical bond is specified precisely. It is not a set of particular techniques, devices, or products, but the set of capabilities that we will have when our technology gets near the limits set by atomic physics. Nanotechnology aims at achieving for control of matter what computers did for our control of information (Hall, 2006).

Limitations of modern farming

Agricultural practices associated with Green Revolution might have increased global food supply, but placed the Earth under crisis. Degradation of soil and environmental quality, damaged C, N, and P cycles, alarming diminished energy balance between input and output, loss of biodiversity, retreating groundwater levels, accelerated rate of weathering of soil minerals, soil acidification and salt build-ups are some such examples. On the other hand, alternate farming proposals like "Conservation Agriculture", "organic farming", "rainfed/ dryland farming" and similar technologies have fallen short of our

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Email: dhillon.navjot@gmail.com

productivity expectations (Mukhopadhyay 2014). The situation becomes worrisome with rising population and accelerated pace of climate change, depleting resources, and shrinking landscape.

Present scenario of herbicide use

Weeds accounts for S! 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.

Allelopathy and its synergism with nanotechnology

Allelopathy is a biological phenomenon by which an organism produces one or more chemicals that influence the growth, survival, and reproduction of other organisms. It is commonly observed in nature, and produced by molecules by molecules. Nanofabrication follows the same principle. Therefore, it is imperative for the nanotechnologists to learn from the principles of allelopathy to design advance chemicals to keep weeds under control. Nanotechnology could possibly be used to synthesize allelochemicals in the similar manners as pheromones and pheromone-carriers are synthesized, so that nano-designed chemicals can act as substitutes to conventional herbicides. Both weeds and crop plants possess allelopathic substances to compete with neighbouring plant species. Nanotechnology has the potential ability to study, design, create, synthesis, manipulation of functional materials, devices, and systems to fabricate structures with atomic precision by controlling the size of the matter at the scale 1–100 nanometers (one nanometer being equal to 1 × 10^{-9} of a meter). The properties and effects of nanoscale particles and materials differ considerably from larger particles of the same chemical composition. By controlling structure accurately at nanoscale dimensions, one can control and tailor properties of nanostructures, such as nanocapsules, in a very precise manner for slow release herbicide to achieve season-long weed control. Degrading phenolic compounds responsible for dormancy of weeds with suitable functionalized nanoparticle would be an intelligent solution for the exhausting the weed seed bank. Regardless of their minuscule size, the zero valent Iron (ZVI) nano particle, a chemical reductant hold the potential to cost-effectively address the issue of atrazine residual toxicity. However, nanotechnology will be successful, if these chemicals are target specific, release them in controlled manner, show superior efficiency, and effective in different ecosystems to thwart weed competition (Subramanian *et al*., 2013).

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 (Bernhardt *et al*., 2010; US-EPA, 2012). 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 nanoherbicides with highly specific, controlled release and increased efficiency to evade the weed competition under different ecosystem of crop production. The properties and effects of nanoscale particles and materials differs signifcantly from larger particles of the identical chemical composition. By controlling structure precisely at nanoscale dimensions, it is possible to control and tailor properties of nanostructures, such as nanocapsules, 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 (Pérez de Luque and Rubiales, 2009). 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.

Developing molecule encapsulated with nano particle to target specific receptor in the roots of weeds, which enters into roots system and translocated to parts that inhibit glycolysis of food reserves in the root system and making the specific weed plant to starve for food. Detoxification of weed residues is necessary as excessive use of herbicides cause damage to succeeding crops (Chinnamuthu and Boopathi, 2009). Up to 88 per cent detoxification of atrazine by Carboxy Methyl Cellulose (CMC) by nano-particles was observed by Satapanajaru *et al.* (2008). Nano-formulations (nanodispersions / nanoemulsions) of herbicide are designed to attack the seed coating of weeds and prevent weed germination. Two-third of Indian agriculture is rainfed farming where herbicide usage is very limited, weeds have the potential to make the total harvest vulnerable in the delicate agro-ecosystems. Keeping in view the need, it is desirable to design and produce nano-herbicide that is protected under natural environment and acts only when there is a spell of rainfall, which truly imitate the rainfed system.

Nanobiosensors

The challenge for weed scientists is to develop innovative, effective, economical, and environmentally safe systems that can be integrated into current and future cropping systems to bring a more diverse and integrated approach to weed management in crops. It is well known that certain biomolecules enhance the life and the growth of the surrounding organisms, thus helping the plants to clear space for itself. This opens up the opportunity of using nano-allelochemicals against weeds would lead the way for the world to use these natural chemicals instead of chemical herbicides. We perceive great future for nano-allelochemicals, because by and large allelochemicals exists in nanoform in nature. Applications of these nano-allelochemicals may be linked with nano-sensors. Nanosensors use nanoscale devices to identify and sense physical, chemical, or biological conditions crucial for weed control, and then translate that response into a signal or output in a useful form, and then transmit it to user. This is also one of the research efforts supported by recently launched "Nanotechnology Platform" by the Indian Council of Agricultural Research. Although miniaturization of structure is an advantage, but the major challenge remains in designing nanosensors that would make them functional in the field, where vagaries of nature are in abundance.

Nano-herbicides for smart weed control

Nanotechnology applications has 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 and pesticides. Seeds imbibed with nano-encapsulations with specific bacterial strain are termed as 'Smart Seed'. Nanoparticles can be used as smart delivery systems for targeting and uploading substances at specific areas within whole plants (González-Melendi *et al.* 2008, Corredor *et al.* 2009). Nano-encapsulated agrochemicals should be designed in such a way that they acquire all necessary properties such as effective concentration (with high solubility, stability and effectiveness), time controlled release in reaction to certain stimuli, improved targeted activity and less ecotoxicity with safe and effortless mode of delivery thus avoiding repeated application (Green *et al.,* 2007, Wang *et al*, 2007, Boehm *et al,* 2003, Tsuji, 2001).

The control of parasitic weeds with nano-capsulated herbicides reducing the phytotoxicity of herbicides was reported by Perez-de-Luque *et al.* (2009). Various types of herbicide formulations, with emphasis on controlled release formulations, micro-encapsulation 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 nanocapsules provide enhanced penetration through cuticle and allow slow and controlled release of active ingredients on reaching the target weed. Nano-encapsulation of chemicals with biodegradable materials also makes the concentrated active ingredients safe and easy to handle by the growers. Nano-encapsulation of herbicides could be used to resolve problems regarding phytotoxicity on the crop. 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 (Pérez-de-Luque and Rubiales, 2009). Bin-Hussein *et al.* (2005) reported development of organic–inorganic nanohybrid 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.

Smart Nano-scale carriers

These are "smart" nano scale devices as they can be organized for the efficient delivery of herbicides, fertilizers, pesticides and plant growth regulators *etc.* The nano scale carriers are designed in such a way that they can fasten the plant roots to the surrounding soil and organic matter. Consequently leading to improve stability against degradation in the environment and eventually reduce the amount to be applied (Johnston, 2010 and Ditta, 2012). Pal *et al.,* (2012) reported that use of arsenic nanoparticle (AsO) against weeds and for some other applications. This must be examined in the light of US-EPA (2009) initiative that prohibited use of several organic arsenical products on the ground that they eventually get converted to more toxic form in soil as inorganic arsenic, and potentially contaminate drinking water through soil runoff. Earlier, disodium methanearsonate (DSMA, or cacodylic acid) was used as herbicides in cotton and some other agricultural crop fields. Incidentally, brake-fern (*Pteris vittata*); a non-agricultural crop was reported as arsenic hyper-accumulator (Sarangi and Chakrabarti, 2008).

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