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Role of nanotechnology in slow release of herbicide and season long weed control: A review

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Abstract
The field of nanotechnology opens up novel potential applications for agriculture. Nanotechnology applications are already being explored and used in medicine and pharmacology, however interest for use in crop protection is just starting. The development of nanodevices as smart delivery systems to target specific sites and nanocarriers for controlled herbicide release. Some nanotechnologies can improve existing crop management techniques in the short to medium term. Nanocapsules would help to avoid phytotoxicity on the crop by using systemic herbicides against parasitic weeds. Nanoencapsulation can also improve herbicide application, providing better penetration through cuticles and tissues and allowing slow and constant release of the active substances. Nanomaterials offer a wider specific surface area to fertilizers and pesticides. In addition, nanomaterials as unique carriers of agrochemicals facilitate the site-targeted controlled delivery of herbicide with season long control. Due to their direct and intended applications in the precise management and control of inputs (fertilizers, pesticides, herbicides) support the development of high-tech agricultural farms. In this review, we summarize recent attempts at innovative uses of nanotechnologies in agriculture that may help to prevent weed growth without hampering environment.

Keywords: Nanotechnology, polymers, microencapsulation, nanoherbicide, weed control

Introduction
As we reduce the size of the particle the properties and behaviour of the molecules shows deviation from bulk characteristics. Surface properties of nanoparticles are the key factors, which determine the *in vivo* fate of such a carrier. Nanoparticles are widely used in several areas of drug delivery and cosmetics. These particles are usually smaller than 100 nm, they are formed by nanocrystals or by drug-polymer complexes or by creating nanoscale shells that entrap drug molecules (Breitenbach, 2002) [1]. Nanoscience and its applied sphere that is known as nanotechnology have potential to bring the next revolutionary breakthrough in agricultural-based natural resource management. It has ushered as a new interdisciplinary venture-field by converging science and engineering into agriculture and food systems (Lal, 2008) [2]. Nanotechnology has the potential to revolutionize the agricultural and food industry with new tools for the molecular treatment of diseases, rapid disease detection, enhancing the ability of plants to absorb nutrients etc. Smart delivery systems will help the agricultural industry combat viruses and other crop pathogens. In the near future nano structured catalysts will be available which will increase the efficiency of pesticides and herbicides, allowing lower doses to be used (Biswal *et al.*, 2012) [3]. As shown in the past, science and technology have a significant and necessary role to play in these areas. Whether by increasing productivity of fields, improving food and water quality, or helping to improve market access, new technologies can enable faster advancements in these directions and provide high returns to investments. Although there are debates on the tradeoff between investing in the development and diffusion of well-known past technologies versus that of new and potentially revolutionary technologies, several examples show that both of these strategies may be beneficial and are sometimes complementary. In some cases, technological advances driven by demand, *viz*., mobile phones, can have an enormous impact and even replace previous technologies (such as land-based telephones) before their complete diffusion. In other cases, *viz*., agricultural biotechnology, continued investment in existing practices (conventional breeding techniques) is necessary to move forward and have an impact on the ground. The question for public authorities is how to approach the prioritization of research and development efforts with limited budgets and scientific capacity. Advances in nanoscale sciences may present a new opportunity to help address these issues and improve the livelihood of the poor (Larkins *et al.*, 2008) [4]. Nanotechnology is research and development that involves measuring and manipulating matter at the atomic, molecular and supramolecular levels at scales measured in

approximately 1 to 100 nanometer (nm) in at least one dimension (NNI, 2007) [5]. At this scale, the physical, chemical and biological properties of materials may be fundamentally different from their corresponding bulk materials.

Role of nanotechnology in agriculture chemicals

One of the first industrial applications is the development of nano-chemical pesticides or nano-pesticides, where the pesticides that contain nano scale toxins. Nano-scale formulations of new and existing pesticidal toxins offer a range of novel properties, such as increased toxicity, stability or dissolvability in water as compared to large-scale molecules of the same chemical toxins. At the same time, the nano-encapsulation of pesticidal toxins offers new possibilities for the controlled or targeted release of pesticides, such as in the alkaline environment of certain insects digestive systems, or under specific moisture and heat levels (FOE, 2008) [6].

Joseph and Morrison (2006) [7] observed that “many companies make formulations which contain nanoparticles within the 100-200 nm size range that are able to dissolve in water more effectively than existing ones (thus increasing their activity). Other companies employ suspension of nanoscale particles (nano-emulsion), which can be either water or oil-based and contain uniform suspensions of pesticide or herbicide nanoparticles in the range of 200-400 nm”. Several developing countries already believe in the potential of nanotechnology. For instance, India has included agricultural productivity as one of its main focuses for public research in nanotechnology (Sreelata, 2008) [8].

Several pesticide manufacturers are developing pesticides encapsulated in nanoparticles (OECD and Allianz, 2008) [9]. These pesticides may be time released or released upon the occurrence of an environmental trigger (for example, temperature, humidity and light). It is unclear whether these pesticide products will be commercially available in the short term.

Adjuvants for herbicide applications are currently available that claim to include nanomaterials. One nano surfactant based on soybean micelles claims to make glyphosate-resistant crops susceptible to glyphosate when it is applied with the nanotechnology derived surfactant (Bio-Based, 2010) [10]. The regulatory structure in developed countries is driving development of nanoscale pesticides and herbicides in the direction of nanoscale adjuvants rather than nanoscale-active ingredients (Observatory NANO, 2010) [11]. Whether the nano application is due to a nanosized active ingredient or the creation of a nanosized formulation through the use of an adjuvant, the benefits of nano application are similar: Less herbicide is required to achieve the weed reduction effects desired. If the active ingredient is combined with a smart delivery system, herbicide will be applied only when necessary according to the conditions present in the field. Improvements in the efficacy of herbicides through the use of nanotechnology could result in greater production of crops and less injury to agricultural workers who must physically remove weeds if herbicides are not used.

Nanoparticles have a great potential as 'magic bullets', loaded with herbicides, chemicals or nucleic acids and targeting specific plant tissues or areas to release their charge. Viral capsids can be altered by mutagenesis to achieve different configurations and deliver specific nucleic acids, enzymes or antimicrobial peptides acting against the parasites. Many issues are still to be addressed, such as increasing the scale of production processes and lowering costs, as well as toxicological issues, however the foundations of a new plant treatment concept have been laid and applications in the field of parasitic plant control can be started (Perez-de-Luque and Rubiales, 2009) [12].

Microencapsulation

Microencapsulation is defined as a technology of packaging solids, liquids or gaseous materials in miniature, sealed capsules that can release their contents at controlled rates under the influences of specific conditions (Kailasapathy and Masondole, 2005) [13]. A microcapsule may be opened by many different means, including fracture by heat, solvation, diffusion and pressure (Brannon-Peppas, 1997) [14]. Polyelectrolyte multilayer microcapsules generated via the LbL self-assembly technique have attracted particular interest as potential vehicles for drug-delivery (Donath *et al.,* 1998) [15].

Microencapsulation of drug microparticles is a useful technique for prolonging release. Polymer-based and liposome-based systems have been used for drug encapsulation, mostly as unordered drug/polymer conjugates (Junyaprasert *et al.*, 2001) [16]. Reduction in volatilization loss of applied herbicides due to micro encapsulation has been reported thus diminishing the presence of herbicide in the atmosphere. Reduction in phyto toxicity in crops due to micro encapsulation has also been reported (Bernards *et al*., 2006) [17].

In recent years, the interest has been focused on the study of polyelectrolyte multilayer microcapsules. In most cases, these capsules have been hollow (water inside), however they have also been filled with neutral or charged polymer solutions (Vinogradova *et al.,* 2004) [18]. Polyelectrolyte multilayer microcapsules have attracted a great deal of interest, due to primarily the fact that their properties, including size, shape, composition, shell thickness, permeability, stability and stiffness, can be tailored fairly readily (Johnston *et al.,* 2006) [19].

Microcapsules can be generated from a variety of materials and polyelectrolytes, proteins, nucleic acids, inorganic nanoparticles, dyes and lipids have all been utilized as components of the shells. Shell properties, including thickness and permeability for certain classes of molecules, can be tuned to match the desired characteristics. Therefore, the well-defined shape of these capsules, their mechanical stability and their ease of preparation allow for their use as a model system for both basic and applied studies. By varying the number of layers and the assembly conditions, *viz*., concentration and nature of the polyelectrolytes used, salt concentration and pH value. The properties of polyelectrolyte multilayer microcapsules can be controlled with ease. In addition, the capsule surface can be modified to alter the functionality of the capsule and/or to improve colloidal stability (Cho *et al.,* 2004) [20].

In general, the polyelectrolyte multilayer shells evidence selective permeability. High molecular weight compounds are hindered by the polyelectrolyte shell, whereas small molecules including dyes and simple ions can readily penetrate the microcapsule shell. This property is of primary importance when using microcapsules as controllable containers in nano-biotechnology. Furthermore, the well-defined shape of these capsules and their mechanical stability, in addition to their ease of preparation, allows using as a model system for basic and applied studies in fields including

drug delivery, catalyst research and biotechnology (Kim and Chio, 2007) [21].
The herbicide Systems of Controlled Liberation (SCL) is a technology wherein an active ingredient is available for a specific goal at a concentration and with a duration designed to achieve the intended effect, aiming to reach optional biological effectiveness and to reduce any harmful effects. Polymeric capsules are held together by strong covalent bonds, which make them more robust and stable than liposomes (Holister *et al.,* 2008) [22].
Layer-by-layer (LbL) adsorption of oppositely charged polyelectrolytes, sodium alginate (Alg) and poly-L-lysine (PLL), novel biodegradable microcapsules have been prepared for delivery of biological active substances (BAS) (Borodina *et al.* (2008) [23]. Porous spherical $CaCO_3$ microparticles were used as templates and EDTA is used for core dissolution. Chymotrypsin the immobilized enzyme retained about 86 per cent of the activity compared to a native Chymotrypsin. The polyelectrolyte PLL of resultant microcapsules were stable in acidic medium and could be easily decomposed in slightly alkaline medium (trypsin). Chymotrypsin is active after its release from the microcapsules decomposed by the trypsin treatment.
Microencapsulation is a well-established dedicated to the preparation, properties and uses of individually encapsulated novel small particles, as well as significant improvements to tried-and-tested techniques relevant to micro and nano particles and their use in a wide variety of industrial, engineering, pharmaceutical, biotechnology and research applications. Its scope extends beyond conventional microcapsules to all other small particulate systems such as self-assembling structures that involve preparative manipulation (Nitika Agnihotri *et al*., 2012) [24].

Microencapsulation of herbicide

Microencapsulation becomes the most industrial process used for the production of controlled release agricultural formulations. In fact, various agrochemicals such as norfluazon, atrazine, metribuzin, diuron and dicamba were formulated by different microencapsulation techniques. These formulations permit the protection of the active agent from evaporation and degradation by photolytic, hydrolytic or microbial reactions. Furthermore, the release rate of herbicide can be controlled and its concentration is maintained within optimum limits over a long period (Bahri and Taverdet, 2007) [25, 39]. Recently, it has been found that alachlor and norflurazon formulations control liberation. Microencapsulated in ethylcellulose (EC) they reduce mobility and protect herbicides against degradation in the soil-water system, regardless of the type of soil involved. These characteristics result in greater herbicide activity than that observed with the commercial formulation (Sopefia *et al.,* 2007) [26].

Control release of encapsulated herbicide

Biodegradable polymers are widely used for drug delivery and controlled release because they eliminate the need of removing delivery systems after administration. Drugs are released from polymer matrix by diffusion, polymer degradation or erosion (Uhrich *et al.,* 1999) [27]. Micro and nanospheres fabricated from a biodegradable polymer for drug delivery systems have become increasingly important owing to the fact that such systems enable controlled drug release at desired sites.
Controlled drug delivery occurs when a polymer, whether natural or synthetic, is judiciously combined with a drug or other active agent in such a way that the active agent is released from the material in a pre-designed manner. The release of active agent may be constant over a long period of time, it may be cyclic over long period, or the environment or other external events may trigger it. In any case the purpose behind controlling the drug delivery is to achieve more effective therapies while eliminating the potential for both under and overdosing. Other advantages of using controlled release drug delivery are; maintenance of drug levels within desired range, need of fewer administration, optimal use of drug in question and patient compliance (Omathanu Pillai and Ramesh Panchagnula, 2001) [28].
Advances in the polymeric science have led to the development of several novel drug-delivery systems. A proper consideration of surface and bulk properties can aid in designing of polymers for various drug-delivery systems. Biodegradable polymers find widespread use in drug delivery, as they can be degraded to non-toxic monomers inside the body. Polymeric delivery systems are mainly intended to achieve either a temporal or spatial control of drug delivery (Omathanu Pillai and Ramesh Panchagnula, 2001) [28].
Controlled drug delivery strategies have made a dramatic impact on medicine. Controlled drug release can be achieved by a combination of carrier materials and active agents. Polymer micro and nanospheres can be employed to deliver medication in a rate-controlled and sometimes targeted manner. Biodegradable polymers can be natural polymers, modified natural because they are always biodegradable (Nair and Laurencin, 2007) [29].
Timed-release technology was designed to release the active ingredient at a predetermined time (the lag time) after application. Although fertilizers and pesticides are widely used in agriculture, they sometimes cause hazards to both humans and the environment (Narutoshi *et al.,* 2007) [30].
Technologies such as encapsulation and controlled release methods have revolutionized the use of pesticides and herbicides. A mechanism frequently referred in the medical field “smart delivery of chemical” enable us to reduce the use of pesticides in agriculture with increased efficiency. Smart delivery of herbicide will be highly useful to exhaust the weed seed bank, responsible for the weeds, causing one hundred per centage crop loss, is a great accomplishment for the farming community (Chinnamuthu and Kokiladevi, 2007) [31].
For controlled release system, micron-scale core materials are encapsulated with an outer shell. The core must be insoluble under some condition, such as low pH and soluble under the conditions at which controlled release is to take place. The release rate generally depends on the thickness of the encapsulating shell and the material used in the coating. Thicker shells lead to longer release times (Arida and Al-Tabakha, 2007) [32].
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 translocated to parts that inhibit glycosis of food reserve in the root system. This will make the specific weed plant to starve for food and gets killed (Chinnamuthu and Kokiladevi, 2007) [31].
In recent years, the development of modified natural polymers as controlled release devices in agro industries has emerged as a new technology with better commercial viability than the use of conventional synthetic polymers since these are known to create some environmental concern (Kumbar *et al.,* 2001) [33]. Therefore, the research orientation has been ongoing to

find a suitable alternative and film-forming membrane material that can be safely used in agro industries.

Recently, Green and Beestman (2007) [34] reported that most of the technologies are based on micro and nanoencapsulation for control release. This may be because herbicide micro encapsulation reduces losses of the active ingredients.

Smart delivery systems are nanoscale devices that have the capability to detect and treat an animal infection or nutrient deficiency and can be designed to provide time controlled release of drugs or nutrients. This application is apparently not currently in widespread or commercial use and will require substantial effort to integrate nanotechnology, biotechnology and information technology with geographic information systems. Some estimate that while the building blocks exist to design smart drug delivery systems, it may be decades before they are in commercial use (Scott, 2007) [35].

Sopefia *et al.* (2009) [36] reported that controlled release formulations of herbicides have become necessary in recent years and important to develop new herbicide formulations that are highly effective, safer, low cost ratio and increase herbicide efficacy at reduce dose. Plaguicide encapsulation aims to control the liberation of the formulation's active ingredients, to enable their use for a specific purpose at an intended concentration, to diminish the disadvantages of the active ingredient and to maintain the highest possible biological effectiveness.

Encapsulation efficiency

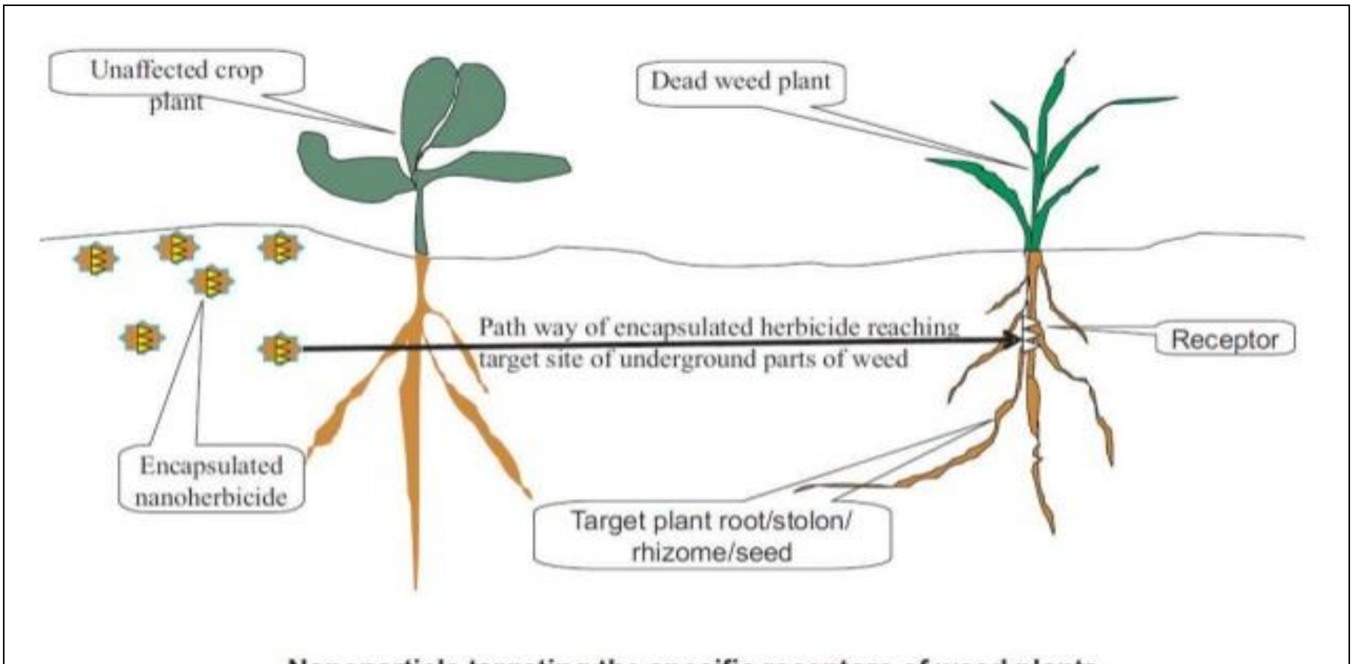
Cetin *et al.* (2007) [37] study describes the preparation and characterization of a model protein bovine serum albumin (BSA)-loaded in alginate microspheres. BSA was encapsulated within alginate microspheres by the emulsification technique. The average particle size was 11.96 ± 0.043 µm of the prepared microspheres. The drug loading and encapsulation efficiency were about 0.73 and 37 per cent, respectively. The in vitro release profile showed a fast release rate of BSA and 90 per cent of the BSA was released from alginate microspheres in 48 hours.

Releasing efficiency

Hussein *et al.* (2005) [38] studied the release property of controlled release formulation of 2, 4-D in the inorganic Zn-Al layered double hydroxide (ZAL) matrix into aqueous solutions containing chloride, carbonate as well as distilled water was found to be rapid initially followed by a more sustained release thereafter and this behaviour was dependent on the type of anions and their concentrations in the release medium, the aqueous solution.

Bahri and Taverdet (2007) [25, 39] study that the release of herbicide from the Gelatin Arabic gum coated Ethylcellulose (EC) or Cellulose acetate butyrate (CAB) microspheres is much slower compared with EC and CAB microspheres. Taking into account the presence of pores in the microspheres structure and by applying the analytical equation derived from Fick's second law, the effective diffusivities of 2, 4-D calculated in short times and with the number mean diameter are in the range of 0.7 to 7.7 x 10^{-11} cm^{-2} sec^{-1} for EC microspheres and 0.3 to 4.4 x 10^{-11} cm^{-2} sec^{-1} for CAB microspheres.

Dimov and Petrov (2008) [40] shown the results of encapsulated Perozin E and Ridomil pesticide in epoxy resins, give emission levels in aqueous medium up to 2.5-3.3 mg l^{-1} and were considered to be sufficiently low. It can be supposed that such capsules can successfully be stored in air or additionally isolated in polymer packing.



Nanoparticle targeting the specific receptors of weed plants

Conclusion

In the field of agriculture, nanotechnology has been used to intensify the crop production with quality enrichment by enlightening farming systems. The emergence of engineered nanomaterials and their actions within the frame of sustainable agriculture have revolutionized world agriculture canvass dramatically by novelty, fast growth and enormity to meet the projection of global food demand. In sustainable agriculture, the protection of the environment from pollution is the crucial target for trade, and nanomaterials provide an assurance of better management and conservation of inputs to plant production. The potential of nanomaterials encourages a new green revolution with reduced farming risks. However, there are still huge gaps in our knowledge of the releasing capacity, permissible limit and the ecotoxicity of different nanomaterials in open field condition. Therefore, further research is urgently needed to unravel the behaviour and fate of altered agriculture inputs and their interaction with biomacromolecules present in living systems and environments.

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