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Nano-Agrochemicals: Risk Assessment and Management Strategies

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Abstract

Application of nanotechnology in agriculture especially in the form of nano agrochemicals is increasing nowadays. Agrochemicals such as fertilizers, soil amendments, soil conditioners, pesticides and plant growth promoting hormones have both pros and cons. To overcome the constraints of conventional agrochemicals researchers are focusing on nano agrochemicals. Apart from the high potential and effectiveness these chemicals also have some threats to the human health, environment and ecological balances. With proper assessment of risks associated to these nano agrochemicals threats can be minimised and the potential of nanotechnology in agriculture can be explored to the greater extent. After assessment the risks could be managed by applying three thumb rules as risk prevention, risk mitigation and risk communication. In depth research is required to explore the potential of nanotechnology in agriculture.

Keywords: Environment, Human health, Nano-Agrochemical, Nano Material, Threats

Introduction

In agriculture several inputs such as seed, irrigation, pesticides, fertilizers, plant growth hormones are required for boost up the quality and production of agricultural products. Agrochemical refers to any substance employed by humans to assist in the maintenance and enhancement of agricultural ecosystems. These substances encompass fertilizers, agents for altering soil pH (liming and acidifying agents), soil enhancers, pesticides, as well as chemicals utilized in livestock farming, such as antibiotics and hormones (Anonymous, 2022). The unregulated application of these chemicals has led to a significant boost in food production, but it has concurrently resulted in a decline in food quality, soil fertility, and overall environmental well-being. According to Bollag *et al.* (1992), approximately 50-70% of chemical inputs are lost due to processes such as leaching, mineralization, and bioconversion, contributing to significant wastage in agricultural practices. Apart from the impact on human health, these chemicals have also disrupted various sublevels of ecosystems, including soil microbial communities, parasites, marine environment, *etc*. (Chhipa, 2017). So there is a need to replace these conventional agrochemicals with new generation smart agrochemicals like nano based agrochemicals for sustainable agriculture. Nanotechnology holds tremendous promise to revolutionize the current agricultural landscape through the development of innovative tools tailored for agricultural applications (Joseph and Morrison, 2006).

Nano-agrochemical is a consolidation of nanotechnology and agrochemicals. Currently, these nano-agrochemicals got popularized owing to their superior efficacy in comparison to conventional agrochemicals, rendering them economically viable and environmentally friendly alternatives (Chhipa, 2017; Qazi and Dar, 2020). All of the leading producers of agrochemicals are focusing on the research about nanotechnology for use in agricultural practices (DeRosa *et al*., 2010). Over the past decade, several companies have already filed patents consisting of a diverse array of production and application protocols for nano-pesticide formulations (Peters *et al*., 2016).

Increasing the uses of nanotechnology in agriculture raises questions in concern with human and environmental health. In this prospective, environmental and human exposure due to nano-agrochemical residues in soil and crops is

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poised to rise with potential exposure routes encompassing contamination and the possibility of bioaccumulation within the environment and food chain (Iavicoli *et al.*, 2017). This raises concerns about the long-term impact on both ecological systems and human health.

From an environmental and human health standpoint, this underscores the increasing urgency of evaluating the risks linked to nano-agrochemicals, especially in light of numerous reports by researchers highlighting adverse effects on environmental elements (Antisari *et al.*, 2013; El-Temsah and Joner, 2012; Jośko *et al.*, 2014; Kim *et al.*, 2011; Roh *et al.*, 2010) and human well-being (Bai *et al.*, 2014; Hossain and Mukherjee, 2013; Iavicoli *et al.*, 2011; Moschini *et al.*, 2010). In this review, we focussed on types of nano agrochemicals, their benefits, potential applications as well as assessment of risks associated with these chemicals and key ways to manage these risks.

Nano Agrochemicals

Nano Pesticides

The term “nano pesticide” is used to describe any pesticide formulation that “involves either very small particles of a pesticide active ingredient or other small engineered structures with useful pesticidal properties” (Kookana *et al.*, 2014). Numerous types of nano pesticides have been developed and documented by researchers (Table 1).

Table 1: Nano pesticides in crop protection

Nano-Formulation	Pesticide	Impact	Reference(s)
Calcium carbonate	validamycin	Control release extended upto 2 weeks	Qian *et al.*, 2011
PEG-400	acephate	Reduced toxicity of acephate and improved stability	Choudhury *et al.*, 2012
Poly(citric acid)-poly(ethylene glycol)-poly(citric acid) (PCA-PEG-PCA) ABA type linear-dendritic copolymers	indoxacarb	Higher loading capacity and slower release rate of indoxacarb	Memarizadeh *et al.*, 2014
Fluorescent photoresponsive organic nanoparticles of perylene-3-ylmethanol	2,4-D	Improved absorption by plant cells and increased water solubility as compared to conventional 2,4-D	Atta *et al.*, 2015
Nano formulation with lemon oil terpenes, polysorbates and Glycerol	natural pyrethrin	Increased insecticidal activity and absence of adverse effects on non-target aphid predators	Papanikolaou *et al.*, 2018

Nano Fertilizers

Nano fertilizers fall into two categories: they are either nano-materials capable of directly supplying one or more vital nutrients to plants, thereby enhancing their growth and yields, or they are substances designed to enhance the effectiveness of conventional fertilizers, albeit without directly providing nutrients to the crops themselves (Chhipa, 2017; Liu and Lal, 2015). Various researchers have examined and documented a range of inorganic, organic, and composite nano-materials or nano-fertilizers, as illustrated in table 2.

Nano Based Soil Remediation Chemicals and Soil Conditioners

The hazards linked to soil pollution are regarded as significant threats to the entire ecosystem. Therefore, it is imperative to prioritize prevention, as well as the remediation and restoration of contaminated soil. Following successful remediation, this rejuvenated land can be harnessed to fulfil global food and energy demands, addressing a pressing need of our time (Bakshi and Abhilash, 2020). Several techniques identified by researchers for soil remediation and these techniques were categorized into 3 categories *viz.*, (i) physical remediation which involves soil washing, thermal desorption and replacement or partial replacement of contaminated soils; (ii) biological remediation including microbial and phytoremediation; and (iii) chemical remediation which comprises of chemical leaching, chemical fixation and electro kinetic methods. These techniques are expensive, time consuming, laborious and less efficient (Dhaliwal *et al.*, 2019). Apart from these several engineered nano materials were identified and tested by researchers in last few decades (Table 3).

Similarly to improve soil physical conditions several nano soil conditioners are prepared and tested recently. Kim *et al.* (2011) and Liu *et al.* (2017) have been prepared nano-submicron mineral-based soil conditioner (NMSC) from potassium-rich feldspar using environmentally friendly hydrothermal technique. In this study they reported that the soil pH was improved by 1-9% as compared to control group, and soil bulk density decreased by 8%. Aluminium concentration in soil and cadmium concentration in rice were decreased by 29-42% and 50%, respectively that indicates that this nano soil conditioner was effective in alleviating the aluminium toxicity as well as to inhibit the Cd accumulation reduction.

Nano-Particles as Plant Growth Promoting Substances

Nano-particles can exert both positive and negative impacts on plant growth (Goswami *et al.*, 2019; Kim *et al.*, 2011). Numerous reports indicate that various types of nanoparticles have the potential to serve as plant growth-promoting (Table 4).

Table 2: Nano Fertilizers used in crop production

Nano Fertilizer	Nutrient	Crop	Effects	References
Zeolite Based	Nitrogen	Maize	The grain N content of nanozeourea on inceptisol (0.32%) and alfisols (0.76%) were higher consistently.	Manikandan and Subramanian, 2016
Zeolite Based	Nitrogen	Kalmi (*Ipomoea aquatica*)	The growth of Kalmi, N uptake and concentration was better in nano fertilizer treatments than in the conventional fertilizer treatments.	Rajonee *et al*., 2016
Nano-scale zinc oxide (ZnO) and ferric oxide (Fe_2O_3)	Zn and Fe	Barley	Days to anthesis and maturity significantly increased after application of both nanofertilizers. Considerable improvement was observed in grain mass, spike length, number of the grains spike^{-1}, chlorophyll content, grain yield and harvest index by application of nano-fertilizer.	Janmohammadi *et al*., 2016
Nano chitosan based	NPK	Wheat	significant increases in harvest index, crop index and mobilization index of the determined wheat yield variables; life cycle of the nano-fertilized wheat plants was shorter (130 Days) than normal-fertilized wheat plants (170 Days)	Abdel-Aziz *et al*., 2016

Table 3: Nano materials used for soil remediation

Nano materials	Pollutant	Process of remediation	References
Nano zero valent iron	Chlorpyrifos	Degradation	Reddy *et al*., 2013
Nanomaghemite and magnetite	Cd, Cu, Pb	Stabilization	Michálková *et al*., 2014
ZnO, Al	Heavy metals	Sorption	Mahdavi *et al*., 2015
Nanosilicone	Lead	Stabilization	Liu *et al*., 2015
Hydroxyapatite	Cd, Zn, Pb, Cu	Adsorption	Chen *et al*., 2010

Table 4: Nano particles as plant growth promoting substances

Nano Particles	Crops	Effect	References
Ag	*Lolium multifolium*	Enhance plant growth.	Vannini *et al*., 2013
Zn	*Vigna radiata*	Increase germination, root and shoot growth.	Zafar *et al*., 2016
TiO_2	*Vigna radiata, Arabidopsis thaliana, Foenticum vulgare, Lemna minor, Triticum aestivum*	Enhance germination, plant growth chlorophyll content.	Scott *et al*., 2018
Carbon Nano tubes (CNTs)	*Glycine max*	Increase seed germination.	Changmei *et al*., 2002
Multi-walled Carbon Nano tubes (MWCNTs)	*Lycopersicum esculentum*	Increase plant growth, height, flower number.	Morla *et al*., 2011

Potential Threats Related to Nano Agrochemicals

There is a substantial gap in the available knowledge concerning the environmental, health and ecological threats associated with the nano-agrochemicals (He *et al*., 2019; Shang *et al*., 2019). Due on their size and physicochemical properties, it is possible to cross the cell wall and bioaccumulation of nano particles when compared to larger molecules of the same material. Literature shows that nano-particles especially engineered nano particles have both chronic and acute toxicological effect (Mwaanga, 2018). For example silver nano particles have several applications in agriculture and it is reported that these silver nano-particles have several toxic effects such as mitochondrial dysfunction due to change in cell permeability for K^+ and Na^+ ions (Kone *et al*., 1988); induce pronounced toxic effects on the proliferation and cytokine expression of peripheral blood mononuclear cells (PBMCs), as reported by Shin *et al.* (2007), and toxic effects on the male reproductive system, as indicated by McAuliffe *et al.* (2007). Such type of toxicity may occur in the person having direct contact while production of nano particles, exposure during application or through bioaccumulation. In addition to their impact on human health, numerous studies have demonstrated the effects of nano-materials on non-target organisms, including soil macro- and micro-organisms, as well as beneficial insects and plants. Karunakaran *et al*. (2013) advocated that plant growth-promoting rhizobacteria (*Bacillus subtilis* and *Pseudomonas fluorescens*) were susceptible to the toxicity of Al_2O_3, TiO_2, ZnO and SiO_2 nanoparticles (Dimkpa, 2014). Chen *et al*. (2011) observed that AgNPs could lead *E. coli* to the induced formation of "pits" in the cell walls and cell membrane distraction, DNA could condense and then leakage of the cytoplasmic components could occur due to Entrance of periplasm through these pits. Similarly toxic effects of engineered nanomaterials on other nitrifying bacteria (Yang *et al*., 2014), nitrogen fixing bacteria (Dimkpa 2014; Fan *et al*., 2014) and soil enzyme activities (Du *et al*., 2011; Zheng *et al*., 2011) are also reported.

Risk Management Strategies

After risk assessment associated to nano agrochemicals it is required to follow-up the effective risk management strategies. There are three most required aspects regarding risk mitigation *viz*., risk prevention, risk mitigation and risk communication (Figure 1).

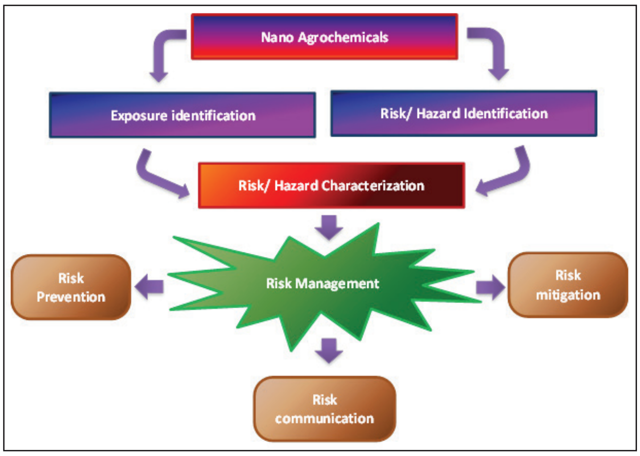

Figure 1: Diagrammatic representation of toxicological risk assessment of nano materials on humans, animals, environment and whole ecosystem and management strategies

Risk prevention and mitigation strategies entail thorough assessment and identification of risk. This includes the adoption of less toxic, biodegradable, or environmentally friendly nano-materials for agrochemicals, ensuring the safe use of nano-materials, and minimizing exposure risks. Effective communication and comprehensive knowledge dissemination to stakeholders, including farmers and the general public, regarding the risks associated with nano-agrochemicals can greatly contribute to the better management of potential hazards and threats (Brunda and Kumawat, 2022).

Future Prospects in Nano-Agrochemicals and their Risk Management

For better understanding and assessment of threats associated to nano agrochemicals there is in depth studies required in relation to fates, modes and extent of exposure of nano agrochemicals, less toxic nano materials, green nano agrochemicals. As compared to other fields (Engineering, medical, sensors, electrical, *etc*.) there is a limited applications of nanotechnology in agricultural practices. To explore the potential of nanotechnology in agricultural sector, a great scope is there to researchers to scrutinise the risk and its management for safer use of nano agrochemicals.

Conclusion

Nanotechnology indeed holds the promise of revolutionizing agriculture in the future, offering a sustainable alternative to conventional agricultural inputs through the use of nano-agrochemicals. These nano-agrochemicals have the potential to deliver active ingredients with precision, enabling controlled release and minimizing runoff and residual contaminations, thus promoting more environmentally friendly and efficient agricultural practices. Although the nano chemicals have several pros over conventional one but they needs to be used carefully to avoid the risks associated. Furthermore research is needed for identification and mitigation of risks associated to nano agrochemicals before commercialization.

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