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A REVIEW: APPLICATIONS OF ZNO NANOPARTICLE IN AGRICULTURE

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ABSTRACT
Importance: ZnO nanoparticles hold excellent properties for its use in agriculture and medical fields due to its small size it can be used in fewer amounts rather than usual fertilizers that are used in high amounts since the need for sustainable and environmentally friendly agriculture is trending now these days. ZnO NPs have proven to be an excellent applicant. **Observation:** A significant increase in crop yields have been recorded when using ZnO nanoparticles on various crops, it has also proven effective in water remediation, water disinfection, and in delivering pesticides without any residues from the pesticides. Hence, the use of nanoparticles in various biotechnological fields must be increased for an eco-friendly approach. **Conclusion and Relevance:** With the growing demand for basic food and eco-friendly methods of growing crops ZnO NPs have proven effective but everything has its pros and cons. Various researches have shown the toxicological effects of ZnO NPs on different organism including humans so we need for research in this nanoparticle field to study the characteristics and then tune these characteristics according to our need so that it possesses less harm to the environment as well as organism.

KEYWORDS: Nanotechnology, ZnO nanoparticle, Agriculture, Remediation, toxicity.

INTRODUCTION
A nanoparticle is an ultrafine particle usually, a particle matter that has a size "between 1 to 100 nanometres (mm) in diameter.[1,2] This term also sometimes used for particle size up to 500nm or tubes and fibres that are 100nm or less in size in only two directions". Metal particles that are smaller than 1nm at the lowest range are called atom Clusters instead of a nanoparticle.[2]

There is a variety of nanoparticles used in agriculture like Fe, Cu, Ag, Si, ZnO, TiO_2, CeO_2, Al_2O_3, Carbon Nanotubes.

Nanoparticles in agriculture
Sustainable agriculture is the requirement nowadays, that is reasonable to opt for a good approach to the ecosystem in the long run. Practices that do long-term harm to the soil and land which includes too much ploughing of the soil which causes soil erosion as well as irrigation deprived of needed drainage, leads towards salinization.

Long-run testing is necessary to point out the outcomes of various practices on soil properties, that are crucial to the sustainability as well as to supply essential data on this objective. "Within USA, an authority, the improvement in Nano-chemicals has seemed to be an assuring means for the growth of plants including the control of pests. Nanomaterials function as fertilizers which can have properties like crop enhancement and with less eco-toxicity". Plants can provide a vital way of bioaccumulation into the natural food series. Modern advancements in agriculture cover the utilization of NPs for new practical as well as secure practice of compounds for plants. The consequences of several "NPs on plant growth and phytotoxicity were described by quite a few personnel including (Fe3O4) nanoparticles. Plant growth, root growth and seed germination of 5 higher plant species; radish, rape, lettuce, corn, and cucumber, silver nanoparticles including seedling growth in wheat, sulphur nanoparticles on tomato, philosopher's wool in mungbean, nanoparticles of ZnO, CuO, MnO, FeO, and AlO. Silver nanoparticles have shown effects on stimulation of wheat germination and increase in yield. Soil applied with 25 ppm SNPs had very favourable growth-promoting effects on wheat growth and yield".[3] Broccoli seeds treated with nano Zinc material increases the plant growth, early flowering, and early setting of flower heads. The secondary metabolites i.e. polyphenol, Glucosinolate, 4-hydroxy and methoxy glucobrassicin, glucoerucin, gluconasturtiin is increased by 10-12% in treated broccoli as compared to Control.[4]

Zinc is acknowledged as a necessary micronutrient needed by plants to perform their metabolic activities and is needed in minimum quantity. It had been discovered that zinc performs a significant role in the managing of ROS and also provides stability against oxidative stresses in plant cells. "Zinc has key roles within the synthesis of auxin (IAA) from tryptophan still, biochemical reactions are required for the production of chlorophyll as well as carbohydrates. Crop quality and yield can be stricken by the deficiency of Zn".[3]

"Zinc oxide nanoparticles has shown good effectiveness as antiseptic agent against typical strains of Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli*" that are produced from pomegranate peels.[3]

Using zinc oxide nanoparticles as fertilizers

The conscious use of nanoparticles in agriculture, though early, but still promising. Because of their smaller size, nanoparticles show diverse properties as of the equivalent material in their natural size. "Essentially, they have a high specific area and high surface energy that generates changes in its physicochemical, optical, and electrical properties, as well as a high reactivity".

These characteristics can be essential to obtain enhancements in the field of agronomy, for example, to develop more effective formulations of phytosanitary and fertilizers. More particularly, there is an increasing curiosity for the use of ZnO nanoparticles in agricultural formulations either for their beneficial properties as an UV light-blocking or else as source of zinc micronutrient by using their fertilizer properties. This micronutrient acts essentially towards the development of plants as its deficiency would decreases the nutritional content and the production of the crops.

Role of ZnO NPs in Agriculture

Zinc oxide Nanoparticles possess the ability to increase the crop production and also the growth of essential crops. "Peanut seeds were treated by various concentrations of zinc oxide nanoparticles. Zinc oxide nanoscale treatment (25 nm mean particle size) at 1000 ppm concentration was used which improved seed germination, seedling vigor, including plant growth, these zinc oxide nanoparticles further proved to be efficient in increasing stem and root growth in peanuts".[6]

Zinc oxide nanoparticles colloidal solution is used as fertilizer. This sort of Nano-fertilizer acts as a significant role in agriculture. Nano-fertilizer given as plant nutrient that is more than a fertilizer because along with providing nutrients to plants it also revives the soil to an organic state without any adverse issues from chemical fertilizers. Benefits of using Nano-fertilizers is that it is needed in short amounts. "An adult tree requires only 40–50 kg of fertilizer whereas an amount of 150 kg would be needed for ordinary fertilizers.[7,8] Nano powders can be actively used as fertilizers and pesticides as well. The yield of wheat plants increased by 20–25% whose seeds were treated with metal nanoparticles".[9] ZnO Nanoparticles also increases the biomass of plant growth promoting fungus *Piriformospora indica.* Fig 1.

Legends for figures

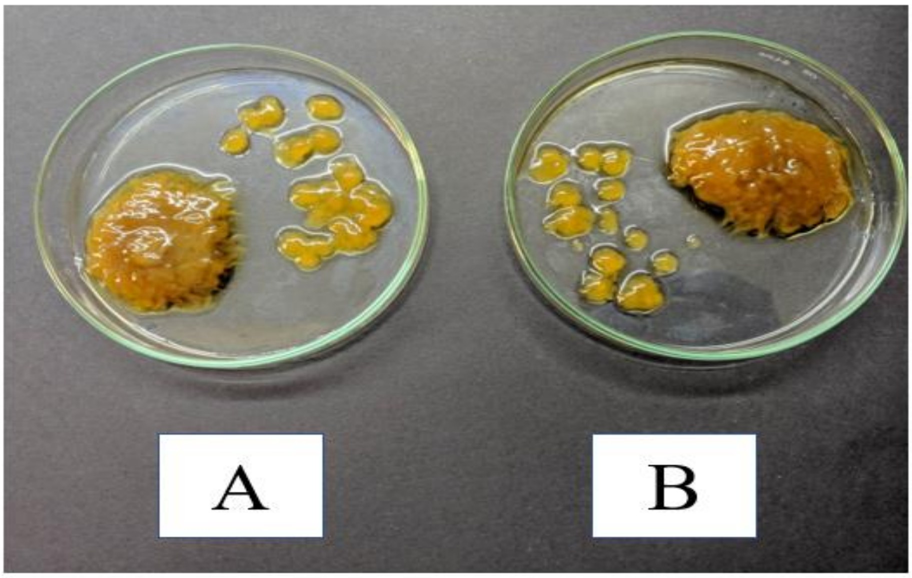

Fig. 1: - *P. indica*(A) and *P. indica* + ZnO 1ml from 100ppm solution(B).

Water remediation with the help of ZnO nanoparticles

Permethrin pesticide can be removed from water by using chitosan– ZnO NPs composite which acts as an adsorbent.

"Synthesis of chitosan–ZnO nanoparticles (CS–ZnO NPs) composite beads were produced by a polymer-based technique. The resultant bionanocomposite was distinguished by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), and spectroscopy. Adsorption applications towards the eradication of pesticide pollutants were conducted". The best conditions as well as agitating time, adsorbent dose, early concentration of pesticide, including the pH on the adsorption of pesticide by chitosan packed with ZnO nanoparticles beads were examined. "Results revealed that 0.5 g of bionanocomposite at pH 7, and in-room temperature could eliminate 99% of the pesticide from permethrin solution (25 ml, 0.1 mg L−1), using UV spectrophotometer at 272 nm. Then, the utilization of the adsorbent for pesticide removal was studied in the on-line column. The column was revived with NaOH solution (0.1 M) completely, and then reused for adsorption application. The CS–ZnO NPs composite beads emerge to become new assuring material in water treatment purpose with regeneration of 56% after 3 cycles".[10]

Zinc oxide NPs for water disinfection

The world stands an increasing challenge for sufficient clean water due to perils arising from growing need and diminishing supplies. Though there are many current technologies for disinfecting of water they have their limitations, "particularly the formation of disinfection-by-products", which needs the researches for alternate approaches. Zinc oxide, a crucial compound used in pharmaceutical and rubber productions, draws attention as an antimicrobial agent. When used as nanoscale, ZnO NPs has displayed antimicrobial qualities and makes it possibly great for numerous applications. "The synthesis of zinc oxide by focusing on precipitation method, its antimicrobial property, and the factors affecting it like disinfection mechanisms and the potential application for water disinfection".

The antimicrobial activity of the "ZnO nanoparticles includes the discharge of oxygen species of the surface of ZnO which causes lethal harm to microorganisms. Reactive oxygen species are known to cause oxidative stress by damaging DNA, cell membranes, and cellular proteins. The breaking of the cell wall is due to the surface activity of ZnO which causes the decomposition of the cell wall and the cell membrane, the leakage of cell contents which ultimately leads to cell death[11,12] The mechanism was presented by Padmavathy and Vijayaraghavan[11] as follows:

ZnO is activated by UV and visible light to form electron-hole pairs: ZnO + hν → e^- + h+

The electron-hole pairs split water molecules from ZnO suspension into OH and H+:h+ + H2O → OH + H+

O2 molecules yield superoxide anion: e− + O2 → O2−

Superoxide anion reacts with H+ to generate HO2 radicals: O2− + H+ → HO2

HO2 interferes with electrons generating hydrogen peroxide anions which react with H+ to produce hydrogen peroxide molecules: HO2 + H+ + e− → H2O2

The hydrogen peroxide can penetrate the cell membrane and kill the bacteria" Fig 2.

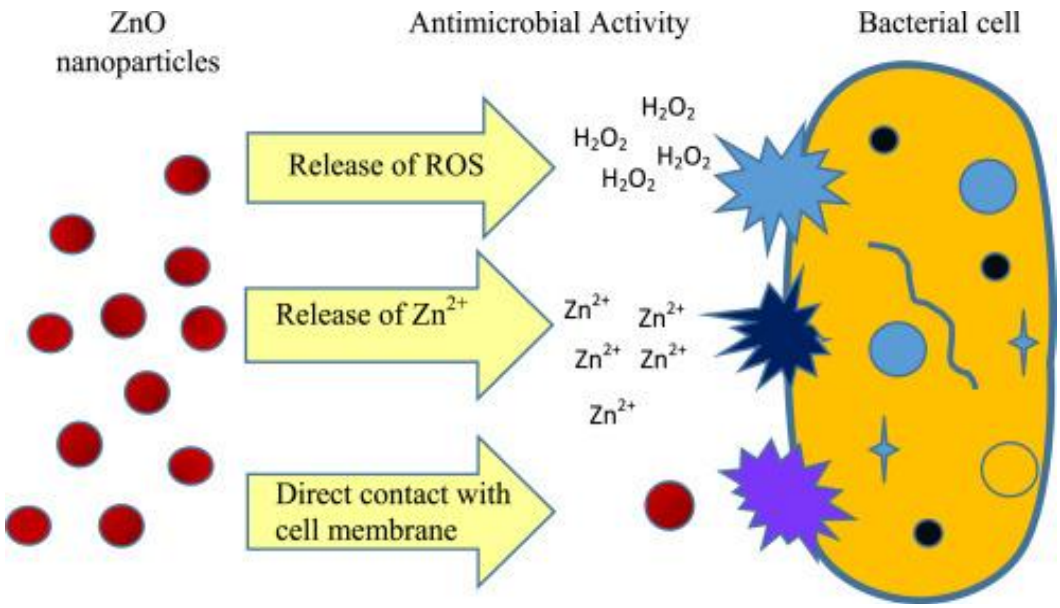

Fig. 2: - ZnO Nanoparticles disinfection mechanism (source Dimapilis et al 2018).

Another feasible "mechanism for the ZnO antibacterial activity is the release of Zn2+ ions which can harm the cell membrane and bore the intracellular contents. In the experiment by Li et al,[13] on the physicochemical characterization and antibacterial tests of ZnO nanoparticles in five media, it was proposed that toxicity of Nano-ZnO against Escherichia coli was associated mainly to the released Zn2+ ions. Likewise, according to Kasemets et al.[14] The toxicity of ZnO nanoparticles against Saccharomyces cerevisiae could result from the solubility of the Zn2+ ions in the microorganism-containing medium".

"According to Heinlaan et al.[15] cell injury does not necessarily appear from the entry of the metal oxide particles into the cell. More importantly, it's the contact between the bacterial cell and the particle which causes changes in microenvironment within the contact area of the organism and particle. Brayner et al.[16] also revealed that after contact with ZnO nanoparticles, bacterial cell walls were damaged and disorganized. The abrasive ZnO caused enhanced membrane permeability leading to consequent cellular internalization of the nanoparticles".

A residue-free green synergistic antifungal nanotechnology for pesticide thiram by ZnO nanoparticles

The research revealed that "0.25 g/L ZnO nanoparticles (NPs) with 0.01 g/L thiram could hinder the growth of fungus in a synergistic mode". "More importantly, the 0.25 g/L ZnO NPs completely degraded 0.01 g/L thiram under simulated sunlight irradiation within 6 hours. It was demonstrated that the formation of the ZnO-thiram antifungal method, electrostatic adsorption of ZnO NPs to fungi cells, and the cellular internalization of ZnO-thiram composites performed important roles in synergy. Oxidative stress test indicated ZnO-induced oxidative damage was enhanced by thiram that finally results in a synergistic antifungal effect. By decreasing the pesticides usage, this nanotechnology could control the plant disease economically, more significantly, the following photocatalytic degradation of pesticide hugely benefit the human society by avoiding the negative impact of pesticide residue on public health and environment" Fig 3.[17]

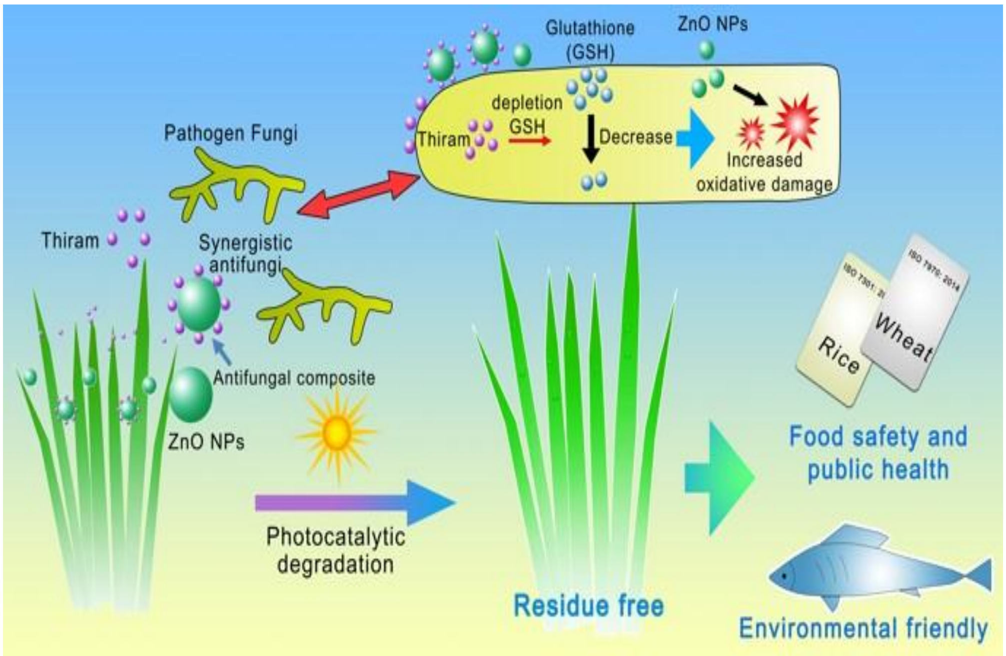

Fig. 3:- "Schematic diagram of residue-free green nanotechnology enhanced the pesticide efficiency and ensured food safety and public health". (source Xue J et al 2014).

Damaging or toxic effects of zinc oxide nanoparticles

Nanoparticles of zinc oxide can perform a significant role in improving "the growth along with yield of plants, but now studies regarding the toxic effects of Nano Particles continue headed for increase with time and only fewer "studies have accompanied to determine toxic effects of Zinc Oxide NPs on plants"[18,19] A study was conducted "on seed development and root growth of some plant species like (rape, radish, ryegrass, cucumber, corn, and lettuce) the harmfulness of five types of Nano Particles (aluminium, alumina, multiwalled carbon nanotubes, and zinc oxide") exposed that sprouting of seed in common, is not affected but elongation of root was inhibited in majority cases. "The IC50 of ZnO Nano Particles was assessed to be about 50 mg/L for radish and about 20 mg/L for rape and ryegrass.

The biomass of ryegrass was significantly reduced, root tip was shrunken and root epidermal as well as cortical cells became highly vacuolated and collapsed when toxicological studies of ZnO NPs were done ryegrass. Most of the ZnO NPs remained adhered to the surface of the root and individual Nano Particles were observed to be existing in the protoplast and apoplast of the root. Some to none dissociated zinc ions were translocated to ryegrasses that are bare to ZnO nanoparticles".[20]

Though ZnO nanoparticles have excellent commercial significance and are already used in numerous "commercial products but the public is getting more concerned regarding the effects ZnO NPs on Environment. Unfortunately, toxicological studies" conducted on ZnO NPs in the past decade reveal that ZnO nanoparticles possess possible danger to the environment as well as human health. Zinc oxide Nanoparticles impose severe toxicity to freshwater microalga, bacteria, mice, Daphnia Magna, and even human cells.[21,16,22]

CONCLUSION

Nanotechnology is one of the emerging technology of the present century operating in the fields of science and technology. “ZnO NPs view out as most the versatile materials, due to their” various properties, applications, and functionalities. ZnO nanoparticles have enormous optical and physical qualities. They also have antimicrobial properties against several fungus and bacteria’s. Regarding the “synthesis of zinc oxide nanoparticles, they can be synthesized by” various chemical techniques but due to green chemistry evolution, biological production of ZnO Nanoparticles “is also possible by using different plant extracts, the plant synthesis of Zinc Oxide NPs is much” more harmless and environment friendly when compared to other chemical syntheses as it doesn't lead to the development of toxic by-product chemicals. As for “their usage is concerned nanoparticles show a substantial part in agriculture”, for that ZnO NPs colloidal solution is used in Nano-fertilizers. The implementation of “these NPs to crops shows increase in their growth as well as yield. As the demand for food is increasing” every day but the yield of essential food crops is significantly low. So, it’s a necessity of the current situation to commercialize ZnO nanoparticles to provide sustainable and stable agriculture.

Future aspects

Concerning the future aspects regarding ZnO nanoparticles, we can say that although there are many reports regarding ZnO nanoparticles with different sizes and shapes, it will still lack the “quality synthesis in terms of crystallinity, size, and sphericity of the” particle and not using the organic solvents (which may limit “its possible application in biomedical sciences”). ZnO NPs that are required for cosmetic applications need to have non-photocatalytic activity, that can be inhibited by uniform coating of ZnO NPs surface via silica or any other molecules plus its toxic effects to human skin is one of the main apprehension. The utilization of ZnO NPs in biological field needs fine-quality ZnO NPs in watery solution with neutral pH along with physiological temperature as biomolecules known to have highly sensitivity regarding the changes in pH along with temperature. Other than, comparatively small in size, its ease of transport within tissues, organs and the ability to cross plasma membranes, and can potentially target the biologically active molecules can help in facilitating the biomedical implementation of nanoparticles in the medicine field. To bring out the best capabilities of zinc oxide nanoparticles we need to better understand the relationship between shape, size, and structure of zinc oxide nanoparticles at a conceptual level and only after that we will be able to tune its capability for the agricultural field, medical field and study its chemical and electronic interaction with biomolecules.

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