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APPLICATIONS OF GREEN NANO MATERIALS AND ITS IMPORTANCE – A REVIEW

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Abstract: Nanotechnology is a new and emerging technology with wealth of applications. It involves the synthesis and application of materials having one of the dimensions in the range of 1–100 nm. A wide variety of physico–chemical approaches are being used these days for the synthesis of nanoparticles (NPs). However, biogenic reduction of metal precursors to produce corresponding NPs is eco-friendly, less expensive, free of chemical contaminants for medical and biological applications where purity of NPs is of major concern. Plants materials or extracts contains lots of inherent phytochemicals, which will further act as reducing agents for the source chemical in nano particles production chain. Present review focuses on plants based green synthesis of Ag, Au, Cu, Fe, Pd, Ru, PbS, CdS, CuO, CeO2, Fe_3O_4, TiO_2, and ZnO NPs and their potential applications. Nano particles are very useful in the field of food industries and pharmaceutical industries, lots of green synthesied nano materials are used effectively in drug delivery and its manufacturing for treatment in medical sciences. It is a broad sector, where it can be used in a very effective manner in almost all sectors.

***Index Terms* - Agriculture; Green; Health; Nano material; Pharmaceutical**

I. INTRODUCTION

Nanoparticles (NPs) having one of the dimension in the range of 1–100 nm act as a bridge between bulk materials and atomic or molecular structures (Kaushik *et al.* 2010). They have notable and interesting properties owing their small sizes, large surface area with free dangling bonds and higher reactivity over their bulk cousins (Zharov *et al.* 2005). Since, from the previous study, the nineteenth century scientists have been well attentive of the ability of biological entities to reduce metal precursors but the mechanisms are still unfamiliar. The progress of efficient green synthesis utilizing natural reducing, capping and stabilizing agents without the use of toxic, expensive chemicals and high energy consumption have attracted researchers towards biological methods (Mukherjee *et al*. 2001). Rapid industrialization, urbanization and population explosion are resulting in deterioration of earth atmosphere and a huge amount of hazardous and superfluous substances are being released. Furthermore NPs are widely applied to human contact areas and there is a growing need to develop processes for synthesis that do not use harsh toxic chemicals.

However, these methods are capital extensive with many problems including use of toxic solvents, generation of hazardous by-products and the blemish of the surface structure. Chemical methods are generally composed by more than one chemical species or molecules that could augment the particle reactivity and toxicity and might harm human health and the environment due to the composition ambiguity and lack of predictability (Li *et al*. 2011).

The particles produced by green synthesis differ from those using physico–chemical approaches. Biological entities possess a huge potential for the production of NPs. Biogenic reduction of metal precursors to corresponding NPs is eco-friendly (Jayaseelana *et al*. 2012), sustainable (Gopinath *et al*. 2014), less expensive (Mittal *et al*. 2013) and can be used for bunch production (Iravani 2011). Moreover, the biological production of NPs allows recycle of expensive metal salts like gold and silver contained in waste streams. These metals have limited resources and have fluctuating prices (Wang *et al.* 2009). We may get green NPs with the required properties. The biological molecules, mostly proteins, enzymes, sugars and even whole cells, that stabilize NPs easily allow NPs to interact with other bio molecules and thus increase the antimicrobial activity by improving the interactions with microorganisms (Botes and Cloete 2010). Biogenic silver NPs when compared to chemically produced NPs showed 20 times higher antimicrobial activity (Sintubin *et al*. 2011).

II. PRINCIPLES OF GREEN BIOSYNTHESIZED CHEMISTRY

1. Prevention: It is better to put off waste than to treat or clean up waste after it has been created. In green synthesis we can easily control the waste and toxic substances.

2. Atom Economy: Synthetic methods should be designed to make the most of the incorporation of all materials used in the process into the final product. We can concise the atom utility.

3. Less Hazardous Chemical Syntheses: Compared to synthetic methods, Green methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals: Chemical products should be designed to affect their desired function while minimizing their toxicity in this method.

5. Safer Solvents and Auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) is not commonly used in green synthesis.

6. Design for Energy Efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.

7. Use of Renewable Feedstock's: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Reuse property of this method.

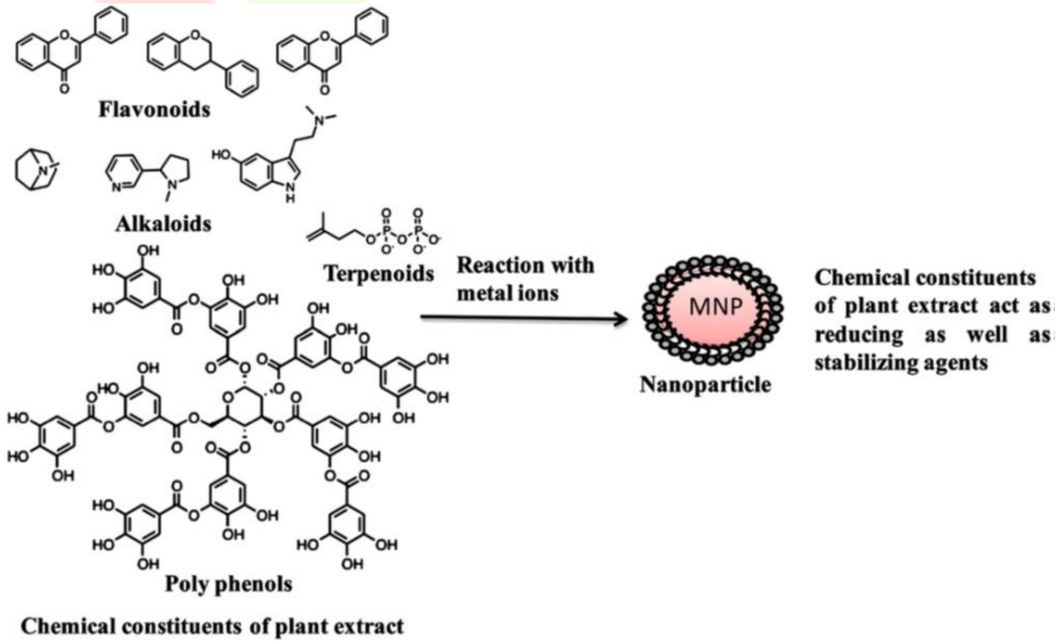
8. Reduce Derivatives: Unnecessary derivatives (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Aim for Degradation: Chemical products should be designed so that at the end of their function they break down into inoffensive degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.



Scheme 1- Possible chemical constituents of plant extract responsible for the bio reduction of metal ions

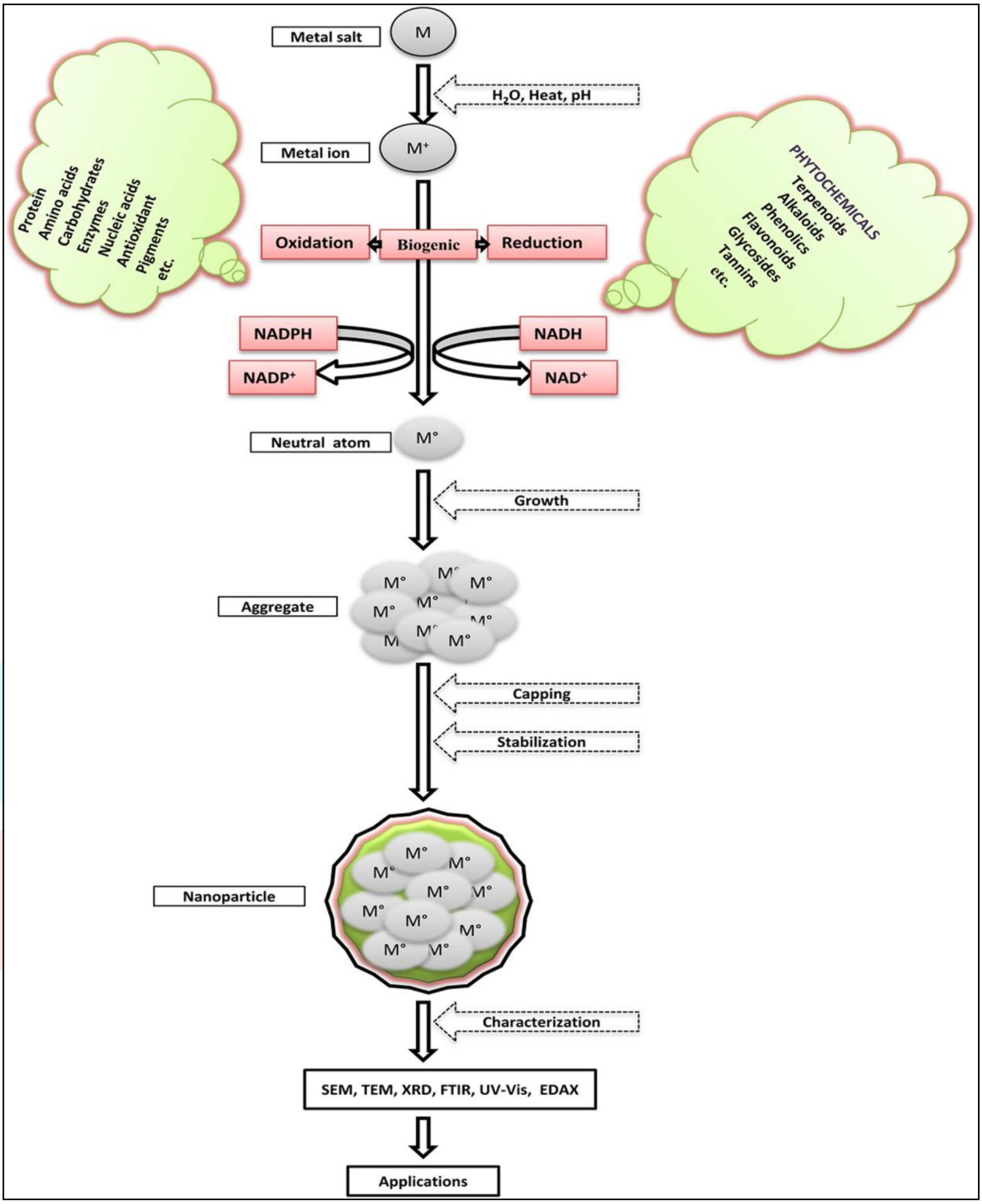


Fig-1 Diagram summarizing the possible mechanism of biologically mediated synthesis of nanoparticles, M metal salt, M^+ Metal ion, M^0 neutral atom. (Hussain *et al.* 2016)

III. UPTAKE, TRANSLOCATION, AND ACCUMULATION OF GREEN NANOPARTICLES IN THE PLANT PARTS

Uptake, translocation, and accumulation of NPs depend on the plant species and the size, kinds, chemical composition and stability of the NPs. Majumdar *et al*. (2011) have been demonstrated the uptake, biotransformation and translocation of various NPs by a model plant.
Whitby & Quirke (2007) reported the interaction of ryegrass with NPs in scanning electron microscopy studies confirmed the adsorption and aggregation of the NPs on the root surface and in TEM images of root cross-sections of the ryegrass also showed the presence of particles in the apoplast, cytoplasm and nuclei of the endodermal cells.
Zhu *et al*. (2008) reported the uptake of Fe_3O_4 NPs by pumpkin seedlings in hydroponic culture. NPs were detected in roots, stems, and leaves of the plants. It suggested that the uptake of the NPs depends on the growth medium this may be due to the adherence of the Fe_3O_4 NPs to the soil and sand grains. *Cucurbita pepo* when treated with Ag NPs, the Ag concentration in the plant shoots was found to be 4.7 times higher in the plants than those treated with bulk Ag powder exposed to 10– 1000 mg L^{-1} Ag NPs .

1. GREEN NANOPARTICLES AS GROWTH PROMOTER

In recent years, the researchers have reported the effects of NMs on germination and growth with the goal to promote their use of agricultural applications. Interaction of NPs with plants caused various physical and physiological changes, depending on the properties of NPs. Effectiveness of NPs depends on their concentration and it varies from plant to plant Efficiency of NPs is determined by their chemical composition, size, surface area, reactivity, and the concentration at which they response positively. NPs have both positive and negative effects on plant growth and development. However, this review deals with the positive roles played by NPs on seed germination, photosynthesis and plant growth.

1.2 EFFECT OF CARBON NANOMATERIALS ON PLANTS

Among the NPs, carbons NMs have acquired a noteworthy place due to their unique mechanical, electrical, thermal and chemical properties. Seeds when exposed to MWCNTs, seed germination and vegetative biomass increased significantly. Some author of various study hypothesized that penetration of the cell wall by NPs leads to the increase in water uptake by seeds which enhanced germination percentage.
Sriniwasan and Sarawathi (2010) reported that the single walled-CNTs (SWCNTs) act as nanotransporters for liberation of dye molecules and DNA into plant cells. In another report MWCNTs enhanced efficiency of water uptake as well as Ca and Fe nutrients uptake which increased the seed germination and plant growth.

1.3 EFFECT OF METAL NANOPARTICLES ON PLANTS

The studies suggest that metal NPs increase plant growth and development. AgNPs increased the root length in maize and cabbage plants in comparison with $AgNO_3$ (Pokhrel & Dubey, 2013). Au NPs influenced the number of leaves, leaf area, plant height and sugar and chlorophyll content that result in better crop yield (Arora *et al*, 2013). Au NPs have a momentous role on seed germination and antioxidant system in *Arabidopsis thaliana* (Kumar *et al*, 2013). Au NPs enhanced seed germination in *Boswellia avalifoliata* (Savithramma *et al*, 2012). Spinach seeds soaked in a solution of Ti NPs increased fresh and dry weight as well as contents of total N, chlorophyll and protein in leaves. More than two fold increases in height and fresh weight of duckweed was found when treated with Ti NPs at 0.5 gL^{-1} conc (Song *et al*, 2012)

1.4 EFFECT OF METAL OXIDE NANOPARTICLES ON PLANTS

A large number of studies on the effects of metal oxide NPs on germination and growth of plants have been documented. Nanosized TiO_2 promoted plant growth when seeds were soaked in NPs or sprayed with NPs (Zheng *et al*, 2005). Parsley seeds exposed to nano anatase, enhanced germination, root and shoot length and chlorophyll content of the seedling. The germination rate of salvia improved when the seeds were treated with TiO_2 NPs (Feize *et al*, 2013). Mixture of TiO_2 and SiO_2 NPs improved the nitrate reductase activity and stimulated the antioxidant system in soybean. In spinach, chlorophyll formation, photosynthesis and plant dry weight increased when exposed to TiO_2 NPs (Zheng *et al*, 2005). Root elongation was promoted at a particular concentration of ZnO NPs in soybean. Iron oxide NPs enhanced root elongation in pumpkin. In another experiment iron oxide NPs increased soybean pod and leaf dry weight (Wang *et al*, 2010). ZnO NPs promoted seed germination root and shoot length in the peanut plant. Plant growth and development improved by nano SiO_2 by increasing photosynthetic rate, transpiration rate, electron transport rate and other physiological parameters. *Cyamopsis tetragonoloba* when exposed to ZnO NPs, improved plant biomass, root and shoot length, chlorophyll and protein synthesis and other growth parameters. TiO_2 NPs increased plant growth by promoting chlorophyll formation and activities of Rubisco. According to Gupta and Tripathi (2011) TiO_2 NPs may be used for decomposition of organic compounds and production of H_2 as a fuel 58.2 and 69.8% increase in fresh and dry weight and significant increase in chlorophyll content, photosynthetic rate and Rubisco activity was recorded in Spinach when treated with anatase TiO_2 NPs ((Lingnel *et al.* 2008).
According to Singh *et al.* (2015) RuO_2 NPs enhanced the germination and early growth of the *Brassica* sps. The growth stimulating function of NPs on plants seems to be significant. Sincere field research is needed to study, promoting effects of these NPs on yields of some important crops. The mode of action of these NPs by which they take part in the growth and development of plants must also be explored.

2. GREEN NANOPARTICLES IN DISEASE SUPPRESSION IN PLANTS

Viruses, bacteria, fungi and nematodes are mainly responsible for plant diseases resulting in decreased yield and poor quality of plant products. Various approaches to manage crop disease are being used including genetic breeding, cultural schemes with sanitation, host indexing, enhanced eradication protocols, new pesticide products, and integrated pest management.

Several studies have reported that NPs can be used to suppress pathogens which increased crop growth. Jo *et al.* (2009) reported that Ag NPs in 200 mg/l conc. reduced 50% colony formation of pathogenic fungi that caused disease in ryegrass. Lamsal *et al.* (2011a) have also reported that application of Ag NPs improved the disease suppression. Combined activities of Ag NP with the fungicide flucanazole were found to be effective against *Candida albicans,* followed by *Phoma glomerata* and *Trichoderma* sps (Gajbhiye *et al,* 2009). ZnO NPs reduced growth by 26% of *Fusarium graminearum* grown in vegetables broth agar. MgO NPs exhibited significant antimicrobial activity due to strong interaction with a negative surface of bacterial membranes (Huang *et al*, 2005). Scientists showed effective concentrations for inhibition of colony formation by silver compounds on *Bipolaris sorokiniana* was greater than that on *Magnaporthe grisea*. Silver compounds inhibited colony formation of *B. sorokiniana* by 50% at optimum concentration. Significant reduction in mycelial growth was observed from spores incubated with silver NPs. Silver NPs greatly reduced the number of germinating fragments relative to the control at 24 hour incubation of spores with a 2.5 ppm solution of NPs.

3. GREEN NANO PLANT TISSUE CULTURES

Plant tissue cultures are the core of plant biology, which is important for conservation, mass propagation; genetic manipulation, bioactive compound production and plant step up. In recent years, the application of nanoparticles (NPs) has productively led to the removal of microbial contaminants from explants and demonstrated the positive role of NPs in callus induction, organogenesis, somatic embryogenesis, somaclonal variation, genetic transformation and secondary metabolite production. Finally, future prospects through the involvement of not merely Ag, TiO_2, and ZnO NPs, but more recent innovations such as graphene, carbon nanotubes, SiO_2, quantum dots, and dendrimers are proposed. The undisclosed shadows hanging in the background, including the repercussions of using nanomaterials without proper awareness, as well as dosage-based adverse effects and nanotoxicity aspects, are highlighted. The need for more research in the pursuit of discrete answers to unresolved questions regarding mechanisms is emphasized as the key to real progress in plant nanobiotechnology.

4. GREEN NANOPSETICIDES AND NANOHERBICIDE IN PLANTS

Pesticides and herbicides are usually used in agriculture to get better crop yield and efficiency. But presently the negative aspects of conventional pesticides and herbicides on environment are under argument. The main disadvantages of pesticides are development of pathogen and pest resistance, decreases nitrogen fixation, reduces soil biodiversity, contributes to bioaccumulation of pesticides, pollinator decline and destroys habitat for birds .Therefore, use of NPs resolve these problem to most extent, its application with herbicides reduces the amount of herbicides requirement for weed eradication. With the active ingredient and smart delivery system, herbicides are released in the soil according to the soil condition (Gruere *et al,* 2011).

Green synthesis of silver nanoparticle of *Tinospora cordifolia* showed maximum cidal effect against the head louse *Pediculus humanus* and fourth instars larvae of *Anopheles subpictus* and *Culex quinquefasciatus* (Jayaseelan *et al*, 2010). Recently, researcher has concluded that nano-agrochemicals are generally nano reformation of existing pesticides and fungicides. Probably the nanoformulations are expected to enhance the solubility of poorly soluble active constituents, release the active constituents in a targeted fashion and resists premature degradation. Nanopseticides significantly controlled delivery of pesticides, low chemical dose and high positive results. Silver NPs at 100 mg/ kg reduced mycelial growth and conidial germination on cucurbits and pumpkins against powdery mildew. Phenolic suspensions of hydrophobic alumina-silicate NPs are significantly effective against grasserie disease in *Bombyx mori* leaves (Gowswami *et al,* 2010). It is also reported that Nano encapsulated pesticides are adsorbed on plant surface, helps in sustained release for longer time as compared to conventional pesticides that washed away in the rain.

Conventional methods to control the pathogens and pests have adverse effects on both the environment and economy of farmers. Therefore the NPs applications are gaining ever escalating demand for sustainable agriculture without disturbing the environment.

The studies conducted under non-sterile conditions make it clear that the increase in crop growth/yield is the result of reduced disease presence. This is possible either from the anti-pathogenic activity of the NP itself, or indirectly through the induction of key defensive pathways and metabolites within the plant.

5. GREEN NANOFERTILIZERS

Nanofertilzers are the NMs which can provide nutrients to the plants or they assist to augment the activities of conventional fertilizers. Replacement of Nanofertilzers for traditional fertilizer is beneficial as its application is to release nutrients into the soil steadily and in a controlled way, thus prevents water pollution.

Hydroxyapatite ($Ca_5(PO_4)_3OH$) NPs of 16 nm in size, synthesized by Liu and Lal (2014) exhibited fertilizing effect on soybean and other vegetable crops. There are so many reports where application of Nanofertilzers reflects positive effect in terms of good crop yield as well as environmental pollution. The application of NPs increased the growth rate and seed germination by 33% and 20% respectively, compared to regular P fertilizer. The result indicated that the roots of soybean can absorb hydroxyapatite NPs as an effective P nutrient source. Soil amended with metallic

Cu NPs significantly increased 15 day lettuce seedling growth by 40% and 91% respectively Shah & Belozerova, (2009). Some studies focused on the characteristics of NPs also revealed that NPs can enter plant cells and transport DNA and chemicals inside the cell. These studies provide a platform on which we can assume that NPs can also deliver nutrients to the plants as fertilizers. The nano-organic iron chelated fertilizers demonstrated high absorption, increase in photosynthesis and expansion in the leaf surface area. Moreover, Nanofertilzers have great impact on the soil as Nanofertilzers can reduce the toxicity of the soil and decrease the frequency of fertilizer application. Scientists reported that in Nanofertilzers, nutrients can be encapsulated by NMs, coated with a thin protective film or delivered as emulsions or NPs.

Gliricidia sepium nanocomposite exhibited a slow and sustained release of nitrogen over time at 3 different pH values (Koteegoda *et al*, 2011). Studies reported that nonporous zeolite used on N fertilizer might be used as alternate strategy to enhance the effectiveness of N used in crop production system.

Nanofertilzers due to their characteristic features have great role in sustainable agriculture. Thus from the above mentioned findings we can articulate that the use of Nanofertilzers leads to an increased efficiency of the micro and macro elements, reduces the toxicity of the soil and reduces the frequency of application of conventional fertilizers.

6. NANOBIOSENSORS

NPs can be used as a diagnostic tool for detection of plant pathogens. However, this research is in initial stage in agriculture. NPs sometime used as an investigative tool to detect compounds which could be indicator of disease. Fundamentally biosensor is derived from the coupling of a ligand-receptor binding reaction to a signal transducer. It consists of a probe, bio receptor and transducer. The interaction of analyte with bio receptor is designed to produce an effect measured by transducer, which converts the information into electrical signal. Lopez *et al.* (2009) reported that nano-chips are known for detecting single nucleotide changes of bacteria and viruses. Yao *et al.* (2009) used fluorescence silica NPs in combination with antibody to detect this microorganism showing potential of NPs in disease detection. Research on nanosensors for detecting pathogens, is yet to be explored specially for its field application. It would be highly valuable for diagnosis and disease management. Nanosensors dispersed in the field can detect the presence of plant viruses, other crop pathogens and the level of soil nutrients. Previous studies reported that nano smart dust i.e. tiny wireless sensors and transponders can evaluate environmental pollution quickly. Insects, disease, pathogens, chemicals and contaminants can be rapidly detected by portable nano devices and results in faster treatment. Nanotechnology based devices will increase the use of sensors for real time monitoring of crops.. It is now clear that nanobiosensors can be effectively used for sensing a wide variety of fertilizers, herbicides, pesticides, insecticides, pathogens and thus can support sustainable agriculture by enhancing crop productivity.

7. GREEN NANO PARTICLES IN FOOD INDUSTRIES

Food nanotechnology has infiltrated into many aspects of customer products, such as food packaging, additives, and food preservation. The recognition of this novel technology has advanced the food processing and storage in ensuring food safety. Many conventional chemicals added as food additives or packaging materials have also been found partially existing at nanometre scale. For example, food-grade TiO_2 NPs now have been found up to approximately 40% in the nanometre range. Although nanomaterials like TiO_2 NPs are generally recognized low toxic at ambient conditions, long-term exposure to such nanomaterials may cause adverse damages. Peter *et al.* (2016) investigated the chemical and microbiological characteristics of white bread during the storage in paper packaging modified with Ag/TiO_2-SiO_2-NPs. The results showed good water retention and prolonged shelf-life of bread for 2 days compared to the unmodified packaging.

8. PHARMACOLOGICAL AND BIOMEDICAL APPLICATIONS OF GREEN NMS

Being super paramagnetic in nature, iron and iron oxide NPs find extensive usage in biomedical applications. Au NPs have proved to be important tool in many potential biomedical applications including an emerging alternative for life-threatening diseases, DNA modelling and biosensor applications, especially in cancer nanotechnology. Nanoparticles have proved to be a likely candidate for antimicrobial agent. AgNPs is a suitable promising agent to inhibit the growth of cancer cells via various mechanistic approaches; the hypothetical mechanism.The plant derived chemical constituents such as quinine; artemisinin and aromatic compound have been successfully used against resistant strains of malaria parasites. Anti-inflammation is a cascade process that produces immune responsive compound.

The bio based nanoparticles are new and revolutionized to treat malignant deposit and without interfering the normal cells. Suman, *et al.* (2013) reported that the green synthesis of silver nanoparticles exhibited a significant cytotoxic effect in HeLa cell lines compared to other chemical based synthetic drugs.

IV Conclusions and Future Prospective

Production of NPs using extracts from natural substances is emerging as an important area in nanotechnology. The use of natural resources for production of NPs is sustainable, eco-friendly, inexpensive and free of chemical contaminants for biological and medical applications where purity of NPs is of major concern. Useful and common nanomaterials can be produced easily on large scale. The biological methods do not need harsh or toxic chemicals. The waste products of plant extracts are non toxic and easier to dispose off. Furthermore, NPs synthesized via green route are more stable and effective in comparison with those produced by physico–chemical methods. The majority of greener synthetic efforts reported earlier are dedicated to Ag and Au NPs, which may be due to their importance in disinfection science. This report devoted to several other metals and its oxides NPs viz. Fe, Pd, Ru, PbS, CdS, CuO, CeO_2, TiO_2, and ZnO NPs synthesized by biological methods which have imperative roles in human welfare. A considerable number of efforts have been taken in order to obtain secondary metabolites from the extract of natural products which may act as reducing, stabilizing and capping agents in the synthesis process of nanomaterials. The nature of biological entities in different concentrations with combination of organic reducing agents influences the size and shape of NPs. The most of these investigations have been carried out in research laboratories in small scale but researchers are engaged to explore the potential and application of NPs at large scale in agricultural field, environment, health science and many more to fulfil the future demands of growing population of world and to provide best service for human welfare.

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