Green synthesis of metal nanoparticles using plants

Science, Biology

Metal nanoparticles have immense uses in various fields of science. The traditional methods of their synthesis are expensive and harmful to environment, thus there is growing interest of researchers in " green" synthesis of metal nanoparticles using plants. Plants are most suitable candidate amongst all organisms as they offer synthesis of stable nanoparticles and variety in shape and size of nanoparticles. This review sheds light on use of plants in synthesis, mechanism, factors affecting, and prospective applications of such biologically produced nanoparticles.

Introduction

" Nanotechnology is the art and science of manipulating matter at the nanoscale to create new and unique materials and products with enormous potential to change society." It is the application of technology to control matter at molecular level. In recent times it is gaining much importance in areas like chemical industry, drug-gene delivery and biomedical sciences i. e. it plays important role in all major technologies. Nanoparticles, in particular are becoming popular because of following attributes: small size large surface to volume ratio. Physical, chemical, optical and electrical properties of theses nanoparticles depend upon size, shape and surface morphology. Nanoparticles have applications in various fields like biological imaging, cell labeling, antimicrobial agents, anticancer nanodrugs, nanocomposites, hyperthermia of tumors and drug delivery. Nanoparticles are produced by using various physical and chemical methods which are costly, labor intensive, and potentially hazardous to the environment. Over the last two decades there has been growing emphasis on adopting a green synthetic approach because it has following advantages: environmentally friendly, lower cost of production, short production time, efficient and without the use of harsh, toxic and expensive chemicals.

Important aspects to be considered in synthesis of metal nanoparticles

Selection of the best organisms: The organism used for this purpose range from simple prokaryotes to complex eukaryotes. Intrinsic properties of the organism like enzyme activities and biochemical pathways are considered while choosing the best candidate. Plants are best choice for nanoparticle synthesis because they have amazing potential in heavy metal accumulation and detoxification.

Optimal conditions for cell growth and enzyme activity: Growth conditions have an undeniable effect on the synthesis process. Inoculum size, light, temperature, pH, mixing speed and nutrients should be optimized.

Optimal reaction conditions: For synthesizing metal nanoparticles on industrial scale, the yield and the production rate are important issues to be thought upon. Bio reduction conditions in the reaction mixture are needed to be optimized. The substrate concentration. The bio catalyst concentration, pH, exposure time, temperature, buffer strength, mixing speed and light need to be controlled and optimized. Researchers use complementary factors like visible light or microwave irradiation and boiling which could affect the size, morphology and rate of reaction.

Solvent medium: Presently H_2O is used as a benign solvent [environmentally friendly] throughout the preparation. Although the use of alternative solvents such as supercritical CO_2 has been successful for the synthesis of nanoparticles, the use of CO_2 –philic surfactants presents difficulty in isolation and recovery of the nanoparticle.

Reducing material: About 75% of methods use reducing agents such as hydrazine, sodium borohydride [$NaBH_4$], and dimethyl formamide [DMF]. But these are highly reactive and hazardous to environment. Currently β-D-glucose is used as the reducing agent. It is a mild, renewable, inexpensive and nontoxic reducing agent.

Capping material: They are used to protect and passivate nanoparticle surface. Choice of capping material depends upon the required size ranges and morphologies of the nanoparticles. Starch is selected as the capping material for several reasons like starch can form dispersion avoiding the use of organic solvents, protection is easily reversible at relatively higher temperatures, it is possible to use place exchange reactions.

The mechanism of metal nanoparticles synthesis in plants

Synthesis of metal nanoparticles synthesis in plants and plant extracts includes three main phases.

The Activation phase – during this phase the reduction of metal ions and nucleation of the reduced metal atoms occur.

The Growth Phase – during this phase the small adjacent nanoparticles spontaneously coalesce into particles of larger size, it is the direct formation of nanoparticles by means of heterogenous nucleation and growth, and further metal ion reduction, this process is often referred to as Ostwald ripening, this is accompanied by increased thermodynamic stability of nanoparticles.

The TerminationPhase – this phase determines the final shape of nanoparticles. In the termination phase, nanoparticles acquire the most energetically favorable conformation. This process is influenced by the ability of plant extract to stabilize metal nanoparticles. This can be understood by taking in account an example of nanotriangles; they have a very high surface energy, which makes them less stable, and if the stability of nanoparticles is not supported in given extracts, then the nanotriangles will acquire a more stable morphology like truncated triangle, so as to minimize the Gibb’s free energy.

Factors affecting the formation of metal nanoparticles in plants

As we know reduction process is associated in metal nanoparticle synthesis. This particular process is affected by various reasons; major one being the nature of plant extract that contains active biomolecules in different concentrations and combinations. Other factors include the pH of the reaction mixture, reaction time, incubation temperature and electrochemical potential of the metal ion.

Effect of pH – There is change in charge of the natural phytochemicals present in the extract with change in pH, this affects their ability to bind and reduce the metal ions, which in turn affects the shape size and yield of nanoparticles. Taking an example of Avena sativa [common oat] in which more numerous small-sized gold nanoparticles were formed at pH 3. 0 and 4. 0, in contrast to formation of more aggregated nanoparticles formation at pH 2. 0. In pears, hexagonal and triangular gold nanoplates are formed at alkaline pH, whereas as nanoparticles do not form at acidic pH.

Effect of temperature – Temperature also have manifolds effects in synthesis of nanoparticles. Generally, increased temperature leads to increased reaction rate and efficiency of nanoparticle synthesis. It was found that triangular silver nanoparticles in alfalfa plants [M. sativa] formed only at temperatures above 30°C. Increase in reaction temperature in lemon verbena extracts caused increase in efficiency of reduction of silver ion. It is assumed that elevation in temperature increases the nucleation rate. In Cassia fistula [golden shower tree] change in temperature changed the structural form of the synthesized nanoparticles; silver nanoribbons are predominantly formed at room temperature, whereas silver particles were mainly formed at temperatures above 60°C. Here it is believed that interaction of phytochemicals with nanoparticle surface is altered with higher temperature which inhibits the incorporation of adjacent nanoparticles into the nanoribbons.

Effect of proteins present in plant extracts – Tryptophan and amino acids such as tyrosine, arginine, and lysine have superiority in ability to reduce metal ions. However, a polypeptide composed only of tryptophan residues is very less effective than a polypeptide that is mixture of tryptophan molecules interspersed with other nanoparticles. This is likely due to strong binding of the reduced ion, which in turn inhibits further reduction. Peptides that are composed of amino acids that weakly bind tetrachloroauric acid ions, such as glutamic acid or aspartic acid are inefficient in synthesis of nanoparticles because of rapid dissociation of the peptide- metal ion complex. Thus, the peptides in which reducing and strongly binding amino acids residues [e. g., tryptophan] alternate with weakly binding amino acids that act as an up regulator are most suitable for synthesis of metal nanoparticles.

Metal nanoparticles synthesis using whole plants

Plants show great potential in heavy metal accumulation and detoxification. The natural phenomenon of heavy metal tolerance of plants has interested the researchers to investigate the related biological mechanisms as well as physiology and genetics of metal tolerance in hyperaccumulator plants.

Disadvantage of using whole plants

The size and shape of nanoparticles depend upon their localization in plant. Different tissues have different metal ion concentration and subsequent possibility of nanoparticle movement and penetration; this in turn affects the localization process. These factors could affect the level of metal deposition around existing nanoparticles and the nucleation process. In applications where specific, finely tuned sizes and shapes are required, the use of nanoparticles produced from whole plants could be hindered because of differences in their morphology and size. Also, efficient extraction, isolation and purification of nanoparticles from plant material is a difficult and a problematic procedure.

Metal nanoparticles synthesis using plant extracts

It is a fast and nontoxic method and a better alternative to using whole plants. It provides a better and easy control over the shape and size of nanoparticles as well as facilitates easy purification. Also, it is a much faster process because reaction proceeds instantaneously as the time required for the uptake and diffusion of metal ions throughout the plant is omitted. This in vitro approach is carried on by using extracts from a variety of acids and salts of metals, such as copper, gold, silver, platinum, iron and many others.

Extraction of metal nanoparticles produced using plants

Armendariz extracted the produced gold nanoparticles from inactivated tissues from wheat and oat biomass. He used cetyltrimethylammonium bromide [CTAB] and citrate in combination with sonication to transfer the nanoparticles from biomass into the aqueous solution. It was found that extraction with citrate was more successful than that with CTAB. TEM analysis of the extracted solution showed that gold nanoparticles of smaller radius were obtained at first and then larger nanoparticles were obtained. Various physicochemical methods like freeze thawing, heating processes, and osmotic shock have also been used for the purpose of extraction. Their limitation being the chances of interference with the structure of the nanoparticles. They may also cause aggregation, precipitation and sedimentation, these may change the shape, size and activity of the nanoparticles. Other method that could be used is the enzymatic lysis of the plant cells containing the nanoparticle, but it is an expensive method and could not be used in up-scalable and industrial production, also, rigid cell wall around plants makes the process difficult. Centrifugation can be used for the extraction and purification of extracellular nanoparticles, but it may cause aggregation of nanoparticles. It is observed that surfactants and organic solvents might be good candidate for extraction as well as stabilization of nanoparticles.

Prospective application of nanoparticles synthesized in plants

Although the green synthesis of nanoparticles is grabbing attention because of its advantages stated above, but its equivalence in terms of potential applications and production scalability with nanoparticles produced form chemical and physical methods are needed to be studied. Nanoparticles produced by traditional physicochemical methods have wider range of applications like the targeted delivery of drugs, molecular imaging, wastewater treatment, catalysis, biosensor development, coatings, cosmetics, as antiseptics and in cancer therapy. Whereas the nanoparticles produced from plant/ plant extracts by far have fewer practical applications. For example, silver nanoparticles produced using Tridaxprocumens [tridax daisy] extract had similar antimicrobial activity to equivalent nanoparticles synthesized by chemical or physical methods, like strong antimicrobial activity against E. coli, S. dysenteriae, and V. cholera. Other applications of biologically produced nanoparticles are as follows: Silver nanoparticles synthesized in plants show significant cytotoxic activity against various tumor cell lines. Silver nanoparticles synthesized in Iresineherbstii [Herbst's bloodleaf] were found to inhibit the survival and growth of HeLa cell lines, and silver nanoparticles produced using Euphorbia nivulia [leafy milk hedge] latex extracts are toxic to the A549 cell line of human lung cancer. Silver nanoparticles synthesized in Nerium oleander [oleander] display strong larvicidal activity against larvae of the malaria vector Anopheles stephensi.

In order to achieve greater efficiency and reduce side effects, these particles are functionalized with antibodies or peptides for the targeted action in certain tissues of the body. Cyamopsistetragonoloba[cluster bean] extracts were used to produce composite silver nanoparticles that acts as a biosensor to determine ammonia, which have potential application in agriculture and medicine.

Main query that arises is that whether the physical, chemical and biological properties of the nanoparticles synthesized from the plants different from the ones produced by traditional methods and what effect these differences have on the efficiency of nanoparticles application for specific practical problems. Organic ligands, proteins, polysaccharides, and polyatomic alcohols are absent in nanoparticles synthesized by physical and chemical methods, but present on the functionalized surface of the nanoparticles synthesized from plant extracts. Their presence increases the stability and may facilitate further attachment molecules like DNA and antibodies to nanoparticles.

Conclusion

Metal nanoparticles are produced by various physical, chemical and biological methods. Each method has its own advantages and disadvantages. General problems faced by all these methods are the stability, aggregation, control of crystal growth, morphology, size and size distribution and separation of produced nanoparticles. Nanoparticles produced from plants have following advantages: more stable in comparison to those produced by other organisms. Plants have better ability to reduce metal ions than fungi or bacteria. In green synthesis, only the cost of metal salts determines the bulk of the cost, whereas in the chemical synthesis, costs of both the metal salts and reducing agents constitute the cost synthesis; in case of plants, cost of reducing agents is omitted because plant extracts and plants themselves serve as reducing agent. Despite of all these advantages, there are certain limitations that are needed to be worked upon. There is much more to be investigated and researched in the field of nanoparticles. Further investigations might be upon optimization of reaction conditions; engineering e recombinant organisms for production of high amounts of proteins, enzymes, and biomolecules involved in synthesis and stabilization of nanoparticles. Genetic modification of plants with improved metal tolerance and accumulation capacity can increase the productivity of plants towards synthesis of metal nanoparticles. Schemes and processes needed to be developed for continuous production of nanoparticles using plants on large scale in a cost-effective manner.