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Green Synthesis And Characterization Of Metal Nanoparticles For Sustainable Applications

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Abstract:

Green synthesis of metal oxide nanoparticles (NPs) has gained significant attention due to its numerous advantages, including simplicity, cost-effectiveness, non-toxicity, and environmental friendliness. Utilizing natural resources such as plant extracts, microorganisms, and biodegradable materials, this approach offers a sustainable alternative to conventional chemical methods. The resulting nanoparticles exhibit excellent stability, functionality, and biocompatibility, making them highly suitable for various applications in medicine, environmental remediation, and catalysis. Additionally, green synthesis methods align with the principles of green chemistry, reducing the ecological impact of nanoparticle production. This study highlights the synthesis approaches, characterization techniques, and potential sustainable applications of green-synthesized metal nanoparticles.

Introduction:

Green Nanotechnology – An Introduction

Nanotechnology is the science of the structure of materials with sizes ranging from 1 to 100 nm in at least one dimension, as well as the production of nanomaterials. The ability to comprehend, create, and engineer materials, devices, and systems in the nanoscale range is critical to nanoscience and nanotechnology. Actually, nanotechnology is predicated on the premise that humans can manipulate matter at the atomic level [1]. Nanotechnology can now help to solve key sustainability challenges. With the march of time, science and technology is moving at a rapid speed while the environment is witnessing drastic changes. Thus, nanotechnology as a field has to be re-envisioned and reinterpreted with scientific rigor today. In the creation of a new field of scientific endeavor known as "Green Nanotechnology", the vision and challenge of environmental engineering science and nanotechnology are broadly merged [2]. The framework of green nanotechnology comprises the creation of nanomaterials, green engineering, green chemistry, indirect and direct environmental applications, as well as the fabrication of nanocatalysts, nanomembranes, and the greater release of harnessed energy. Nanotechnology for green innovation – green nanotechnology – attempts to develop products and processes that are safe, energy efficient, decrease industrial waste, and reduce greenhouse gas emissions. As a result, for the synthesis of nanoparticles green nanotechnology has gained popularity in recent years. Though there are immense challenges in the field of green nanotechnology, it surely opened windows of innovation for the continuance of science in years to come [3].

Nanoparticles:

Definition:

By definition, particles that vary from 1 nm to 100 nm in size in at least one dimension out of three, are considered as nanoparticles. The characteristics (biological, physical, and chemical) of nanoparticles alter at the atomic/ molecular level according to the size of this range, making these nanoparticles unique [4]. Metals and their oxides, non-oxide ceramics, silicates, organics, carbon, and polymers are all examples of materials that may be used to make nanoparticles. Nanoparticles come in a variety of morphologies, including spheres, tubes, cylinders, platelets and so on. These, on the other hand, are designed and customized expressly for the purposes they are utilized for [5]. Figure 1 depicts the diversity of nanoparticles based on their form, chemical origin, morphology, medium, surface modification, and state of dispersion. These are the characteristics that have made nanoparticles such a significant component of research in recent years.

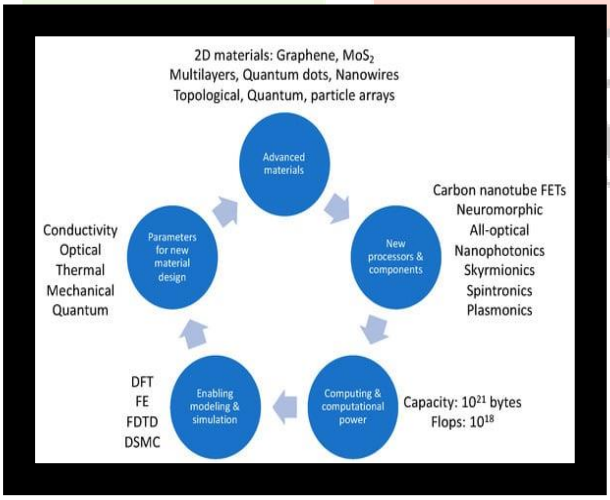

Figure.1.The diversity of nanomaterials

Nanoparticle Categories:

The classification of nanoparticles is based on several categories. Depending on dimension, there are zero dimensional nanoparticles – all dimensions are at nanoscale, i.e., no dimensions are greater than 100 nm, one dimensional nanoparticles – two dimensions are at nanoscale and the other is outside the nanoscale, two dimensional nanoparticles – one dimension is at nanoscale and the other two are outside the nanoscale, three dimensional nanoparticles – they are not confined to the nanoscale in any dimension. Based on origin and composition, nanoparticles are of two types including natural nanoparticles and synthetic nanoparticles. Ocean, dust, fine sand, volcanic ash is the common place to find natural nanoparticles. On the other hand, synthetic nanoparticles are carbon based, metal based (noble metal including silver, gold, etc.), inorganic (semiconductor nanoparticles like zinc oxide and titanium oxide) based precursors. Inorganic nanoparticles, on the other hand, have piqued the curiosity of researchers due to their many functionalities. Inorganic particles have also been shown to offer a significant potential for application as medical treatments and imaging instruments. Inorganic nanoparticles are also suitable for cellular delivery because they have useful properties such as high functionality, wide accessibility, the ability to administer targeted medications, good compatibility, and precise drug release [6]

Nanoparticle Applications:

Sensors, medical diagnostics, catalysts, magnetic recorder, biotechnology, high performance engineering materials, cancer therapeutics, drug delivery, conducting adhesives, and optics are only some of the potential scientific uses of metal oxide nanoparticles presented by scientists. Although nanoparticles cannot be utilized as a food additive, they may have uses in the food industry, such as food safety. Microbe-resistant textiles and non-biofouling surfaces are the most emerging nanomaterial application in the food industry. Nanoparticles have a hazardous effect on the environment because they leach into soil and water, yet it has been shown that they may be cleansed automatically by microbial protein interactions with NPs. For medication delivery systems, nanotechnology has produced a tailored solution. The materials employed in drug delivery systems must be able to bind the substance in question and be quickly digested or excreted through the regular excretory process. The nanoparticles have the capacity to recreate or mend damaged (injured) tissues by stimulating cell proliferation artificially utilizing nano-sized scaffolding and growth factors. Because of their enormous surface to volume ratio, nanoparticles might be used as a catalyst in a variety of applications, including fuel cells, catalytic converters, and photocatalytic devices. For example, TiO_2 NPs (anatase titanium dioxide nanoparticles) are employed as photo-catalysts and have the ability to convert hazardous organic dyes and CO_2 to non-toxic compounds [7-14].

Synthesis Approaches of Metal Nanoparticles:

In general, there are two ways to synthesize metal nanoparticles (MNPs), namely, top-down approach and bottom-up approach. The “Top-Down” procedures rely heavily on the generation of isolated atoms from bulk materials via various distribution mechanisms. Some of the fundamental techniques used in top-down manufacturing procedures include milling or attrition, repeated quenching, and photolithography [15]. The “Bottom-Up” techniques, on the other hand, begin with a metal salt precursor (dissolved in a solvent) that is reduced in a chemical reaction, and the NPs are created by a nucleation process, followed by cluster formation [16]. A comparative schematic view of the both approaches is illustrated in the figure.

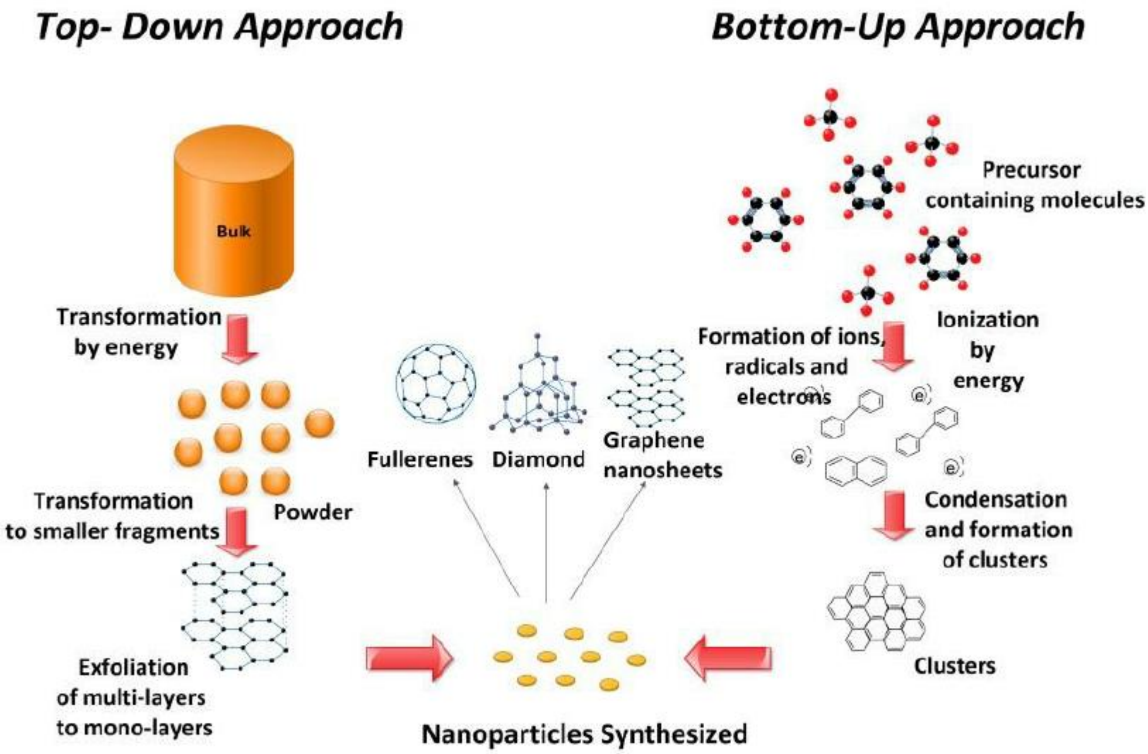

Figure.2.Schematic illustration of both top-down and bottom-up approaches for the synthesis of metal nanoparticles.

Top-Down Approaches:

The top-down method is a physical technique for producing nanoparticles from bulk materials. The two physical processes employed in the top-down approach for the formation of nanoparticles from their bulk antecedents are cutting and grinding. For the synthesis of very complex structures and the mass manufacture of MNPs, top-down techniques (Figure 2) are the preferred methodologies. The fundamental downside of these top-down techniques is that the surface structure might be imperfect, which can have a significant impact on the characteristics of the resultant MNPs [17]. The bottom-up techniques are an effective strategy for resolving this issue.

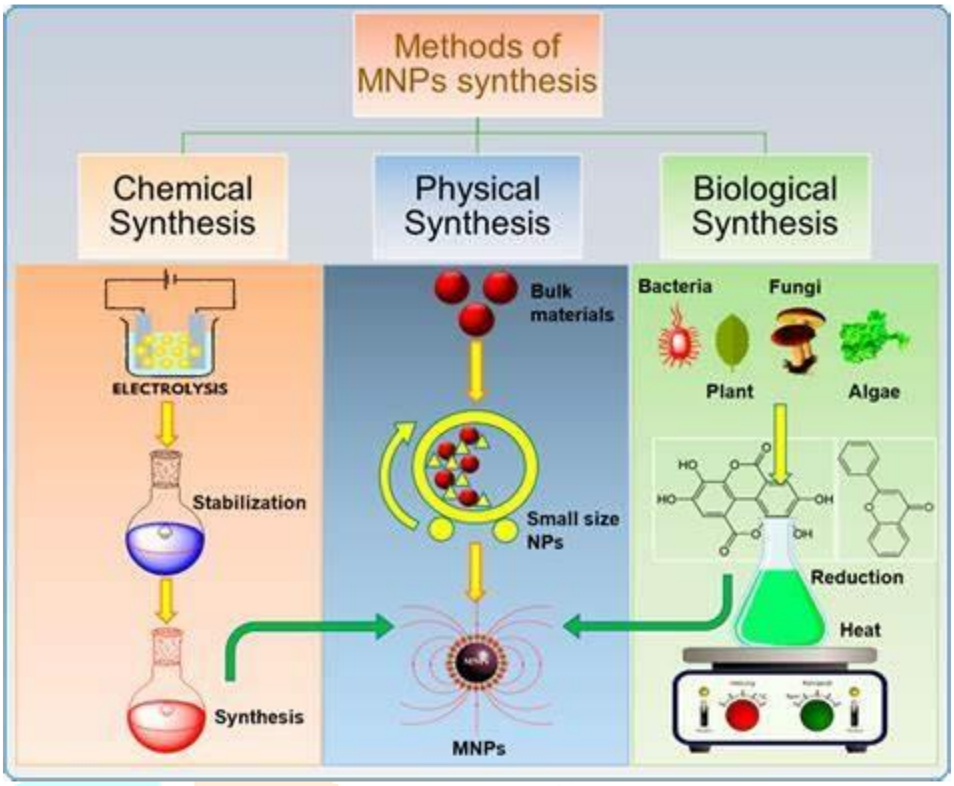

Figure.3: Classification of top-down approaches for the synthesis of MNPs

Bottom-Up Approaches:

Bottom-up tactics have been used specifically to avoid the drawbacks of top-down approaches by creating homogeneous and stable MNPs. This process results in the production of target products through the collection (nucleation) and growth of building block units with the desired size, shape, and crystallinity. Self-assembly, chemical synthesis, and colloidal aggregation are classic examples of the bottom-up technique [18]. To synthesis MNPs utilizing wet chemical techniques, the reaction mixture must contain three key reactants: a metal salt precursor, a capping agent and a reducing agent. Some of the reaction parameters that govern the morphology and surface chemistry of the resultant MNPs are the chemical nature of the capping agent, its molar ratio to the metal salt, and the redox potential of the reducing agent. The concentration of the capping agent, perhaps, may have the greatest influence, notably on the size. Capping agents are sometimes employed as reducing agents for metal salt precursors. The mass manufacture of MNPs is an issue in bottom-up approaches since not all technologies can be employed to mass-produce enough MNPs for industrial usage. A classification of bottom-up approach is depicted in figure.

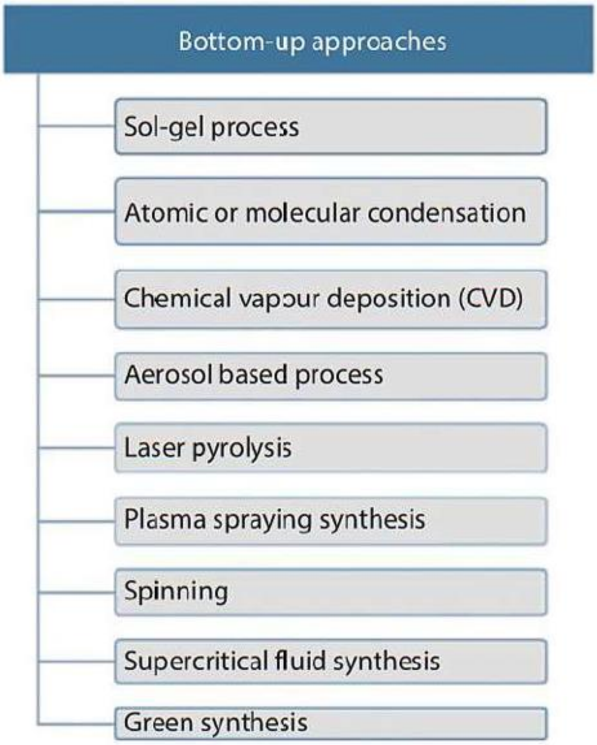

Figure 4: Classification of bottom-up approaches for the synthesis of MNPs.

Sub-Category of Nanoparticle Synthesis Routes:

The nanoparticles synthesis techniques are sub-divided into three more categories, such as, chemical approaches, physical approaches, and biogenic approaches as shown in figure 3. Nanoparticles have been manufactured physically and chemically for many years, but recent modifications and advancements use microorganisms and a variety of biological systems in the synthesis and production of metal nanoparticles.

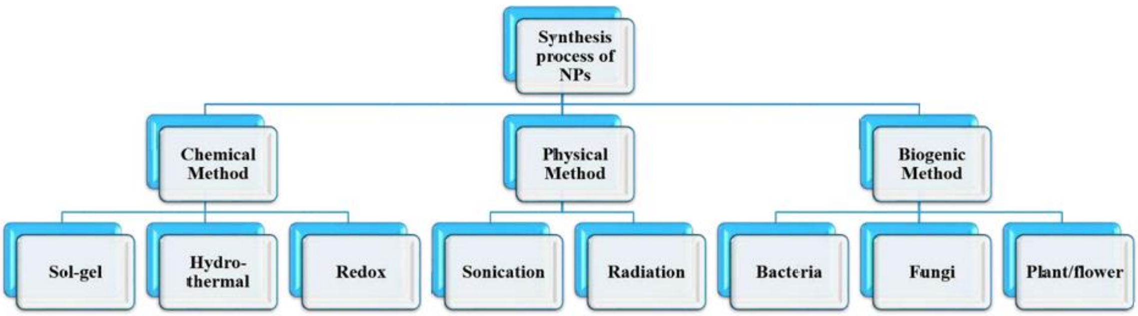

Figure.5: Sub-classification of the bottom-up approach.

Chemical Approaches:

Chemical reduction, chemical precipitation, sol-gel, etc. are well-known methods for producing nanoparticles by employing inorganic and organic reducing agents. In these methods, the use of protective agents allows for the stabilization of dispersive nanoparticles throughout the metal nanoparticle formulation process, as well as the protection of nanoparticles. As a result, they are crucial because they aid in absorption on the desired surface and prevent agglomeration.

Physical Approaches:

The most widely utilized and important physical techniques are evaporation-condensation and laser ablations. Unlike chemical techniques, physical approaches do not have the danger of solvent contamination in thin films and have a homogeneous distribution of nanoparticles.

Biogenic/Green Approach:

The biogenic route mitigates the shortcomings of chemical and physical methods by forming and stabilizing MNPs with ecologically friendly ingredients such as biopolymers and plant extracts. The biogenic route conforms to the bottom-up approach. The next section will contain elaborate discussion on the definition, types, mechanism of green synthesis or biogenic route of nanoparticle fabrication.

Biogenic Synthesis of Nanoparticles:

Biogenic synthesis is a process in which metal ions get reduced and stabilized in presence of living organisms, such as, fungi, algae, microbes, flower extract, plant extracts as shown in figure 4. All these organisms can produce NPs in vivo. However, plant extract-mediated in vitro green synthesis of NPs has gained popularity, because of its simplicity, low cost, eco-friendliness, and ease of scale-up. In the green synthesis of NPs, extracts taken from various plant species, their organs, and isolated compounds have been effectively employed. NPs synthesized by biogenic route demonstrate better bioactivities and catalytic characteristics compared to their counterparts fabricated by other methods. The capacity of plant extracts to reduce metal ions might be explained by the ubiquitous presence of phenolic chemicals throughout the plant kingdom.

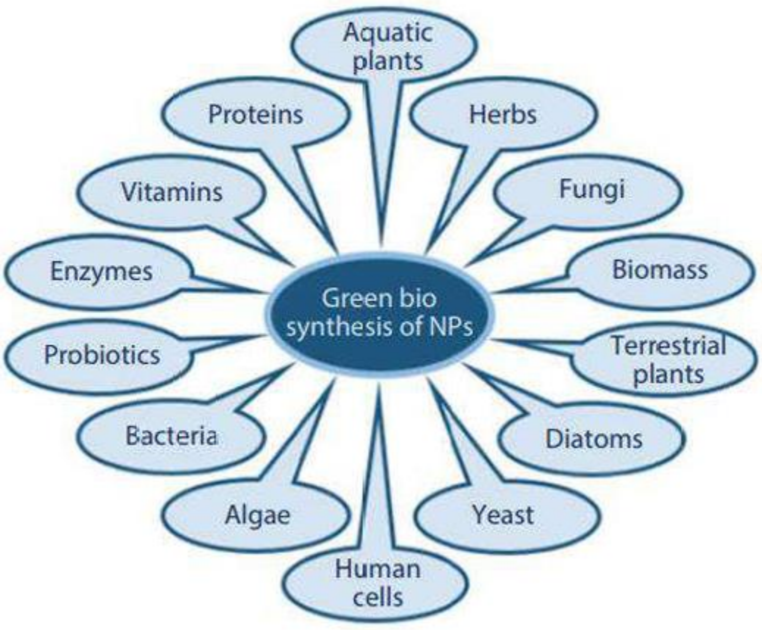

Figure.6: Various living organisms to synthesize nanoparticles.

In Vivo Biogenic Synthesis of Nanoparticles:

The mechanism of NP production by plants, as shown in figure 7, can be explained by a process known as bioaccumulation, which gives plants the ability to detoxify metal ions. When plants receive metal ions at a quicker pace than catabolism can remove them, the excess metal ions build up in the plant tissues. When metals are present at very high levels, excessive reactive oxygen species (ROS) formation in cells and damage to cellular macromolecules can cause major morphological, metabolic, and physiological abnormalities in plants. Plants have complex chelation processes to detoxify metals in order to counteract metal toxicity. When metal poisoning occurs, cellular enzymatic antioxidant mechanisms (Homeostasis) are engaged to preserve ROS equilibrium. Plant secondary metabolites, such as phenolic compounds, can help cells maintain ROS homeostasis in addition to enzymatic antioxidant processes. In essence, the metabolites present in the plant reduce the metal ions to reduce the toxicity and hence form NPs in vivo.

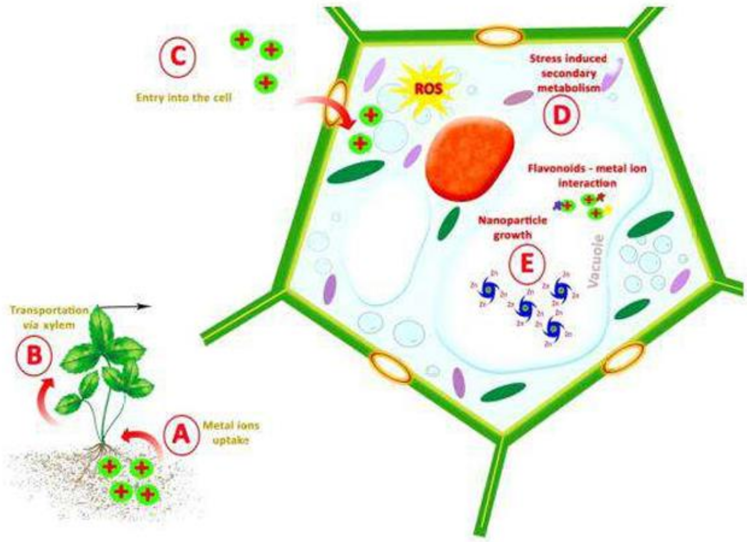

Figure.7: Schematics of in vivo synthesis of nanoparticles

In Vitro Biogenic Synthesis of Nanoparticles:

In vitro biogenic/green synthesis of NPs from plant extract utilizes the same principle discussed above. The cations will be saturated to form hydroxyl complexes when a metallic salt dissociates into cation and anion. Crystallite formation of metal with oxygen species begins immediately after the super-saturation of hydroxyl complexes. This causes the creation of crystalline planes with various energy levels. Heat is an important source of energy for the reaction system. The process continues until the plant extracts activate the capping agent, which eventually stops the formation of high-energy atomic growth planes. As a result, particular types of NPs are formed. The reducing agents usually give electrons to the metal ions and convert them to NPs throughout the synthesis. These NPs are in a high-surface-energy state and tend to aggregate against one another to convert to their low-surface-energy conformations. As a result, the presence of more reducing and stabilizing chemicals reduces nanoparticle aggregation and promotes the formation of smaller NPs. Furthermore, proteins may capture metal ions on their surfaces and convert them to their corresponding nuclei, which can then assemble and form NPs . A flow chart of the whole process is depicted in figure .8.

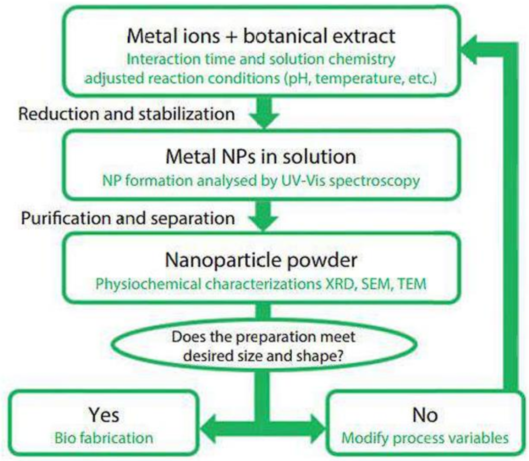

Figure .8: Flow chart of the biogenic synthesis route for nanoparticles.

Plant-mediated green NP synthesis process can be divided into three stages as shown in figure.9. They are the activation phase, growth phase and termination phase. The activation phase is the first step in the process of recovering metal ions from their salt predecessors using plant metabolites, which are biomolecules with reduction abilities. The metal ion's oxidation states are changed from mono-valent/di-valent states to zero-valent states and subsequently nucleation of the condensed metal atoms occurs. The growth stage follows, during which the separated metal atoms merge to form metal NPs, with further biological metal ion reduction taking place. Nanoparticles accumulate a range of morphologies as they develop, including shapes such as cubes, spheres, triangles, rods, hexagons, pentagons, and wires. The increased thermodynamic stability of NPs occurs as the development stage progresses, but excessive nucleation may cause aggregation of produced NPs, modifying their morphologies. The termination phase is the final stage in the green NP synthesis process. When plant metabolites cap the NPs, they achieve their most promising and stable shape. The working principle of the biogenic synthesis of NPs is illustrated below.

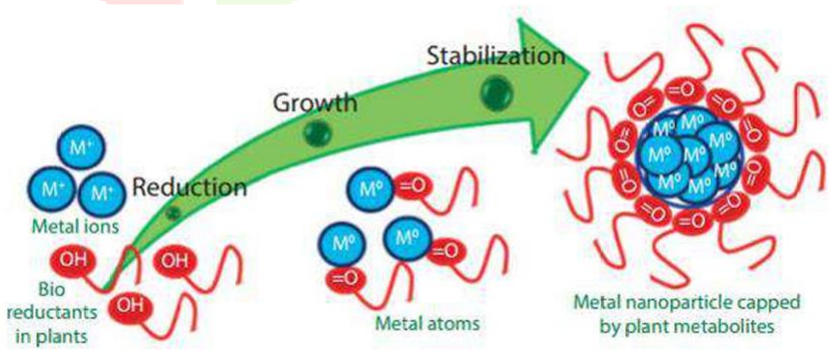

Figure.9 Illustration of the step by step formation of NPs in biogenic route

Importance of Metabolites in Plant Extract-Mediated Biogenic Synthesis of NPs

Metabolites, also known as bio-reductants/ phytochemicals, act as the stabilizing and capping agent during the fabrication of NPs in the green synthesis route. The inclusion of these compounds may increase the bioactivities of these NPs in addition to giving stability to the NPs as capping agents or stabilizers. A wide range of molecules, ranging from proteins to various low molecular weight compounds such as alkaloids, terpenoids, amino acids, polyphenols (flavones, catechin, taxifolin and phenolic acids), alcoholic compounds, antioxidants, glutathiones, polysaccharides, organic acids (ascorbic, oxalic, malic, tartaric acid), quinones etc., have been reported to play a role in the green synthesis of NPs . Sugars, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins have all been implicated in the reduction of metal ions into NPs and in promoting their subsequent stability. The key supporting element in the diverse sizes and forms of produced nanoparticles is thought to be the discrepancy in concentration and conformation of these active bio molecules across different plants, as well as their subsequent connection with aqueous metal ions. Among the various metabolites mentioned above, proteins, flavonoids, terpenoids, alkaloids, saponins, phenols are the most important according to some literature. So, before undertaking synthesis of NPs utilizing biogenic route, one must ensure the presence of such metabolites

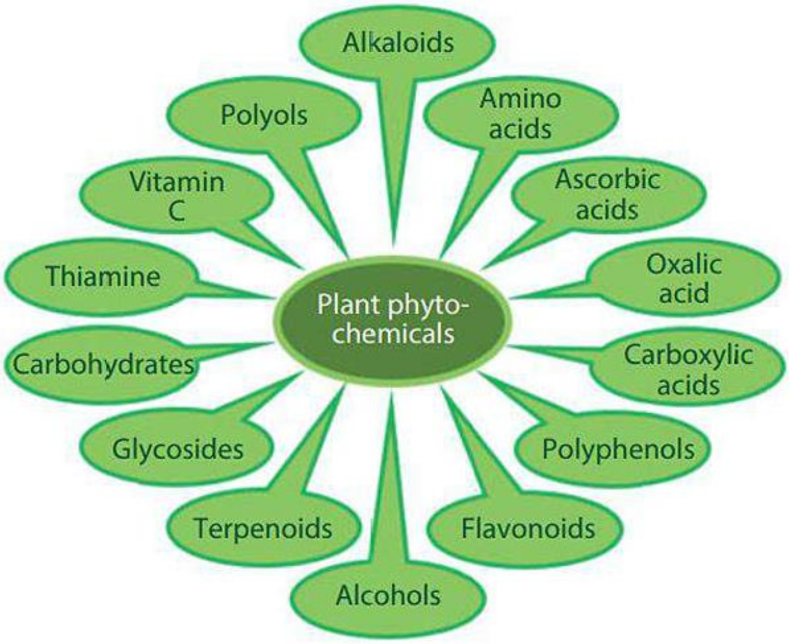

Figure.10: Illustrates important metabolites present for NP synthesis.

Conclusion

Green synthesis of metal nanoparticles presents a sustainable and eco-friendly alternative to conventional chemical and physical methods. By utilizing biological agents such as plant extracts, microbes, or natural polymers, these methods reduce the need for toxic chemicals and harsh reaction conditions, making them more environmentally responsible. The characterization of these nanoparticles is essential to understand their properties and potential applications in areas such as medicine, environmental remediation, and catalysis. Within the broader field of nanoparticle synthesis, green methods form a crucial sub-category that aligns with global efforts toward greener technologies. As the demand for sustainable solutions continues to grow, green synthesis approaches offer promising pathways for the scalable and safe production of metal nanoparticles..

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