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Green Synthesis of Nickel Nanoparticles from Extract of *Coriandrum Sativum* Leaves along with Comparative Analysis using Chemical Reduction Method

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Abstract- For comparative study on characteristics of nickel nanoparticles, they were synthesized by using green synthesis method as well as chemical reduction method at an optimum conditions. Nickel nanoparticles were biologically synthesized using aqueous extracts of coriandrum sativum L. and this extract was used as reducing and capping agent which was purchased from local market, while in chemical synthesis hydrazine was used as capping and reducing agent. Nickel chloride ($NiCl_2$. $6H_2O$) was used as the precursor. The plant adopted for the current study due to its regarded medicinal properties, easily available in all seasons and everywhere in INDIA. The synthesized Ni nanoparticles have been characterized and analyzed by using X-ray diffraction (XRD), UV-Vis spectroscopy, SEM, and FT-IR techniques.

Index Terms- Comparative study, Green Synthesis, Chemical Reduction, Nickel Nanoparticles

1. INTRODUCTION

In modern years, the preparation, characterization, and applications of the nanosized substances have been involved in many researchers in quite a wide variety fields, such as chemistry, physics, material science, and biology [1]. Metal particles that are organized in nanoscale have extraordinarily desirable properties with remarkable purity, size, shape, and shape will enormously have an impact on the ultimate performance of the devices, accordingly, preparation of nanoparticles with preferred quality and low price through using the conventional method in large scale is of incredible importance. In metal particles as the particle size decreases, the surface-to-volume ratio will extend and all properties might also additionally depend on the surface-to-volume ratio changes. Thus, nanoparticles exhibit many unique chemical and physical properties in contrast to the bulk. The significance of nickel nanoparticles is due to their particular properties, such as magnetism, thermal resistance, chemical activity and additionally a massive range of functions along with hard alloys, conducting paints, rechargeable batteries, chemical catalysts, optoelectronics, and magnetic recording media [2].

The instruction of economically and non-agglomerated spherical powders with a narrow dimension distribution is the most desirable. For the preparation of nanosized metallic particles, ball milling electro-deposition, thermal plasma, polyol process, chemical vapor deposition, gas deposition method, radiolytic reduction, sonochemical method, and many extraordinary strategies have been utilized [3, 4]. Among these methods, the chemical reduction of nickel compounds via the use of a reducing agent in aqueous solution has been investigated [5, 6]. As per our understanding, the chemical reduction is often used in the preparation of metallic powders and has many advantages in distinction to different techniques. It is a convenient, less expensive and effortless to manage technique. Hydrazine in aqueous solutions is a sturdy reducing agent. In aqueous solution, hydrazine is a convenient reductant due to the fact its by-product is usually nitrogen fuel [7-9]. It is used for the reduction of metallic ions into free metal in the shape of nanoparticles. In case of biosynthesis of nickel nanoparticles, the environmentally benign reducing agents are used [9-13]. The uses of several bio organisms to grow the nickel nanoparticles have been also reported [14].

The nickel nanoparticles synthesis using plant leaves extract is an emerging field because plant part acts as reducing agent as well as capping agent and free from toxic chemical. In recent years, the green synthesis of metal and semiconductor nanoparticles is an interesting issue of the nanoscience and

nanobiotechnology. Synthesis of nanopartices is a vast area of research due to its potential applications and shows completely new properties in size, distribution and morphology of nanoparticles. For large-scale production of antibacterial nickel nanoparticles using plant part, the synthesis route should be very simple, rapid, cost effective and environmentally pollution free, easy availability and non-toxic in nature [15-21].

In green synthesis method, we select coriander leaf extract for the synthesis of Ni nanoparticles. The coriander has a whole lot significance due to its medicinal properties and versatile use as an herb as well as a spice. Coriandrum sativum is an annual herb which belongs to the family Apiaceae (Umbelliferae), native to the Mediterranean and Middle Eastern regions and recognized as medicinal plants. India is the biggest producer, consumer and exporter of coriander in the world with an annual manufacturing of around three lakh tones [22-25]. All factors of this herb are in use as a flavoring agent and/or as standard remedies for the remedy of specific problems in the folks medication systems of distinct civilizations. This plant is highly fragrant and has multiple uses in food and in other industries. Plants have carried out a necessary function in keeping human health and civilizing the quality of human life for lots of years [26, 28].

Fresh juice of coriander is exceedingly great in curing many deficiencies related to nutritional vitamins and iron. One to two teaspoons of its juice delivered to clean buttermilk is particularly recommended in curing many diseases. Moreover, this plant is used to treatment illnesses like digestive tract disorders, respiratory tract disorders, urinary tract infections. Coriander has been stated to possess many pharmacological matters to do like antioxidant, anti-diabetic, anti-mutagenic, anti-anxiety and antimicrobial exercise alongside with analgesic and hormone balancing impact that promotes its use in ingredients due to numerous health benefits and its protective impact to maintain the food for a longer duration [27-29].

2. EXPERIMENTAL WORK

2.1 *Synthesis of Nickel Nanoparticles:*

Nickel nanoparticles were biologically synthesized using aqueous extracts of coriandrum sativum L. and this extract was used as reducing and capping agent which was purchased from local market, while in chemical synthesis hydrazine was used as capping and reducing agent. Nickel chloride ($NiCl_2$. $6H_2O$) was used as the precursor, which was from SL scientific (Ananthapuramu, India).

2.2 Green Synthesis of Nickel Nanoparticles:

A. Preparation of coriander leaf extract:

The fresh coriander leaves have been bought from nearby vegetable market, Ananthapur, Andhra Pradesh-515002, India. The coriander leaves have been absolutely washed with distilled water and dried in shade. For making ready the plant broth solution, 50 grams dried leaves of coriander have been taken and cut into small portions and made a powder form. The powder was taken into a 500 ml beaker with 250 ml of distilled water and then boiled for 30 min at 80°C. After the period of time solution gets cooled and separated out by the use of whatman No.1 filter paper. The extract used was then stored at 5°C and for further approaches within 7 days.

B. Synthesis of Nickel nanoparticles from the coriander leaf extract:

Synthesis of Nickel nanoparticles from the coriander leaf extract: A volume ratio of 1: 10 of coriander leaves extract and nickel chloride solution mixture was used. A volume of 15 ml of coriander leaf extract (B) was delivered to 150 ml. 0.1 M aqueous nickel chloride solution(C) in a 250 ml conical flask. Both B and C are combined and the mixture solution found to be light yellow color. Then after continuous stirring with a magnetic stirrer around 30-45 minutes, the solution changed from diminished yellow to green. After the development of the homogeneous solution the flask was stored at room temperature in dark for 36 hours. After aduration of 36hrs, darkish green colored Ni nanoparticles were formed. The particles formed were separated via centrifugation at 5000 rpm for 20 min accompanied through re- dispersion of the particles in distilled water. The obtained Ni nanoparticles were dried in an oven at 80°C. Repeated the same procedure with

2.3 *Chemical Synthesis of Nickel Nanoparticles:*

The nickel nanoparticles were synthesized by reduction of nickel chloride in an aqueous solution with hydrazine hydrate acting as the reductant. Solution A was prepared in 500ml of conical flask of 0.05M of Nickel chloride ($Nicl_2.6H_20$) dissolved in 480ml of distilled water and 4.8g of PVP was added. The colour of the solution observed to be green. Solution B was prepared by adding 1.5M of Sodium hydroxide (NaOH) in 160ml of water and adding of

160ml of Hydrazine hydrate ($N_2H_4.H_2O$). The colour of solution was white. Solution A and solution B were mixed together and stirred for 2minutes with a magnetic stirrer. The Mixture turned from green to royal blue and at pH were 12.5. The final solution was sonicated for 15 min at a temperature of 50°C to 60°C for proper dissolution of the mixture product. During the activation period, the solution initially became grey and a thin layer of coating was formed along the sides of the wall of the conical flask. The obtained product was centrifuged for 30min at 1500rpm and washed with distilled water for several times. The obtained product was collected in the petridish and allowed to dry at room temperature and the sample was taken for further characterizations.

3 RESULTS AND DISCUSSION

Nickel nanoparticles have been synthesized and characterized the usage of some techniques such as X-ray diffraction (XRD), UV-Vis spectroscopy (UV analysis), Fourier-Transform Infrared Spectroscopy (FT-IR) and finally, Scanning Electron Microscopy (SEM) for studying the properties of the obtained nickel nanoparticles.

3.1 Morphological Analysis:

a. Green Synthesis Method:

SEM analysis was used to monitor the size and shape of nickel nanoparticles was carried out and SEM image was used to study the average particle size. SEM image of nickel nanoparticles produced by green synthesis method is shown in figures 3.1(a) – 3.1(c). The prepared nanoparticles were found to be spherical and poly-dispersed with diameters ranging from 50nm to 114 nm.

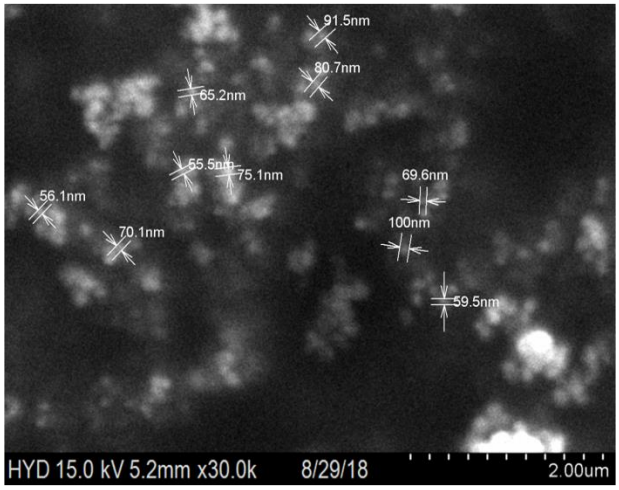

Fig. 3.1(a): SEM image for Nickel Nanoparticles (0.01 M Nickel chloride solution)

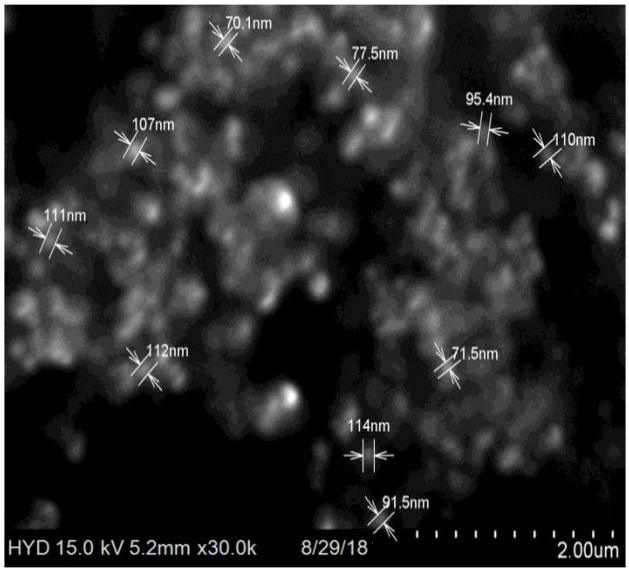

Fig. 3.1(b): SEM image for Nickel Nanoparticles (0.1 M Nickel chloride solution)

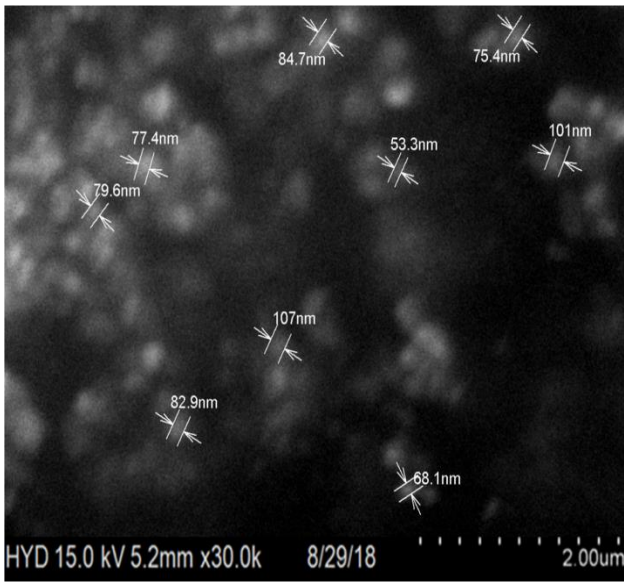

Fig. 3.1(c): SEM image for Nickel Nanoparticles (0.05 M Nickel chloride solution)

b. Chemical Reduction Method:

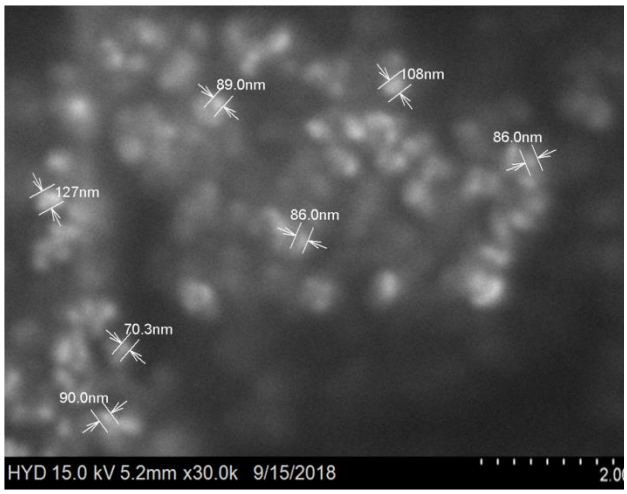

Fig. 3.1(d): SEM image for Nickel Nanoparticles (0.05 M Nickel chloride solution)

The average size for nickel nanoparticles in above figures was observed to be 72 nm, 96 nm, 81 nm for 0.01 M, 0.1 M 0.05 M $NiCl_2$ solution respectively. It is found that the average particles size increases from about 72 nm to 96 nm as the concentration of Ni^{2+} increases from 0.01 M to 0.1 M. The result could be explained by the reaction rate on the nucleation. With the increase of Ni^{2+} concentration, the nuclei concentration and nucleation rate increase. It would induce the growth of larger size particles. Fig 3.1 (d) shows the average particles size of nickel nanoparticles synthesized using chemical reduction method with 0.05 M $NiCl_2$ solution and it was found to be at 93 nm.

3.2 Crystallite Analysis

XRD analysis was done to know the crystallite size and structure of any unknown sample. The obtained product sample was analyzed to investigate the crystalline nature of synthesized particles. The diffractogram pattern were indexed properly for all crystalline peaks and compared with JCPDS data file. The X-ray diffraction patterns of the samples are shown in Fig. 3.2. The XRD patterns for all samples present the typical Ni face centered cubic (FCC) signal (JCPDS 87-0712), but peaks associated with FCC NiO (JCPDS 78-0643) were observed in the sample prepared with chemical reduction method. The appearance of NiO peaks indicates that only oxidized nickel nanoparticles because there is no capping agent. The broad peaks of Ni indicate that the particles have a short crystalline diameter. It is clear from Fig. 3.2 that the decrease in the amount of $NiCl_2$ causes the XRD peaks broadens, indicating that the average size of the particles decreases. The crystallite diameters for each sample were estimated by Scherrer's law to be 6.5, 3.8 and 3.4 nm for the samples prepared from concentrations of 0.1 M, 0.05 M and 0.01 M, respectively. Apart from NiO, NiNP's obtained from chemical reduction method have 11.06 nm.

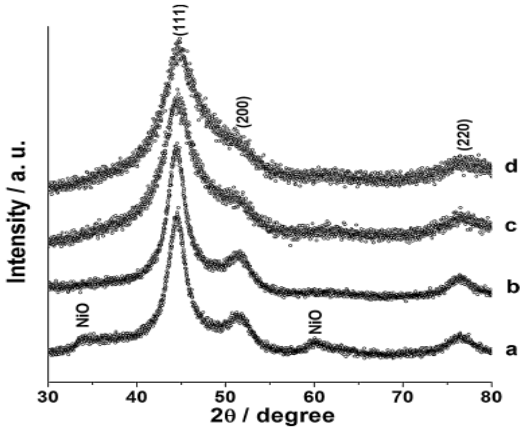

Fig. 3.2: XRD pattern of Nickel nanoparticles (a). Chemical Reduction Method (0.05 M) (b). 0.1 M (c). 0.05 M (d). 0.01 M

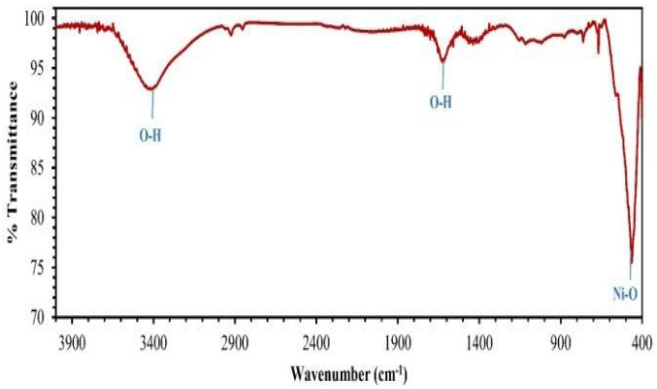

Fig. 3.3(1): FT-IR spectrum of 0.1 M Ni nanoparticles

3.3 Functional group Analysis

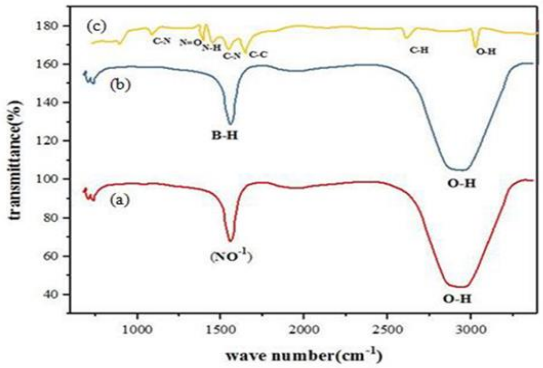

Fig. 3.3(2): FT-IR spectrum of Ni nanoparticles (a). 0.01 M (b). 0.05 M (c). Chemical Reduction Method

FTIR analysis was done to know the functional groups of any unknown sample. The FTIR spectrum shows peaks at 463.8 cm-1, 668.2 cm^{-1}, 1101.6 cm^{-1}, 1617.0 cm^{-1}, 2922.6 cm^{-1} and 3412.4 cm^{-1}. The strong band, corresponding to the Ni-O stretching vibration mode of Ni nanoparticles is seen at 463.8 cm^{-1}. The bands at 3412.4 cm^{-1} and 1617.02 cm^{-1} are characteristic for hydroxyl group (O-H), this is due to the adsorptions of water molecules onto the Ni surface when samples are exposed to the atmosphere. The broad band observed at 3285 cm^{-1} was assigned to the asymmetrical and symmetrical stretching vibrations of hydroxyl group (O-H) of nanoparticles, the band at 1636.35 cm^{-1} was corresponds to deformative vibration of C=O stretching modes in (a) and (b) and (c) shows the functional groups on the surface of particle. The wave numbers 2920 and 3428 cm-1 correspond to C–H and O–H bond. The wave numbers 1363 and 1288 cm^{-1} was due to bond vibrations of the NO^{-3}. But the C–N absorption peak at 1019 cm-1 is separated into two peaks at 1037 and 1021 cm^{-1}

3.4 *.Absorbance Analysis:*

Figure 3.4 shows the absorbance spectrum of Ni nanoparticles. It can be clearly seen that the surface Plasmon resonance (SPR) of nickel nanoparticles centered in fig 3.4(A) at 329.5nm with an absorbance of 0.465, in fig 3.4(B) at 429 nm with an absorbance of 0.589, in fig 3.4(C) at 438 nm with an absorbance of 0.625, in fig 3.4(D) at 404 nm with an absorbance of 0.526. The position of the SPR band in UV-Vis spectra depended on the particle shape, particle size and its interaction with the medium, local refractive index, and the extent of charge transfers between medium and particles.

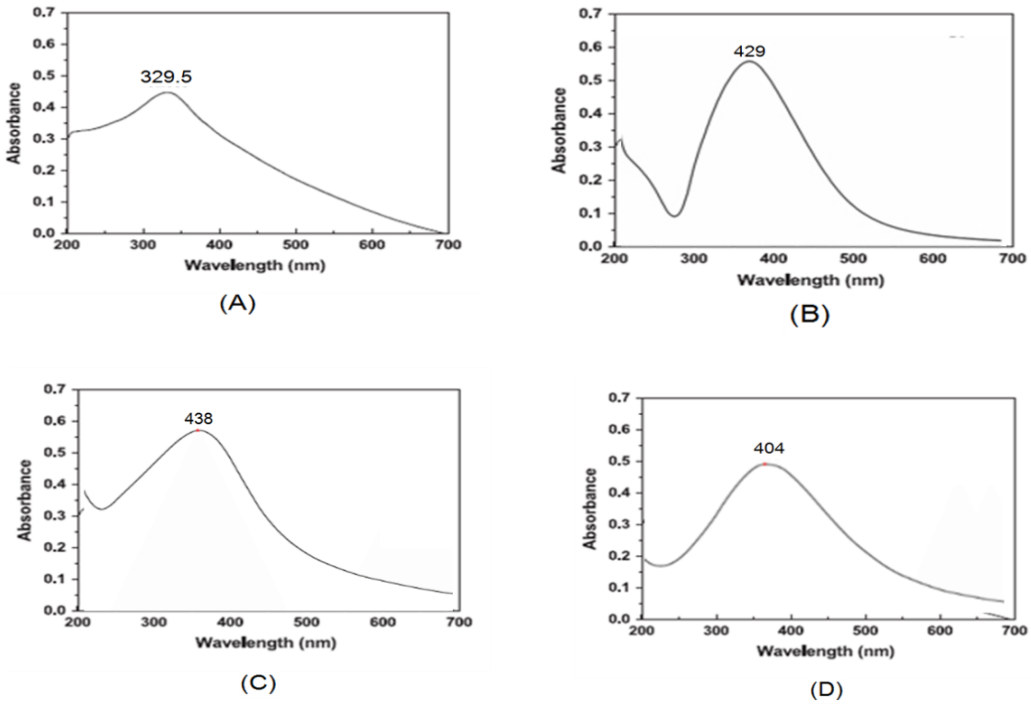

Fig. 3.4: UV-Vis spectrum of Ni nanoparticles (A) 0.1 M (B). 0.05 M (C). 0.01 M (D). Chemical Reduction Method

3.5 Comparative Analysis

To compare and differentiate two different synthesis methods of nickel nanoparticles, I choose green synthesis and chemical reduction methods. During the synthesis process I came to know many variations including cost, health and environmental pollution. As per my knowledge and observation, I tabulated major differences between these two methods in the table. 3.5.

Green Synthesis Method	Chemical Reduction Method
Coriander leaves acts as reductant as well as capping agent.	Hydrazine hydrate acts as only reductant
No. of chemicals used is 1	No. of chemicals used are 3
Coriander is a medicinal plant and easily available material	Hydrazine and NaOH are chemical materials and are available at very few places.
Stability of the resulted nanoparticles is high	Stability of the resulted nanoparticles is low
Average particle size is small	Average particles size is high
Cost effective	Expensive

Table. 3.5: Comparison between Green Synthesis Method and Chemical Reduction Method

4 CONCLUSION

Nanoparticles, in particular nickel nanoparticles have attracted considerable interest in many and diverse fields such as electronics, photonics, and medicine. However, owing to the diversity of biological entities ranging from microorganisms to plants, much of this field remains largely unknown and still remains to be discovered. The production of nanoparticles using biological entities has the potential to deliver new sources of novel materials that are stable, nontoxic, cost effective, environment-friendly, and synthesized using green chemistry approach. This green chemistry approach is in complete contrast with conventional chemical and physical processes that often use toxic materials that

have the potential to cause environmental toxicity, cytotoxicity, and carcinogenicity. Whilst biological entities have been extensively used to produce nanoparticles, the use of plants offers a straightforward, clean, non-toxic, and robust procedure that does not need any special culture preparation or isolation techniques. In particular, the use of plant extracts for synthesizing nanoparticles is inexpensive, easily scaled up, and environment-friendly. Plant extracts have the potential to produce nanoparticles with a specific size, shape and composition. On another front, plant synthesized nanoparticles have the potential to be used for the delivery of anti-microbiological compounds. Despite the environmental advantages of using green chemistry based biological synthesis over traditional methods as discussed in this article there are some unresolved issues such as particle size and shape consistency, reproducibility of the synthesis process, and understanding of the mechanisms involved in producing metallic nanoparticles via biological entities. In the case of plant extracts, nanoparticle formation mechanisms vary between different plant species. Therefore, there is a need for more studies to evaluate and understand the actual plant dependent mechanisms. This is a grossly unexplored field and requires much more research investment to fully utilize the green synthesis of metallic nanoparticles via biological entities.

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