

FORMULATION OF SILVER NANO GROWTH PROMOTERS FOR CARNATION

Main Project Report

Submitted by

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In partial fulfillment of the requirement of the degree of

BACHELOR OF TECHNOLOGY

IN

AGRICULTURAL BIOTECHNOLOGY

Under the guidance of

Dr. L. JEYANTHI REBECCA



(Declared u/s 3 of UGC Act, 1956)

**DEPARTMENT OF AGRICULTURAL BIOTECHNOLOGY
BHARAT INSTITUTE OF HIGHER EDUCATION AND RESEARCH**

(Declared as a deemed university under section 3 of UGC Act 1956)

Chennai-73

May, 2022



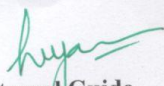
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This is to certify that the Main project work entitled “**Formulation of silver nano growth promoters for carnation**” is a bonafied work done by (Anudeepika I (U18AC055), G Manoj (U18ACO43) for the fulfillment of the requirements of Bachelor of Technology in AGRICULTURAL BIOTECHNOLOGY, during the academic year 2021-2022.


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DECLARATION

I hereby declare that the Main project report entitled "**Formulation of silver nano growth promoters for carnation**" was submitted to Bharath Institute of Higher Education and Research, Chennai in partial fulfillment of the requirement for the award of the degree of Bachelor of Technology in Agricultural Biotechnology, is the record of the original work carried out by me under the guidance of **Dr. L. Jeyanthi Rebecca**.

I further declare that the results of the work have not been submitted to any other University or Institution for the award of any degree or diploma.

Place: Chennai

Date: 23.05.22.

Anudeepika
Signature of the student

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to our respected President **Dr. J. SUNDEEP AANAND** and Managing Director **Dr. SWETHA SUNDEEP AANAND** for their valuable support and encouragement in technological upgrades and novel projects and for providing us much more facilities.

I take great pleasure in expressing my sincere thanks to our Vice-Chancellor (I/C) **Dr. K. VIJAYA BHASKAR RAJU** for his continuous support. I also like to thank our Pro-Vice-Chancellor **Dr. R. M. SURESH**, Pro-vice chancellor **Dr. M. SUNDARARAJAN** and our Additional Register **DR. R. HARI PRAKASH**, for their kind support. I thank our Dean of Engineering **Dr. J. HAMEED HUSSAIN**, for providing sufficient facilities for the completion of the project.

I express my sincere thanks to the Head of the Department **Dr. L. JEYANTHI REBECCA** for providing sufficient facilities for the completion of this project.

I express my sincere thanks to my internal guide, **Dr. L. JEYANTHI REBECCA** for her guidance and encouragement in the accomplishment of this project. I wish to express my thanks to all the **STAFF MEMBERS** of the **DEPARTMENT OF AGRICULTURAL BIOTECHNOLOGY**, Bharat Institute of Higher Education and Research, Chennai for their valuable support throughout the project. I also thank my parents and all my friends for their moral support and suggestion for this project.

Finally, I think everyone who has rendered help directly or indirectly at various stages to do the project successfully.

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ABSTRACT

Nano growth promoter is an ideal multipurpose plant growth promoter. Nano-particles of metals can be routinely synthesize the seeds or plants treated with the particles can improve early growth and crop production. The stabilized silver nano-particles were synthesized and applied to seeds or plants, the germination rate, early plant development. They also increase the growth of the plant and number of flowers, prevents pre-dropping of fruits & flowers. In this, we go through the carnation [fig.4.2]. plant species for the study of effects of nano-growth promoters. The main purpose of using this fertilizer in agriculture give full-fledged macro and micronutrients, which usually lack in the soil. This investigation aims to highlight the use of nanotechnology in the fertilizer system and also provide information on nano-fertilizers that are used for plant growth and nutrition.

With the rising global population growth and the limitation of traditional agricultural technology, Nano-fertilizers and Nano-pesticides have 20-30% higher efficacy than conventional products. Nanotechnology is the best and potential solution for problems caused by conventional fertilizer in the agricultural system. The present review focuses on the application of nanotechnology in agriculture and its possible impact on plant growth and soil micro flora. It emphasizes on more research to study the impact of nanotechnology on agriculture and develop regulatory protocols for safe production, use and release of nanomaterials to minimize environmental nanotoxicity.

KEYWORDS:

Nanotechnology, carnation, nano-particles, micronutrients, fertilizers, Nano-growth promoter, Plant development, nanotoxicity.

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1. INTRODUCTION

Nanotechnology can be defined as the systematic study of nanometer-ordered materials that have properties critically dependent on length scales. Such new and improved properties create promising candidates for a wide range of applications for nanoscale materials that are expected to improve our lifestyles. The chemical substances or materials developed and used on a very small scale are chemical substances or materials. Compared to the same material, nanomaterials are designed to exhibit novel features without nanoscale features, such as enhanced power, chemical reactivity or conductivity [1,2].

Silver nanoparticles (AgNPs) are increasingly used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical and chemical properties [3-5]. These include optical, electrical, and thermal, high electrical conductivity, and biological properties. Due to their peculiar properties, they have been used for several applications, including as antibacterial agents, in industrial, household, and healthcare-related products, in consumer products, medical device coatings, optical sensors, and cosmetics, in the pharmaceutical industry, the food industry, in diagnostics, orthopedics, drug delivery, as anticancer agents, and have ultimately enhanced the tumor-killing effects of anticancer drugs [6,7]. Recently, AgNPs have been frequently used in many textiles, keyboards, wound dressings, and biomedical devices. Nanosized metallic particles are unique and can considerably change physical, chemical, and biological properties due to their surface-to-volume ratio; therefore, these nanoparticles have been exploited for various purposes. In order to fulfill the requirement of AgNPs, various methods have been adopted for synthesis. Generally, conventional physical and chemical methods seem to be very expensive and hazardous. Interestingly, biologically-prepared AgNPs show high yield, solubility, and high stability. Among several synthetic methods for AgNPs, biological methods seem to be simple, rapid, non-toxic, dependable, and green approaches that can produce well-defined size and morphology under optimized conditions for translational research. In the end, a green chemistry approach for the synthesis of AgNPs shows much promise [8-10].

1.1. PROPERTIES OF SILVER

Table-1: Silver properties

1	Chemical formula	Ag
2	Molar mass	107.86 g/mol
3	Structure	FCC
4	Lattice constant	a = 0.409 nm
5	Appearance	Nearly white
6	Density	10.49 g/cm ³
7	Melting point	961°C
8	Boiling point	2162°C
9	Band gap Magnetic	3.19 eV
10	Susceptibility(x)	-19.5×10 ⁻⁶ cm ³ /mol

1.2. CRYSTAL STRUCTURE OF SILVER

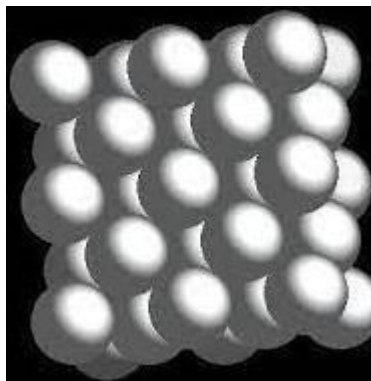


Fig:1: FCC structure of silver

1.3 APPLICATIONS OF SILVER NANOPARTICLES

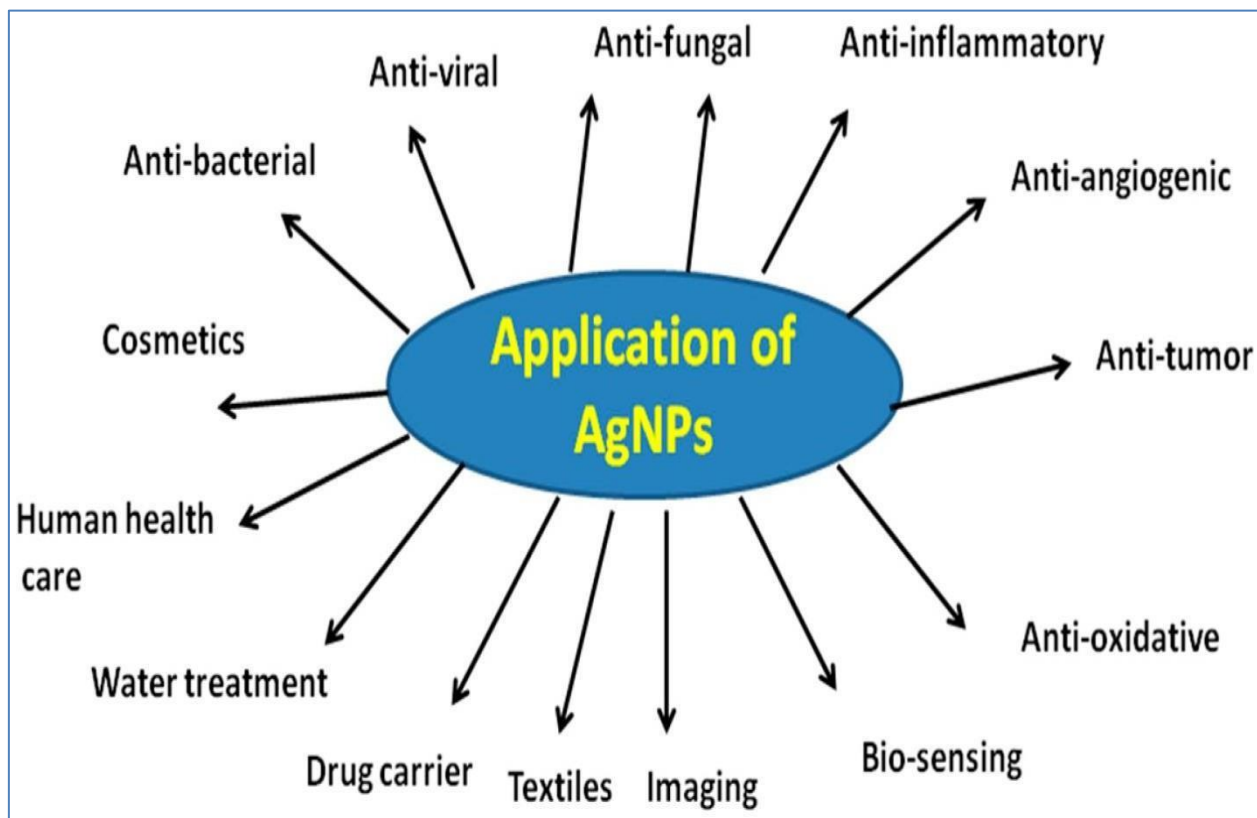


Fig:2: Applications of Ag-NP's

1.4. SYNTHESIS OF METHODS OF NANOPARTICLES:

By consolidating tiny clusters or splitting the polycrystalline bulk content into crystalline groups, nanomaterials can be prepared. These approaches are called bottom-up and top-down strategies.

- (i) Top-down approach: the size of bulk materials is lowered to the nanoscale.
- (ii) Bottom-up approach: Atomic level precursors were used for the synthesis of nanoscale materials

Over the last few decades, nanomaterials are the subject of widespread study, with substantial progress in their understanding, particularly in the last few years. They are single or

multi-phase polycrystals with, as the name indicates, a nanoscale (1×10^{-9} - 250×10^{-9} m) grain dimension. The word 'ultrafine grain size' is also used at the upper limit of this scheme.

Top-down synthesis is the solid state processing of materials where the bulk materials are broken to nanoparticles by crushing, ball milling or grinding. It is difficult to obtain nano particles with uniform formed materials. This causes defects in surface structures, resulting in a substantial change in nanostructured material properties and surface chemistry.

Bottom-up approach is the simplest method of building-up of nanomaterials from the atomic level precursors. ie., atom, molecule or cluster. This method of preparation will lead to perfect nanomaterials with uniform size and shape, which involves chemical synthesis with controlled reaction to reduce the growth. The bottom-up process plays a vital role in the processing of nanostructures. In this technique, there are several techniques are available for the synthesis of nano-structured materials, such as hydrothermal, combustion synthesis, precipitation method, microwave method and sol-gel technique

1.5. SOLVOTHERMAL METHOD

Solvothermal technique is a method to synthesis variety of nanomaterials in the presence of organic solvents under the influence of moderate to high pressure and range of temperatures (100-1000°C), where the temperature facilitate the reaction and interaction between the precursors. Instead of solvent, water is mainly used in hydrothermal method for the synthesis of nanomaterials. Solvothermal is a flexible method for the preparation of many different nanoparticles ranging different nanosized structures, especially controlling over size and shape with uniformity and high crystallinity.

1.6. MICROWAVE METHOD

Microwave radiation is the key factor in the preparation of various nanomaterials for the microwave method. This technique eliminates the usage of high temperature and calcination for extended periods of time, rather synthesis process is a fast procedure to reproduce crystalline nanomaterials. Heating the materials using microwaves will lead to rapid uniform heating. In recent past, many kind of nanomaterials are prepared with controlled microstructures from microwave synthesis.

2. REVIEW OF LITERATURE

This work explores several chemical synthesis strategies that are routinely used to prepare silver nanoparticles. Some synthesis methods with aspects of green silver nanoparticles synthesis, particularly toxicity of reducing and capping agents and energy consumption, are also covered. Selected techniques used to characterize silver nanoparticles to determine how different synthesis parameters influence size and shape and elucidate the size/shape property correlation are provided, as well as an outlook on future considerations in silver nanoparticles synthesis [14].

In this study we present the synthesis of copper silver bimetallic composites utilizing a fast, microwave assisted chemical reduction method. The method requires low reaction times and yields nanocomposites with a morphology best described as nano silver decorated copper particles. Water leaching studies show that copper follows a fast exponential leaching kinetics compared to silver. The release of silver remains slow and is sustained over a much longer period compared to copper. Consequently, the antibacterial effects of the composites will be dictated by the fast leaching copper and modulated by the composition of silver in the composite [15].

Microbial surface area is one of the battlegrounds for invading microbes and host defense. Hence, infectious diseases caused by drug resistant microbes with large surface area are more difficult to treat than small size microbes. Nanobiology offers opportunities to re-explore the biological properties of conventional drugs at molecular level to combat these microbes. The purpose of the present study was to examine size depended susceptibility of Gram-positive bacteria towards nano silver particles [16].

Ceria supported silver nano catalyst was synthesized using a simple, fast and cost-effective gel-casting technique. The gel was made of acryl amide monomer (AM) to disperse, stabilize and control the size of metal nanoparticles. The obtained results revealed that nano particles can easily be confined into the three dimensional network of the polymeric gel. The polymer matrix

was then removed by calcination under a controlled atmosphere and temperature. In the process optimization, the maximum amount of surface area was achieved concurrently with the minimum values for particle size at 5.38 m²/g and 190 nm, respectively [17].

The impact of electrolytes, stabilizing and/or capping agents on morphology of colloidal silver nano materials (AgNPs) is studied spectroscopically. Sodium thiosulfate acts as reducing-, stabilizing- and damping-agents. Stoichiometric ratios of S₂O₃²⁻ and Ag⁺ ions were responsible to the formation stable and perfect transparent dark yellow colored AgNPs. The S₂O₃²⁻-stabilized AgNPs were significantly more stable in inorganic electrolytes (NaNO₃, Na₂SO₄, Na₂CO₃ and KBr). S₂O₃²⁻ is adsorbed more strongly than the used other anions. The addition of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) has significant effects on the absorbance of S₂O₃²⁻-stabilized AgNPs which can be rationalized in terms of electrostatic attraction and repulsion between the adsorbed S₂O₃²⁻ ions on to the surface of AgNPs and cationic and/or anionic head groups of used surfactants, respectively. Transmission electron microscopy images suggest that AgNPs are polydispersed, spherical and exhibiting an interesting irregular morphology [18].

The silver nanoparticles can be synthesized by various methods: Reduction either by using Citrate or Sodium Borohydride, Ion Implantation and Biogenic Synthesis. Amongst these, Sodium Borohydride is used in excess for reduction of silver nitrate and stabilize the silver nano particles. Sodium Borohydride being a strong reducing agent may lead to secondary reaction. An ice bath facilitates to slow down the reaction rate and eliminates secondary reactions. If agglomeration of nano particles occurs, PVP is added during reaction. To characterize the nano particles Ultraviolet Visual Spectroscopy, Borohydride reduction method produces 30-100 nm particles [22].

Silver nanoparticles were synthesized via a reduction reaction carried out in a spinning disk reactor, to which an AgNO₃ solution containing a protecting agent and an alkaline solution containing a reducing agent were added simultaneously and then recycled for a certain period. Besides starch, which has been used for producing silver particles above 10 nm, two more

protecting agents, i.e. polyvinyl pyrrolidone (PVP) and hydroxypropyl methyl cellulose (HPMC), were tested in order to prepare silver particles below 10 nm. Then, the effects of other operating variables, such as rotation speed of disk, flow rates of reactant streams, concentration of reducing agent, and type and concentration of alkali, were investigated, aiming at a high production rate of silver nanoparticles with a size below 10 nm. The produced silver particles were recovered using a centrifuge, and the size did not change after redispersion. The sintering temperature of the 10 nm silver particles was greatly reduced [23].

Soft gamma ray irradiation is done on Silver nano colloids prepared using Pepper Nigrum as reducing and stabilizing agent. Change in surface morphology and the structure of the colloid is obtained from Transmission Electron Microscope images and Selected area Electron Diffractogram. Morphology of the gamma irradiated sample is devoid of nano particle clusters and the Selected Area Electron Diffraction pattern confirms the crystal nature as face centered cubic structure of nano silver. UV–visible spectroscopic analysis gives the absorption peaks in the green region. Gamma irradiation results in the reduction in peak intensity without any change in wavelength. A statistical approach is done on treating the gamma irradiated colloidal sample with the as prepared silver nano colloid for measuring the area of affecting fungal infection on a potato-agar medium. It is found that the fungal growth is declined rapidly with the introduction of gamma irradiated silver nano colloid than the as prepared colloid [24].

Silver nanoparticles (NPs) have been the subjects of researchers because of their unique properties (*e.g.*, size and shape depending optical, antimicrobial, and electrical properties). A variety of preparation techniques have been reported for the synthesis of silver NPs; notable examples include, laser ablation, gamma irradiation, electron irradiation, chemical reduction, photochemical methods, microwave processing, and biological synthetic methods. This review presents an overview of silver nanoparticle preparation by physical, chemical, and biological synthesis. The aim of this review article is, therefore, to reflect on the current state and future prospects, especially the potentials and limitations of the above mentioned techniques for industries [25].

2.1. EXPERIMENTAL TECHNIQUES

The prepared nanoparticles is characterized using the XRD, FTIR, UV-Visible spectroscopy, FESEM to investigate the structural, optical and morphological properties. In addition we attempt the foliar applications of these citric acid doped silver as nutrient to the plants.

2.2. X-RAY DIFFRACTION (XRD)

Working Principle

The incident X-rays with sample gives interference when Bragg's conditions are satisfied.

$$\text{Braggs law: } 2 d \sin\theta = n\lambda$$

where n is an integer and λ is the wavelength of X-ray wave

The observed XRD profiles are distribution of intensities $I(2\theta)$ defined by many parameters. The crystalline phases and orientation of all the thin films of the present work were identified by matching the XRD peaks with those given in the data base (JCPDS). In this study Rigaku Japan X-ray Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$) was used for the analysis. The X-ray scans were performed with 2θ values 20° - 90° with a step size of 0.02° . The diffracted rays are collected by means of the detector [26].

Crystallite Size Analysis

Scherrer's formula is used for calculating the crystallite size, from the XRD pattern.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where β = FWHM, θ -Angle of diffraction and k -Scherrer constant.

2.3. FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM)

Scanning electron microscope (SEM) is primarily employed to study the surface morphology. SEM, which consists of a tungsten filament, which produces electrons. FESEM uses a focused beam of electrons to generate an image or to analyze the specimen. For operation, the gun head, the column and specimen chamber have to be evacuated. The pre-vacuum pump and turbo pump evacuate the specimen chamber. Vacuum in the specimen chamber is measure by penning penning gauge.

Column chamber valve remains closed until the detected pressure is not ready for operation. After vent command, column chamber valve closes and N₂ gas flows into the specimen chamber through vent valve.

A field-emission cathode in the electron gun provides probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Under vacuum, electrons generated by a field emission source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focussing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam and finally the image is displayed on the monitor [27].

FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nm. That's 3 to 6 times better than conventional SEM. Smaller-area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy. Reduced penetration of low kinetic energy electrons probes closer to the immediate material surface. High quality, low voltage images are obtained with negligible electrical charging of samples. (Accelerating voltages range from 0.5 to 30 kV.) Need for placing conducting coatings on insulating materials is virtually eliminated.

2.4. UV-VISIBLE SPECTROPHOTOMETER

The molecules/atoms in the gas and in solution can be excited using UV/Visible radiation based on the Beer-Lamberts law. Absorbance (A) = ϵbc , where, l is the path length, c is the concentration of the solution/substance, ϵ is a proportionality constant (Absorbitivity). Absorption is strongly depends on the types of samples. Spectrophotometer quantitatively measures the fraction of light that passes through a given sample. In spectrophotometer, a light from the lamp is passed through a monochromator, which choose light of one particular wavelength from the continuous spectrum. This light passes through the sample (solution), which is being measured. The intensity of the light is measured using a photodiode, and transmittance is calculated.

There is different kind of spectrophotometers i.e single and double beam. Double beam provides the intensity ratio of beam from different paths. The UV region 200-400 nm and 400-800 visible region is scanned. The light passes through thin film sample. Absorption coefficient is calculated

by

$$\alpha(\lambda) = 2.303 \left(\frac{A}{t} \right)$$

where t -thickness of the film and A -Absorbance.

Extinction coefficient is obtained from

$$K = \frac{\lambda\alpha}{4\pi} \quad \text{Absorption coefficient is written as follows}$$

$$\alpha h\nu = A(h\nu - E_g)^n$$

A -Constant and E_g -Energy band gap and 'n'-kind of optical transitions. 'n'= 1/2, 3/2, 1, 2 and 3, depends of the electronic transition [28].

2.5. FOURIER –TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral resolution data over a wide spectral range.

Principles of FTIR Spectroscopy

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range is measured as wave numbers typically over the range 4000- 600 cm^{-1} . When IR light impinges on a sample (solid, liquid or gas), particular frequencies of the incident radiation is absorbed by the substance leading to the molecular vibrations. The absorbed radiation is unique, provides the characteristics of a substance. FTIR can also be used for some quantitative analysis.

FTIR is used for identifying the chemical bonding (structural properties) of the substances like solids and liquids. There is an interaction between IR radiation and substance and the nature of interaction [29].

3. OBJECTIVE

- To collect the healthy plants.
- To formulate the nano-particles of different formulations.
- To analysis the size, shape and structure of the nano-particles with the use of different spectroscopic methods.
- To treat the plants with different treatments to see the effects of nano-particles on plants.

4. MATERIALS AND METHODS

Table-2: Materials

Silver Nitrate	1.7g
tri-Sodium citrate	2.94g
Choline chloride	0.175g
Citric acid	0.105g
Distilled water	Required amount
Hot air oven	1
Petri dish	2
Thermometer	1

4.1 : PREPARATION OF CITRIC ACID DOPED SILVER NANOPARTICLES BY SOL-GEL METHOD:

- 1.7 g of silver nitrate is dissolved in 100 ml of DI water. [fig.4.1.1]
- The solution is heated to boil and under vigorous stirring. After 3 min of boiling, the aqueous solution of sodium citrate is added rapidly.
- Then the 0.005 M of citric acid is added to the solution. The solution gradually turned to grey color [fig.4.1.2].
- The solution is kept boiling for 5 min continuously and then allowed to cool.
- The grey color solution indicates the formation of silver. Sodium citrate 2.94 gm is dissolved in 10 ml of DI water.
- Then the water content is dried with hot air oven at 200°C for 3 hours and then calcinated at 400°C or 2 hrs [fig.4.1.3].
- Then the powder is used for the further analysis.



Fig:3: Silver nitrate dissolved in distilled water



Fig:4: Cloudy precipitate formation after adding Sodium citrate



Fig:5: Dried silver Nano-particles.

4.2 : Carnation:

Family : Caryophyllaceae

Genus : Dianthus

Species : *Dianthus caryophyllus*

Dianthus caryophyllus commonly known as the Carnation or clove pink, belongs to the species of dianthus. It is probably native to Mediterranean. It is a herbaceous plant.



Fig:6: Carnation

4.2.1. Plantation tips:

Carnations should be planted in an area that gets 4-6 hours sunlight. They are long day plants and required high light levels, to produce high quality flowers.

Plant type : Perennial flowering

Mature size : 12-18 inches

Soil type : drained Alkaline, fertile, well

Bloom time : Late spring

Soil PH : 6.7-6.9

4.2.2. Watering schedule:

- Plants should be watered once or twice a week if the top 3 inches of soil is dry.
- Better to Misting or about 1 inch of water. Be careful not to get the plant too wet, because “**excess watering may cause leaves to turn yellow**”.
- Over watering also causes Bacterial and Fungal disease.
- The plant is Drought Tolerant.

4.2.3. Importance & Uses of Carnation:

- Used for treating Muscle spasms and improves heart health.
- It is also useful for treating the problems of hair loss & sore muscles.

4.3. CITRIC ACID DOPED SILVER NANOPARTICLES ANALYSIS:

4.3.1. X-ray diffraction (XRD)

XRD technique is broadly used to study the structure of crystalline metallic nanoparticles using X-rays. The XRD pattern confirms the formation of silver nanoparticles with crystalline structure. Ag Nanoparticles showed many significant peaks in the range of 10-100°. The pattern showed strongest peaks at an angles 32.2, 38.11, 44.30 and 64.4 corresponding to the lattice planes of (111), (200), and (220) respectively, indicating the of cubic crystal structure. Scherrer equation is applied to calculate the particle size from the XRD data.

$$d = K\lambda/\beta \cos \theta,$$

where d is the particle size (nm), K is the Scherrer constant, λ is the wavelength of X-ray, β is the full width half maximum and θ is the diffraction angle. The average crystallite size is found to be 29 nm.

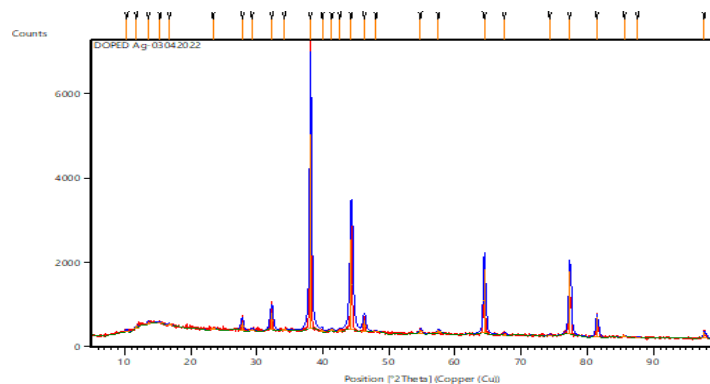


Fig:7: XRD pattern of the citric acid doped silver nanoparticles annealed at 400 °C

4.3.2. FT-IR Spectroscopy

FTIR is used to the study of nanoscale materials, such as confirmation of functional molecules covalently grafted onto silver, carbon nanotubes, graphene and gold nanoparticles, or interactions occurring between enzyme and substrate during the catalytic process. The FTIR spectra of synthesized Ag NPs represented intense peaks at 3700-3800 cm^{-1} (N-H stretch), 3000 cm^{-1} (Stretching vibration of aliphatic C-H), (C-H stretching of aromatic compound), ~ 2200-2000 cm^{-1} denotes O-H stretch carboxylic acids), Alkyne $\text{C}\equiv\text{C}$ stretching, C-C stretching were recorded. After the reduction with the AgNO_3 , the peak about 500-600 cm^{-1} is attributed to the formation of nanoparticles. The stretching frequency of N-O is observed at above 1300 cm^{-1} .

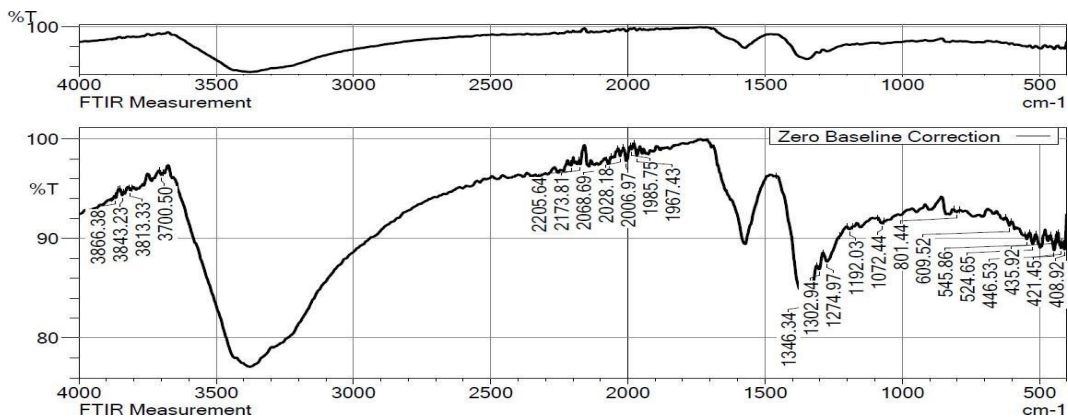


Fig:8: FTIR spectrum of the citric acid doped silver nanoparticles

4.3.3. UV-VISIBLE SPECTROSCOPY STUDIES

Optical experiments were studied by using a UV-Visible spectrophotometer in the wavelength range 200-1000 nm. Figure shows the sharp absorbance ~ 350 nm. The band gap can be assessed from the Tauc map: $(\alpha h\nu)^2$ versus $h\nu$; where α is the absorption coefficient and γ is the frequency of radiation. The coefficient of absorption, alpha (alpha) was calculated using the relation,

$$\alpha(\omega) = 2.303*(A), \text{ where 'A' is the absorbance}$$

The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the value of the optical band gap energy. The formation of Ag NPs displayed a well-defined absorbance band at 350 nm, as shown in figure. The fact that

the bands developed well indicate that the reducing agent was successful in forming nanoparticles. According to earlier literature, the absorption peaks of Ag NPs are in the 350–450 nm range. The bandgap is calculated from the formula $1240/350 \text{ nm} = 3.54 \text{ eV}$. These findings were supported by the present study and indicated t

Fig:9: UV-Visible absorbance spectrum of the citric acid doped silver nanoparticles

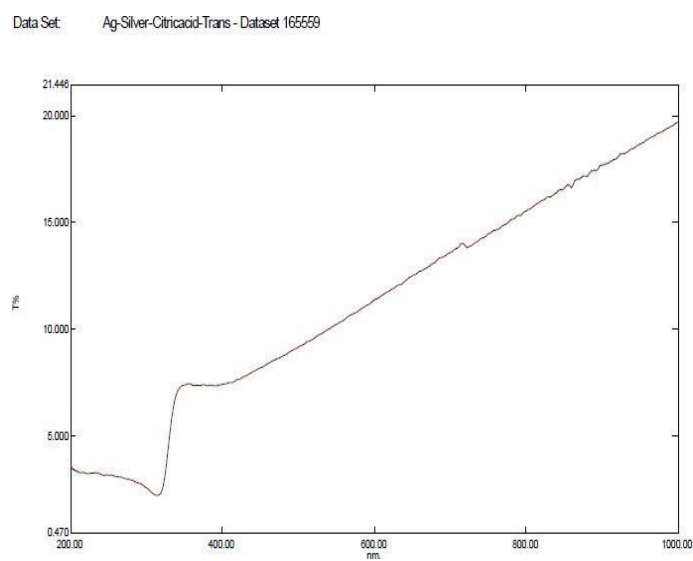


Fig:10: UV-Visible transmittance spectrum of the citric acid doped silver nanoparticles

4.3.4. FE-SEM ANALYSIS

The morphological features of synthesized silver nanoparticles were studied by Field emission Scanning Electron Microscope. FE-SEM provided further insight into the morphology and size details of the doped silver nanoparticles. The result showed that the particles are of spherical shape but also shows some nanorods shape in case of 60 and 40 KX magnifications (20, 40 and 60 KX). It is observed that the nanoparticles are agglomerated. The EDX spectrum indicated the presence of Ag, C, O and Na.

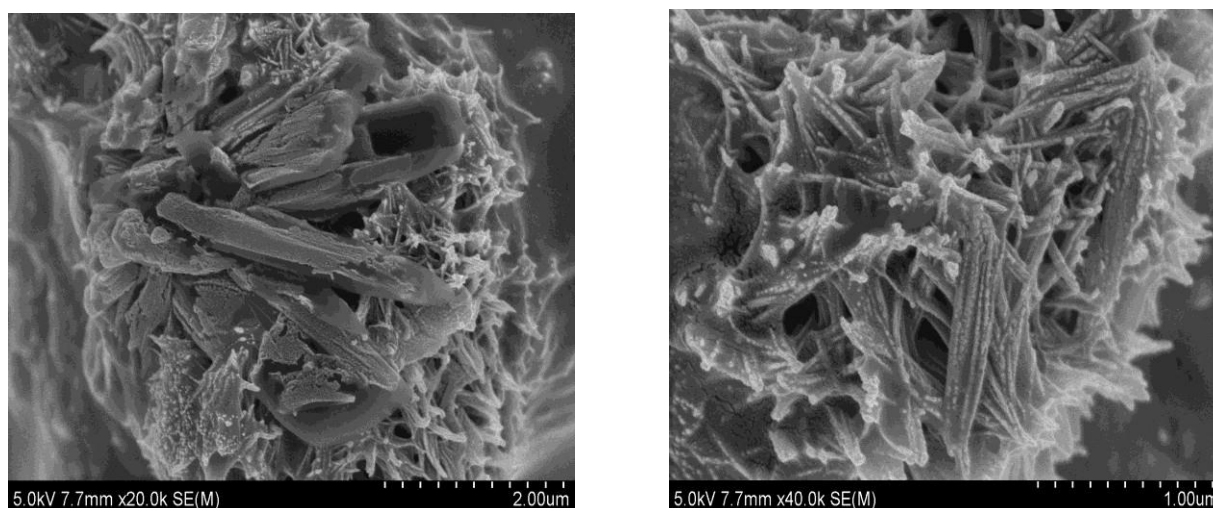


Fig:11: FE-SEM image of the citric acid doped silver nanoparticles with different magnifications (20 and 40 KX)

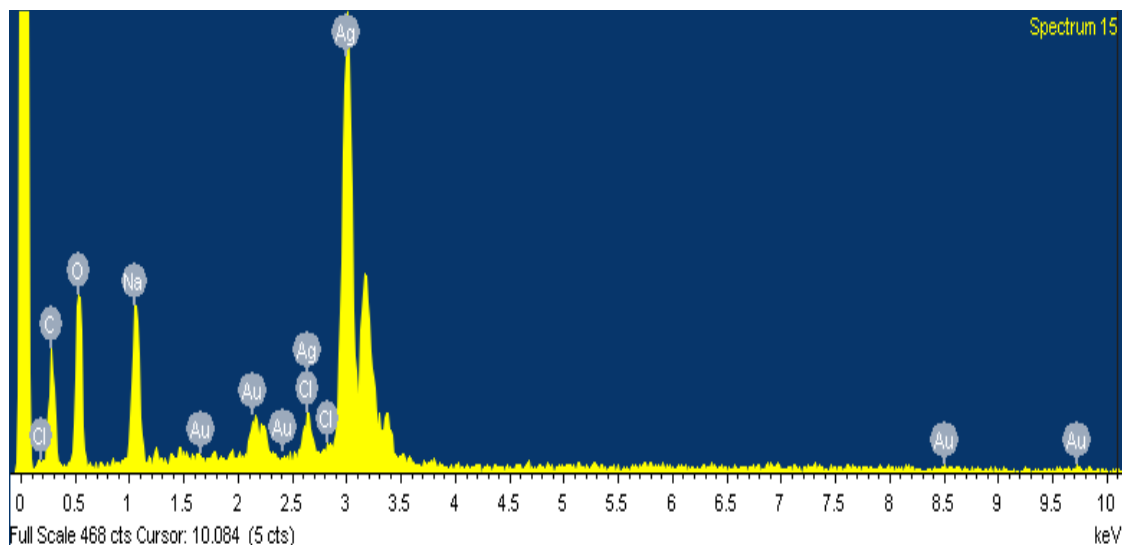


Fig:12: EDS spectrum of the citric acid doped silver nanoparticles

5. RESULTS AND DISCUSSIONS:

Silver nanoparticles were prepared using sol-gel method. The nanoparticles are annealed at 400 °C and its structural, optical and morphological properties have been investigated. XRD studies indicated the well defined crystalline structure and the crystallite size of 29 nm. The optical studies indicated that the sharp absorption about 350 nm indicating the bandgap of 3.5 eV of silver nanoparticles. The FTIR studies confirm the formation of bonds and confirm the silver nano crystallites formation. The FE-SEM studies indicated the formation of silver nano crystallites along with nanorods structure and agglomeration.

6. FIELD APPLICATION:

6.1. Foliar Applications

Foliar feeding is a technique of feeding plants by applying liquid fertilizer directly to the leaves. Plants are able to absorb essential elements through their leaves. The absorption takes place through their stomata and also through their epidermis.

Foliar spray fertilizer is a good way to supplement the nutritional needs of your plants. There are various types of foliar spraying options available to the home gardener, so finding a recipe or suitable solution to accommodate your needs should be easy. Keep reading to find more about using foliar sprays to maintain the health of your plants. Foliar spray, although not a substitute for healthy soil, can be beneficial when a plant is suffering from certain nutrient deficiencies. Foliar plant spray involves applying fertilizer directly to a plant's leaves as opposed to putting it in the soil. Foliar feeding is similar to humans putting an aspirin under their tongue; the aspirin is more readily absorbed into the body than it would be if it were swallowed. A plant takes nutrients through the leaf much quicker than it does through the root and stem. There is a wide variety of foliar feeds to choose from. Usually water-soluble powder or liquid fertilizers are used. If you purchase a fertilizer, be sure that there are directions for foliar application. Foliar sprays are generally less concentrated than fertilizers that are placed on the soil. Many people use natural materials for foliar sprays such as kelp, compost tea, weed tea, herbal tea, and fish emulsion.

Foliar feed should be applied in the early morning when the air is cool. Spray plants until you see the mixture dripping from the leaves. To help the foliar application stick to plants, add a small amount of insecticidal soap or horticultural oil. Do not forget to spray the underside of leaves as well.

6.2. Mechanism of Foliar Fertilization

In order for a foliar fertilizer nutrient to be utilized by the plant for growth, it must first gain entry into the leaf prior to entering the cytoplasm of a cell in the leaf. To achieve this nutrient must effectively penetrate the outer cuticle and the wall of the underlying epidermal cell. Once penetration has occurred, nutrient absorption by the cell is similar to absorption by the roots. Of all the components of the pathway of foliar-applied nutrients, the cuticle offers the greatest resistance.

Plants require 16 nutrients for their growth and development. Three of these, carbon, hydrogen and oxygen, are obtained from the atmosphere and from soil water. If proper conditions of aeration

and moisture are maintained in the soil, there is no problem with these three nutrients. However, if any of the other 13 elements, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, boron, copper, manganese, molybdenum, zinc, or chlorine, are deficient, they must be applied for the plants' use. These nutrients may be applied to the soil or they may be applied to the foliage of the plants. When applied to the foliage they are known as foliar sprays.

However, when soil conditions are unfavorable, when micronutrients are needed, or when spraying for insects and disease, it may be desirable to make foliar applications of the plant nutrient

Nutrients applied to the foliage are generally absorbed more rapidly than when applied to the soil. Foliar application provides a means of quickly correcting plant nutrient deficiencies, when identified on the plant. It often provides a convenient method of applying fertilizer materials, especially those required in very small amounts and the highly soluble materials.

6.3. Limitations of Foliar Application

Those fertilizer materials suitable for foliar application must be soluble in water. Most of these are salts and when applied in too high' concentration the solution will cause "burning" of the plant tissue. Often the safe concentration of the fertilizer material in the solution is so low that repeated applications are required to supply the needs of the plant. This is especially true of nitrogen, phosphorus, and potassium. Foliar applications become soil applications if excess solution is applied or if rain falls shortly after application. This results in inadequate absorption of the nutrient by the foliage and loss of time, machinery use and labor for the application of the material. However, it is not a complete loss as some of the material that gets to the soil will be absorbed by the plant roots. Fertilizer materials are not compatible with all insecticides, fungicides, etc. If mixed with incompatible materials, loss of effectiveness of the fertilizer, the insecticide, etc., or of both may result. In addition, this may also increase the danger of burning to the plant

When mixing fertilizers for foliar application use the recommended amounts of the fertilizer material. For most fertilizer materials this is 2 to 4 pounds of the fertilizer in 100 gallons of water. Urea may be used at 12 lbs/100 gallons, sodium molybdate or molybdic acid at the rate of 2 lb/100 gallons but only 4 to 8 ounces per acre of these are needed for plant growth. Borax or other Boron sources should be used at only 1 to 2 lbs/100 gallons of water. The chelate sources of iron, zinc, copper and manganese are used at 2 to 3 lbs/100 gallons of water. These materials are more likely to be compatible with insecticides, etc., than are the sulfates and chlorides of these plant nutrients. A sticker-spreader is required to reduce the surface tension of the water so that the spray solution will spread evenly over the foliage to give uniform application of the plant nutrients. The non-ionic sticker-spreaders are generally better than the ionic types. Household detergents may be used also. The sticker-spreaders are generally used at about one cupful per 100 gallons of water or 1 teaspoonful per gallon. Always follow the directions on the containers when using materials of this nature. For small quantities of spray use 1 teaspoonful/gallon for each 1 lb/100 gallons of

fertilizer material recommended. Apply the solution to both the upper and lower surfaces of the foliage. Apply until the solution just begins to drip from the foliage.

6.4. Process:

- The plants are kept under the shaded net at nursery.
- After that, taking the necessary observations like number of leaves per plant, number of buds, number of flowers and height of the plant before the treatment gets started.
- The plants are kept under the water stress (i.e, do not watered for three days).
- The stressed plants are divided as 3-units as each unit contain three plants.
- Each unit of the plants are named according to their treatments to be given.
 - 1. Control plants** : only water is given
 - 2. Treatment-1** : citric acid doped with silver nano particles.
 - 3. Treatment-2** : citric acid doped with silver nano particles+
Choline chloride
- After giving water stress, the treatment is started.
- The treatment is given for every 3-days (i.e, twice a week)
- For every 3-days the plants are treated with their respective treatments.
- This entire process is continued for 3 weeks.

7. OBSERVATIONS:

After the foliar application of nano-materials, the observations should be noted down. 3 plants should be kept as controlled plants (no chemical is added), other 3 plants should be treated with citric acid dopped with silver NP's (i.e, Treatment-1) and another 3 plants are treated with Nano-citric acid + choline chloride (i.e, Treatment-2).

The following tables shows the day to day observations of the plants of different treatments.

- **Control plants : Only water is given to plants.**
- **Treatment-1 : Citric acid with doped silver nano-particles.**
- **Treatment-2 : Citric acid+silver nano-particles+choline chloride**

Table-3: Number of leaves per plant [fig:13]

Type of treatment	Week-0	Week-1	Week-2	Week-3
Control plants	110	115	113	117
Treatment-1	105	113	120	130
Treatment-2	120	127	137	151



Fig:13: Observation of leaves with different treatments

Table-4: Number of buds per plant [fig: 14]

Type of treatment	Week-0	Week-1	Week-2	Week-3
Control plants	Ab	2	3	2
Treatment-1	3	4	4	4
Treatment-2	2	4	5	6



Fig:14: Observation of buds with different treatments

Table-5: Number of flowers per plant [fig:15]

Type of Treatment	Week-0	Week-1	Week-2	Week-3
Control plants	2	2	1	1
Treatment-1	3	4	4	3
Treatment-2	3	4	5	5



Fig:15: Observation of flowers with different treatments

Table-6: Height of the plants [fig:16]

Type of Treatment	Week-0	Week-1	Week-2	Week-3
Control plants	9.1cm	10cm	10.5cm	11cm
Treatment-1	9.3cm	10.5cm	11.3cm	12.3cm
Treatment-2	9.2cm	10.5cm	11.8cm	13cm



Fig:16: Observation of height of the plants with different treatments

8. CONCLUSION: From the observations, we can conclude that different treatments on plants have shown the different outputs. The plants with treatment-2 (i.e, citric acid doped with silver NP's + choline chloride) have shown the great results, such as increase number of leaves, number of buds, increased flowering and length of the plant.

8.1. FUTURE SCOPE:

The shortage of natural resources and the world's growing population requires agricultural development to be economically sustainable, profitable, ecologically friendly and efficient. Traditional fertilizers are expensive and time consuming to prepare. Therefore, there is a need for developing environmental-friendly fertilizers having high nutrient value as well compatibility with soil and environment. Following are the some of the advantages of nanotechnology in agriculture;

- Greater biocompatibility and less influence on non-targeted species.
- Used as Anti-microbial agents against wide variety of plant pathogens.
- Improves plant growth.
- They also increase crop productivity.
- Many of them used as Herbicides and pesticides.
- Nano-fertilizers boost the crop output by increasing the plant's availability of vital nutrients.

9. REFERENCES

1. Ratyakshi and R.P. Chauhan, Colloidal Synthesis of Silver Nano particles , *Asian Journal of Chemistry* Vol. 21, No. 10 (2009), S113-116.
2. Aziz, M. Khalid, M. Saeed akhtar, M. Nadeem, Z. A. Gilani, H. M. N. Ulhuda khan asghar, J. Rehman, Z. Ullah, M. Saleem. Structural, morphological and optical investigations of silver nanoparticles synthesized by sol-gel auto combustion method. *Digest Journal of Nanomaterials and Biostructures* Vol. 13, No. 3, July - September 2018, p. 679 – 683.
3. Remziye Güzel and Gülbahar Erdal. Synthesis of Silver Nanoparticles. Intech publications doi.org/10.5772/intechopen.75363.
4. Thi My Dung Dang, Thi Thu Tuyet Le, Eric Fribourg-Blanc, and Mau Chien Dang. Influence of surfactant on the preparation of silver nanoparticles by polyol method. *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 3 (2012) 035004 (4pp) doi:10.1088/2043-6262/3/3/035004.
5. Noralvis Fleitas-Salazar & Erika Silva-Campa & Seidy Pedroso-Santana & Judith Tanori & Martín R. Pedroza-Montero & Raúl Riera. Effect of temperature on the synthesis of silver nanoparticles with polyethylene glycol: new insights into the reduction Mechanism. *J Nanopart Res* (2017) 19:113.
6. G. Alagumuthu, R. Kirubha, Synthesis and Characterisation of Silver Nanoparticles in Different Medium. *Open Journal of Synthesis Theory and Applications*, 2012, 1, 13-17.
7. B. Choi, H.Lee, S. Jin, S.Chun, S.H Kim, *Nanotechnology*, 1-5 (2007).
8. J. H. Jung, et al., *Journal of Aerosol Science* **37**(12), 1662 (2006).
9. V. K. Sharma, R. A. Yngard, Y. Lin, *Advances in Colloid and Interface Science.* **145**(1), 83 (2009).
10. R. Manikandan, R. Anjali, M. Beulaja, N.M. Prabhu, A. Koodalingam, G. Saiprasad, P. Chitra, M. Arumugam Synthesis of nano particles, *Process Biochemistry*, Volume 79, 2019, Pages 135-141,
11. Amal Kallivalappil Puthalath, Sanya Hazel, Revathi Kottappara, Asha Srinivasan, Baiju K. Vijayan, Shajesh Palantavida, Synthesis of silver-copper nano-composites formed by microwave assisted chemical reduction, *Materials Today: Proceedings*, Volume 41, Part 3, 2021, Pages 525-529.

13. Samir A. Anuj, Harsukh P. Gajera, Darshna G. Hirpara, Baljibhai A. Golakiya, The impact of nano-silver particles on plants, *Journal of Trace Elements in Medicine and Biology*, Volume 61, 2020, 126517.
14. S. Ahmadi, M. Manteghian, H. Kazemian, S. Rohani, J. Towfighi Darian, Synthesis of silver nano catalyst by gel-casting using response surface methodology, *Powder Technology*, Volume 228, 2012, Pages 163-170.
15. Abdullah Yousif Obaid, Shaeel Ahmed AL-Thabaiti, E.H. El-Mossalamy, Javed Ijaz Hussain, Zaheer Khan, Effects of electrolytes and surfactants on the morphology and stability of advanced silver nanomaterials, *Materials Research Bulletin*, Volume 48, Issue 3, 2013, Pages 1137-114.
16. Ommer Bashir, Zaheer Khan, Silver nano-disks: Synthesis, encapsulation, and role of water soluble starch, *Journal of Molecular Liquids*, Volume 199, 2014, Pages 524-529.
17. Samy M. Shaban, Ismail Aiad, Mohamed M. El-Sukkary, E.A. Soliman, Moshira Y. El-Awady, Preparation of capped silver nanoparticles using sunlight and cationic surfactants and their biological activity, *Chinese Chemical Letters*, Volume 26, Issue 11, 2015, Pages 1415-1420.
18. Zhihan Li, Ming Zhang, Dong Cheng, Rendang Yang, Preparation of silver nano-particles immobilized onto chitin nano-crystals and their application to plants, *Carbohydrate Polymers*, Volume 151, 2016, Pages 834-840.
19. Shivaji V. Banne, M.S. Patil, R.M. Kulkarni, S.J. Patil, Synthesis and Characterization of Silver Nano Particles for EDM Applications, *Materials Today: Proceedings*, Volume 4, Issue 11, Part 3, 2017, Pages 12054-12060.
20. C.Y. Tai, Y.H. Wang, Y.W. Kuo, M.H. Chang, H.S. Liu, Synthesis of silver particles below 10nm using spinning disk reactor, *Chemical Engineering Science*, Volume 64, Issue 13, 2009, Pages 3112-3119.
21. Rachel G. Varghese, M.K. Anu, I. Dhanya, Gamma radiation on silver nano colloid for antifungal activity, *Materials Today: Proceedings*, 2021.
22. Iravani S, Korbekandi H, Mirmohammadi SV, Zolfaghari B. Synthesis of silver nanoparticles: chemical, physical and biological methods. *Res Pharm Sci*. 2014;9(6):385-406.

23. Guinier, A. (1963). X-ray diffraction in Crystals, Imperfect Crystals and Amorphous Bodies. San Francisco: W.H. Freeman & Co.
24. Zworykin VA, Hillier J, Snyder RL (1942) A scanning electron microscope. ASTM Bull 117, 15–23.
25. Skoog, Douglas A.; Holler, F. James; Crouch, Stanley R. (2007). Principles of Instrumental Analysis (6th ed.). Belmont, CA: Thomson Brooks/Cole. pp. 169–173. ISBN 978-0-495-01201-6.
26. Griffiths, P.; de Haseth, J. A. (18 May 2007). Fourier Transform Infrared Spectrometry (2nd ed.). Wiley-Blackwell. ISBN 978-0-471-19404-0.
27. Scott, N. and Chen, H. (2013) Nanoscale science and engineering for agriculture and food systems. Industrial Biotechnology.
28. Manikandan, A. and Subramanian, K. S. (2014) Fabrication and characterisation of nanoporous zeolite based N fertilizer, African Journal of Agricultural Research.
29. Azizi, M. and Z. Safaei, 2017. Effect of foliar application of humic acid and Nano fertilizer (Farmks®) on growth index, yield, yield components essential oil content and yield of agriculture.

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