ZINGIBER OFFICINALE EXTRACT MEDIATED GREEN SYNTHESIS OF SILVER NANOPARTICLES AND THEIR INTENSIFIED CATALYTIC ACTIVITY

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF DEGREE
OF

MASTER OF TECHNOLOGY

IN

[NANOSCIENCE AND TECHNOLOGY]

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CANDIDATE'S DECLARATION

I, Jyotsna Singh, Roll No. 2K17/NST/02 of M.Tech. Nanoscience and Technology, hereby declare that the project Dissertation titled "**Zingiber officinale extract mediated green synthesis of silver nanoparticles, and their intensified catalytic activity"** which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "**Zingiber officinale extract mediated green synthesis of silver nanoparticles, and their intensified catalytic activity"** by **Jyotsna Singh,** Roll No. **2K17/NST/02**, Department of Applied Physics, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the student under my supervision. To the best of my knowledge, this work has not been submitted or full for any Degree or Diploma to this University or elsewhere.

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Jyotsna Singh

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ABSTRACT

The payoff to using plants and plant metabolic pathway over the other biotic process for silver nanoparticles (AgNPs) synthesis have excited researchers to search mechanism of Ag^{+} ion reduction to Ag^{0}. Here we report an aqueous based simple route using ginger (Zingiber officinale) extract as capping and reducing agent which neither makes the need for high temperature nor toxic chemicals to produce spherical and well-distributed silver nanoparticles. The appearance of flavonoids, phenolic, and enzymatic functional group in the fabrication of AgNPs was investigated using the absorption spectroscopy and FT-IR. A various physiochemical set-up like pH, extract concentration, time and, the temperature varied for adjusting the shape and size of synthesized AgNPs and analyzed via absorption spectroscopy in the range of 250 to 700nm. For examining the size, shape and surface nature of synthesized nanoparticles (NPs) several characterization techniques such as absorption and photoluminescence (PL) spectroscopy, XRD, Fourier transformation infrared spectroscopy and, transmission electron microscope were used.

In this study, we interpret the homogeneous catalytic activity of synthesized silver nanoparticles on methylene blue (MB) dye reduction and analyzed the percentage of reduced capacity using absorption spectroscopy in the range of 250 to 800 nm. In this study also comparative study with different methods using different parts of plants (leaf, peel), honey and, fructose and analyzed via absorption spectroscopy in the range of 250-700 nm.

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List of Symbols, abbreviations

NPs	Nanoparticles
AgNPs	Silver nanoparticles
mM	millimolar
%	Percentage
°C	Degree centigrade
/	Per
~	Approximately
µm	Micro mole
Ag+	Silver ions
AgNO3	Silver nitrate
DI	Deionized water
DW	Distilled water
DMSO	Di methyl sulphoxide
Fig	Figure
FT-IR	Fourier Transform -Infra Red
mm	Millimeter
min	Minute
MB	Methylene Blue
NaOH	Sodium Hydroxide
nm	nano meter
A	Absorbance
T	Transmittance
pH	Potential of hydrogen
SPR	Surface Plasmon Resonance

I	Intensity
XRD	X-Ray diffraction
PL	Photoluminescent
TEM	Transmission Electron Microscope
λ	Wavelength
F.C.C	Face Centered Cubic
FWHM	Full Width Half Maxima
$NaBH_4$	Sodium Borohydride
ROS	Reactive Oxygen Species
AgCl	Silver Chloride
D	Dimension
$\triangle$	Heat

CHAPTER-1

INTRODUCTION

Nanoscience and Nanotechnology is a multi-skilled field that conducts together researchers in various scientific disciplines such as biotechnology, chemistry, material science, and physics for improvement of material nature at the nanoscale level [1]. Nanotechnology contributes to the fabrication and processing of the metal nanoparticles by adjusting their shape and size [2]. Metal nanoparticles have unique properties at a nanoscale level within size range 1-100nm and have drawn great attention due to their large surface area- to- volume ratio and their large optical field enhacement appearing in powerful scattering and absorption of light. Nanoscience has been established recently as a new multidisciplinary science. At nano dimension noble metal particles silver, gold changes its properties and applicable in various field like the conversion of solar energy, nanomedicine, wastewater treatment, catalyst, and sensing, etc. As well as nanotechnology applied in various field like textile, biomedicine, cosmetics, drug delivery, food packing, biochip, biosensor, nonlinear devices, photonics, single electron transistors, space industries etc [3], [4], [5].

During the last decade, metal nanoparticles have received strong attention because of their unique size and adjustable properties. Metal nanoparticles have unique chemical and physical properties, i.e., high surface area to volume ratio, optical properties like surface Plasmon resonance, more reactivity, different shape, and nondispersive size [2]. Silver has a strong attention for researchers because of their unique antibacterial action and catalytic properties. Metallic silver has the highest thermal conductivity, electrical conductivity and lowest contact resistance in relation to other metal. Silver nanoparticles (AgNPs) have gained great attention because of their use in optoelectronics, microbe killing, sports clothes, etc. Basically, applied two main approaches for the fabrication of nanoparticles top-down and bottom-up, Top-down means fabrication of nanostructures

by high energy ball milling and etching process, whereas bottom-up means building up of nanostructure at an atomic level [6-11].

In comparison with other methods, the green synthesis of AgNPs has drawn more interest in the past few years due to reduced toxicity, lower temperature, cost-effective and, eco-friendly. Green fabrication route has received strong attention due to the presence of reducing as well as a stabilizing agent in the plant. Expensive chemicals are not required in green synthesis, various numbers phytochemicals, flavonoids, tannin, resins, enzymes, carbohydrates, etc present in plants which are capable of the formation of the nanoparticles. A different part of plants has known to a large range of chemicals that are responsible for the green synthesis of metal nanoparticles [10], [18]. The rapidly growing demand for green nanoparticles synthesis has now great attention for researchers than physical and chemical methods. Green fabrication route of nanoparticles reduces toxicity to the environment. Green approaches, exclusively plant parts like leaf, peel, seed, root and plant nectar (honey) provides a better platform in producing specific phytochemicals for the fabrication of nanoparticles and quantum dots. Plant extracts are prepared under appropriate conditions low temperature (<70°C) an aqueous medium. However, the plant-mediated colloidal synthesis of metal nanoparticles is the one way that offers the opportunity by which such materials can be achieved, which has already shown itself to be a curious field for future nanotechnologies [12-17]. Today developments in plant-mediated techniques in the fabrication of NPs have shown promising results to improve and maintain the size. Plants eliminate the chemical toxicity by making the nanoparticles more biocompatible than other physical, chemical and biological method. It is necessary to explain the possible mechanism which is responsible for nanoparticles green synthesis.

1.1. ORGANIZATION OF DISSERTATION

Here we report on ginger (Zingiber officinale) extract mediated green synthesis of silver nanoparticles (AgNpS) and comparative study with different methods mediated by several parts of plant extract (neem leaf, pomegranate peel), plant nectar (honey) and white sugar (fructose) which are completed in aqueous medium. To study the effect of different physical parameters like temperature, pH, extract concentration, time intervals in the fabrication of silver nanoparticles and observed the effect through absorption spectroscopy. To investigate the size, shape and, morphology of ginger capped AgNPs

various characterization technique were used such as absorption and photoluminescent (PL) spectroscopy, FT-IR, XRD and transmission electron microscope. Thus, these ginger-capped synthesized silver nanoparticles offer the opportunity for intensified the catalytic reduction of dye and observed the percentage degradation via absorption spectroscopy.

1.2. Literature review:

1.2.1. Nanoscience and Nanotechnology:

Nanoscience is a term in which we study the structures of material on the nano meters scale (one nm equivalent to the billionth meter). For an understanding the nanoscale object, we take the example of human hair, the human hair is 100,000 nano meters wide. When materials are maintained at the nano meter scale, then a very interesting change in their physical and chemical properties [1]. Nanostructures have existed in nature when life starts on earth, single strand DNA, building the block of a living organism, red blood cells, etc all about 3nm. The wing of butterfly and feather of peacock contain nanostructures that absorbed and scattered the light which looks dazzling blue and green hues [19]. Figure: 1.1 shows the nanoscale objects and comparative dimension with different things (Å to cm) such as atom (1Å) to football (22cm) for understanding the nanoscale objects.

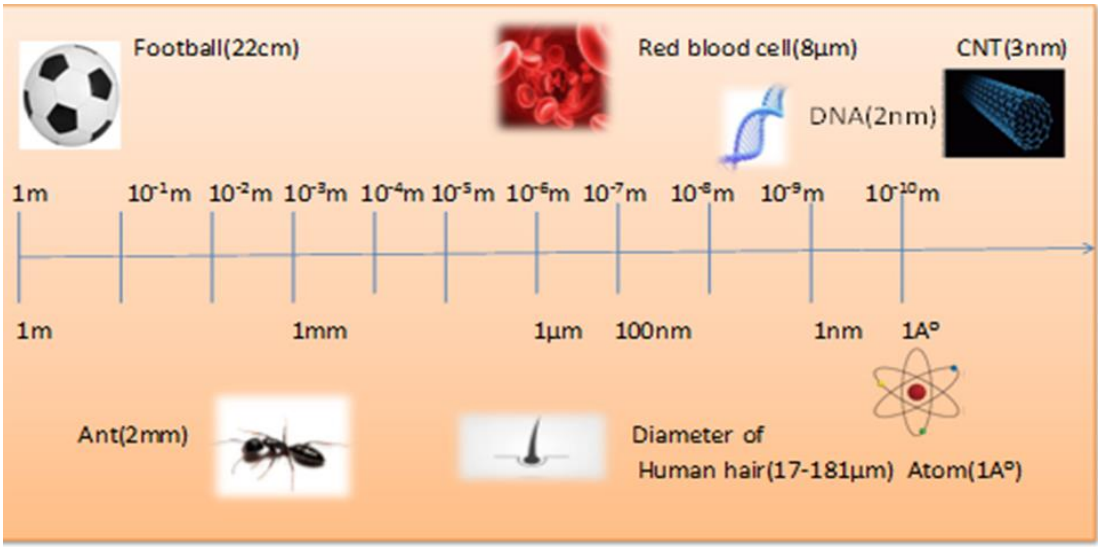


Fig:1.1 A scale to show the comparative dimensions of the different things.

Nanotechnology is the technology that handling and engineering the matter on the atomic and molecular level. Initially, nanotechnology considered in the speech of American physicist Richard Feynman in 1959. He gave the title "There's Plenty of Room at the Bottom." Richard Feynman talked about the significance of engineering and managing things on a tiny level. Initially, nanotechnology term was used by Japanese scientist Norio Taniguchi in 1974. After the discovery of scanning tunnelling microscope (STM) and atomic force microscope (AFM) scientists can visualize the material at the atomic level. Each material on the earth is formed from atoms and spacing between two atoms is approximately in the range of 0.011 Å to 0.014 Å. Once particles are synthesized at nanoscale level considering one to hundred nano meters of materials, properties change significantly from that at the larger scale. Quantum effect dominates the properties of the material at nano meter scale range, properties like fluorescence, melting point, electrical conductivity, and magnetic permeability as a dimension of particles decrease. Nanotechnology is accomplished to fabricate various material and devices with a huge range of applications, like nanomedicine, biocompatible energy production, electronics, and consumer products [17], [19-21].

1.2.2. Nanoparticles:

Nanoparticles term is used to the particle with a minimum of one dimension below 100nm. Material properties changes as their size approach the nanometre scale range and surface plasmonic properties considerable. As to the size range between one nanometre to hundred nano meters, the noble particle like silver, gold and, platinum have surface plasmon resonance significantly. Semiconductor particles show large band gap at the nanoscale and magnetic particles considerable superparamagnetism at nano dimension. Such nanoparticles are employed in the biomedical application like drug delivery, an imaging agent, biosensor and biochip [45], [46].

1.2.3. Classification of nanoparticles:

Nanoparticles can be classified according to their dimension, characteristic, size, shape and properties, such as ceramic nanoparticles, carbon-based nanoparticles, metal nanoparticles, polymeric nanoparticles, viral nanoparticles, lipid-based nanoparticles, magnetic nanoparticles, etc [53]. types of nanoparticles and their applications in medical field shown in figure:1.2. On the basis of dimension nanoparticles are classified in, one dimension (1D), two-dimension (2D) and three dimensions (3D). [21-25]. Table-1

illustrate the examples of nanostructures, confinement and their applications of every dimensional nanostructure.

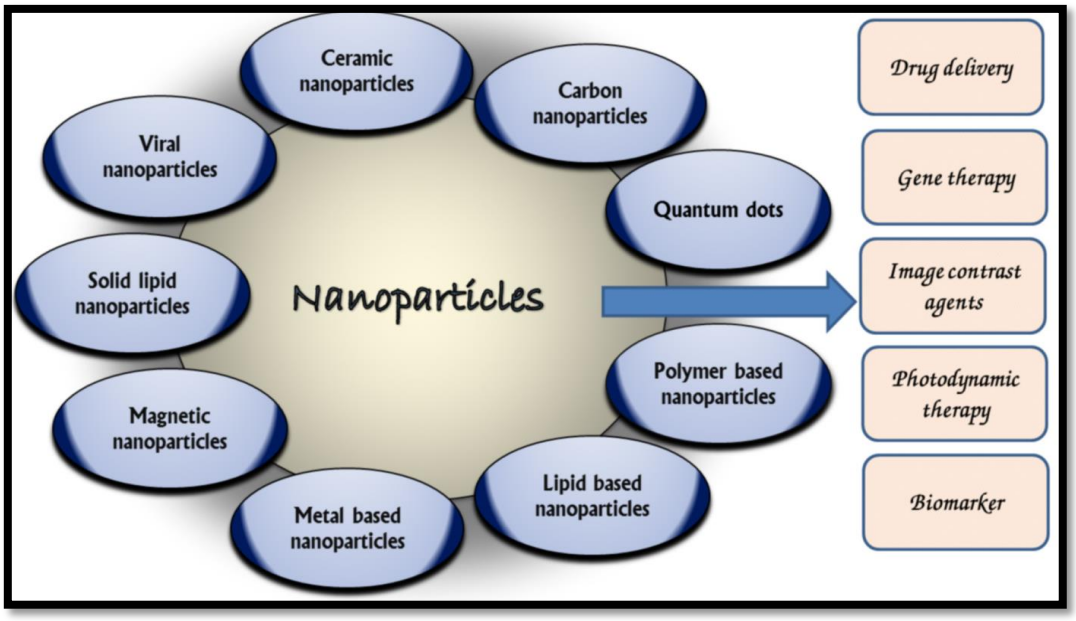


Fig: 1.2 Types of nanoparticles and their biomedical application [53].

Table - i) Dimension based nanoparticles:

Serial no.	Dimensionally Confinement	Size range	Examples	Application
1	1D	1 to 100nm	Thin film or monolayer	Sensors, data storage, fiber-optic, optical devices, fuel cell, field effect transistor, etc.
2	2D	1 to 100nm	CNT, nanowires	photoemitters, photodetectors, high-speed field effect transistors, and high-temperature/high-power electronic devices.
3	3D	1 to 10nm	Quantum dots	Biosensors, drug delivery, light emitting device, biochip, tumors targeting, drug testing, etc.

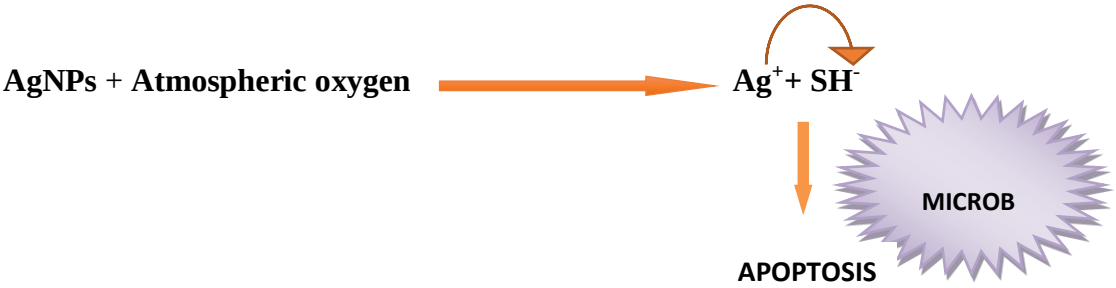
Natural and anthropogenic (anthropogenic is an adjective that describes changes in nature made by people) origins of nanoparticles (NPs), Nanoparticles are truly not new and have

antiqueness as long that of the earth itself. e.g: NPs could be generated through a volcanic eruption. Hence NPs can be designed either purposely as engineered nanoparticles (ENPs) and incidentally, by the lattice including origins like aerosols from a volcanic explosion, woodland fires, microspores pieces, and viruses as well as anthropogenic causes [21]. Nanoparticles in the meteorological environment may grow from unless stable or free sources. A part of nanoparticles is directly released from agitation sources, others are made by nucleation and reduction process of the hot supersaturated vapor compression process when being cooled to ambient temperature. Chemical reactions in the atmosphere may start to chemical species by very low saturation vapor pressure, which will finally produce particle by nucleation [22].

1.2.4. Silver nanoparticles (AgNPs):

Silver is a transition metal of group 11 and period 5 of the periodic table with symbol 'Ag' their atomic number 47 and mass number 107.8682amu. It shows the highest electrical and thermal conductivity (429W/m.K) than any other metal. Silver has soft, white, face-centred and diamagnetic in nature. It is not reactive on microbe in metallic form, the only ionic form of silver kills the bacteria [23]

The use of silver for a cure of wound dressing and burn infection about a hundred years. Silver nanoparticles exhibit different properties than that of bulk material, like as increased catalytic properties because of the large surface area to volume ratio. Nanoparticles especially silver nanoparticles attended great attraction due to their unique antibacterial action, silver ion (Ag^{+}) released when silver nanoparticles (Ag^{0}) reacts to atmospheric oxygen, reaction with silver nanoparticles and atmospheric oxygen depend upon the surface morphology of AgNPs. Ag^{+} reacts with the sulfur-containing enzyme of a microbe and destroyed the DNA and causing the apoptosis (cell death) shown in following reaction.



1.2.6. Fabrication methods of AgNPs:

Generally, silver nanoparticles are synthesized through physical, chemical biological and green methods, these methods have divided into two parts top-down (physical, mechanical) and bottom-up (chemical, biological and plant-mediated) approach. In biological and plant-mediated fabrication process are divided into two parts such as extracellular and intracellular mechanism. Microbe-based synthesis followed by both extracellular and intracellular mechanism and plant-based synthesis is extracellular because in plant-based method only specific part use rather than the whole plant [18]. Figure: 1.3 shows the diagrammatic representation of fabrication technique of nanoparticles, their transformation at each step and examples.

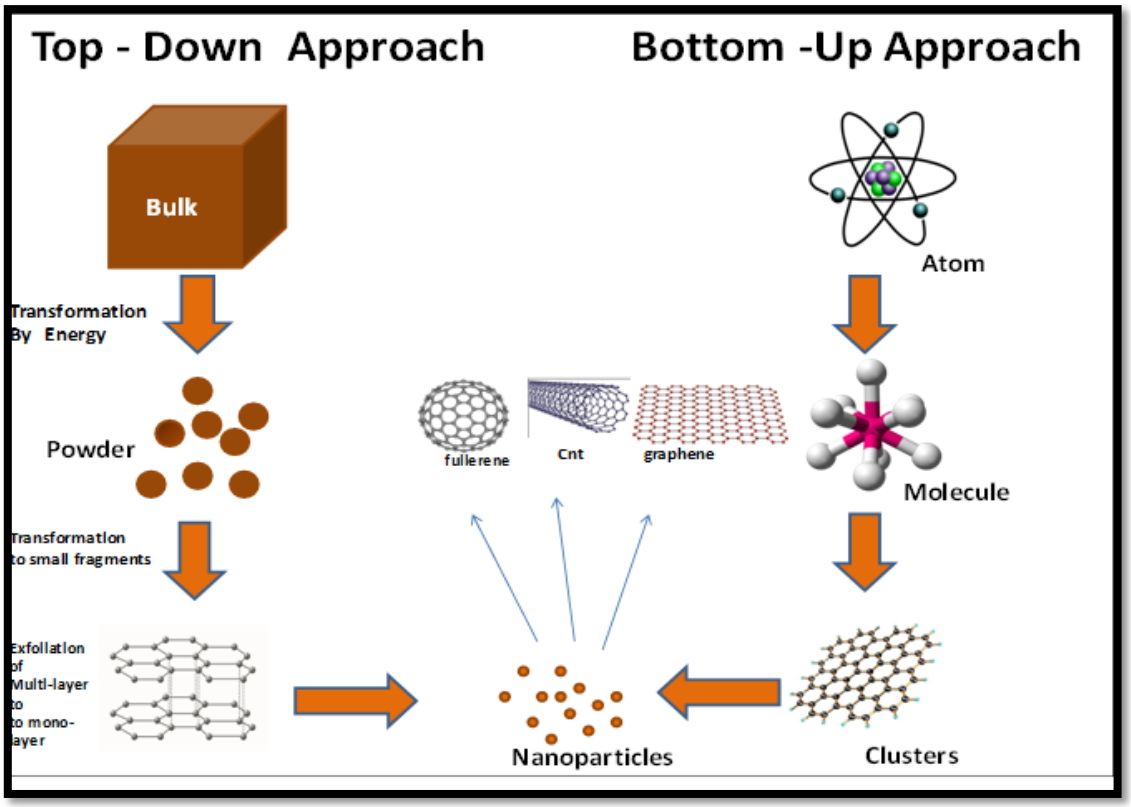


Fig:1.3 Diagrammatic representation of the fabrication of nanoparticles via top-down and bottom-up routes.

1.2.6.1. Physical methods:

The most important physical method is physical vapor deposition (PVD) in which involves the various technical process such as laser ablation, coating under vacuum (low

pressure) condition, sputtering and pulse laser deposition various application like industrial, surface modification of textile improvement, luminescent material. AgNPs fabricated by this process depends upon the various parameter like the wavelength of the laser, The duration of the laser pulses (in the femto-, pico- and nanosecond regime), The ablation time duration, The liquid medium, The presence of surfactant, etc. Many advantages of physical approaches like uniform distribution of nanoparticles, uncontaminated metal nanoparticles, the formation of very small nanoparticles in high concentration and not require toxic chemicals. A major disadvantage of high temperature and good vacuum conditions, this process more expensive and time taking [10],[18].

1.2.6.2. Chemical methods:

Fabrication of AgNPs via chemical method is a bottom-up approach, which is basically used as a reduction and stabilization of metal nanoparticles. Reducing as citric acid ($C_6H_8O_7$), ascorbic acid ($C_6H_8O_6$), ethylene glycol ($C_2H_8O_2$), ethanol (C_2H_5OH), sodium borohydride ($NaBH_4$), DMF (N, N dimethyl formamide), etc. Only reducing agent are not sufficient for nanoparticles synthesis after some time passes these nanoparticles are aggregate for prevention of aggregation it is necessary to use stabilizer during the fabrication process of nanoparticles. These chemicals which are used as reducing and stabilizing agent are expensive and toxic. Although these chemicals are hazardous for the environment [1].

1.2.6.3. Biological methods:

The biological approach or green approach is growing the concept of nanotechnology in which different shape and size of nanoparticles are fabricated from plant extract, plant nectar (honey) and microbes like bacteria, fungi, yeast, etc. Biological methods of AgNPs is a bottom-up approach that mostly involves phytochemicals or biomolecules such as protein, amino acid, DNA, glucose, and fructose as precursors. Since the reaction takes place in a single step because plant precursor acting like both reducing and stabilizing agent, plants like tulsi, neem, aloe Vera, ginger, honey, mango, amla, marigold, lemon, etc [2], [8],[10],[15],[16],[30-32]. The phytochemicals like flavonoids and their functional group, groups such as aldehyde (-CHO), ketone (-CO), hydroxyl (-OH), carboxylic (-COOH) use as reducing agent and enzyme and their functional group like amine(-NH2) and carboxylic group act as stabilizing agent [10]

Fabrication methods are shown in figure: 1.4 and figure:1.5 shows the various parts of plants for fabrication of AgNPs.

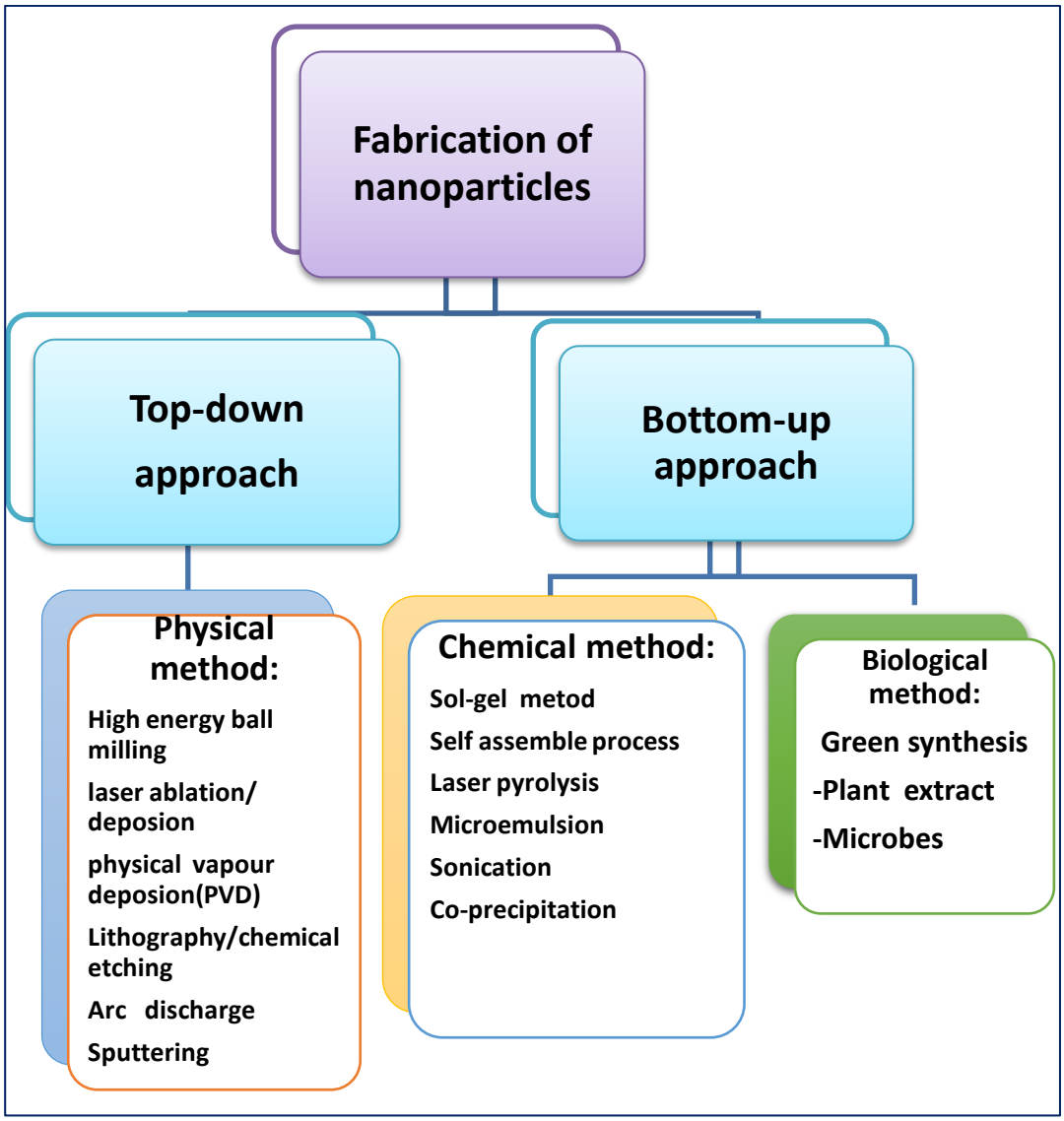


Fig:1.4. Different methods for fabrication of AgNPs.

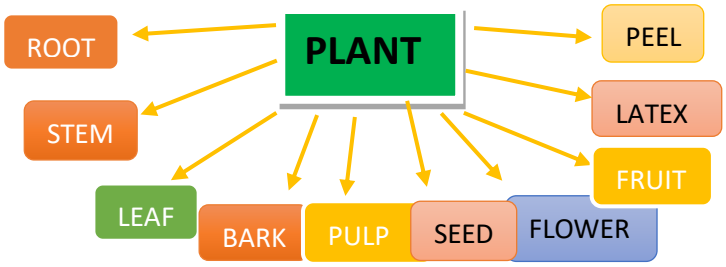


Fig: 1.5 Parts of plants which are used for the fabrication of AgNPs.

1.2.7. Need for the green approach:

The physical and chemical fabrication methods are expensive as well as harmful and toxic for the environment while the green approach is clean, eco-friendly and, low coast. In green fabrication method, the component present in plants acts as reducing as well as a stabilizing agent which are stabilized the nanoparticles about six month and largescale nanoparticles synthesized without any external condition like high temperature, pressure, energy, and toxic chemical. The green approach can be performed via plant extract and microbes but microbes mediated synthesis is costly plant due to the maintenance of culture, more chances of contamination. In chemical approach, by-products are formed which are toxic for the environment and human being, due to this reason nanoparticles which are synthesized through chemical and physical approach are restricted for medical application (WHO,2002). Nanoparticles synthesized through green route are more attention for researchers because of the low cost, easily available, low contamination, both reducing & stabilizing agent, eco-friendly and simple procedure shown in figure: 1.6. Although this method is nontoxic and biocompatible enhanced their potential in medical application [2],[10],[18].

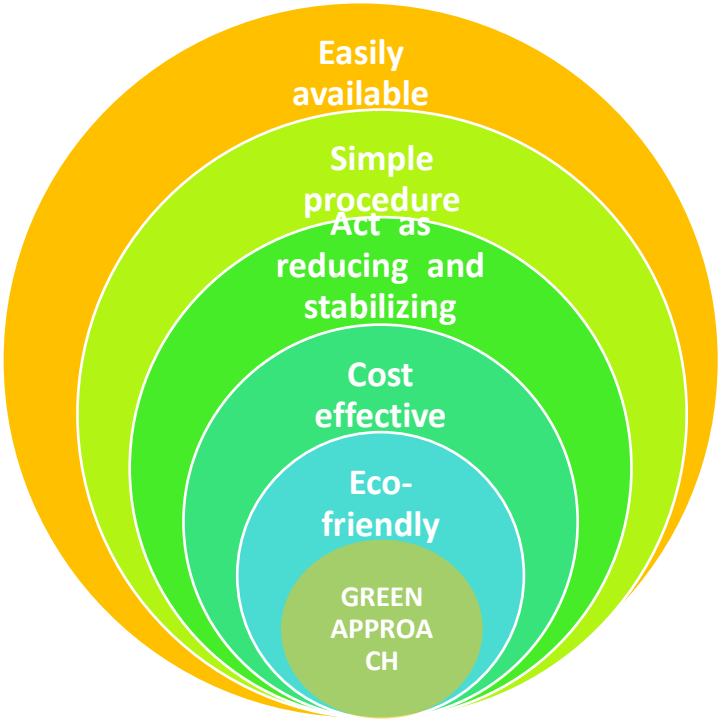


Fig:1.6 Benefit of the green synthesis of AgNPs by plant extract.

1.2.8. Depending factors and Possible mechanism for the green synthesis of AgNPs:

1.2.8.1. Factors:

Plant extract and plant nectar mediated fabrication methods are dependent on the following factors such as pH, temperature, period and extract concentration and their properties like size, shape, and surface nature of silver nanoparticles depend on these factors, shown in figure:1.7.

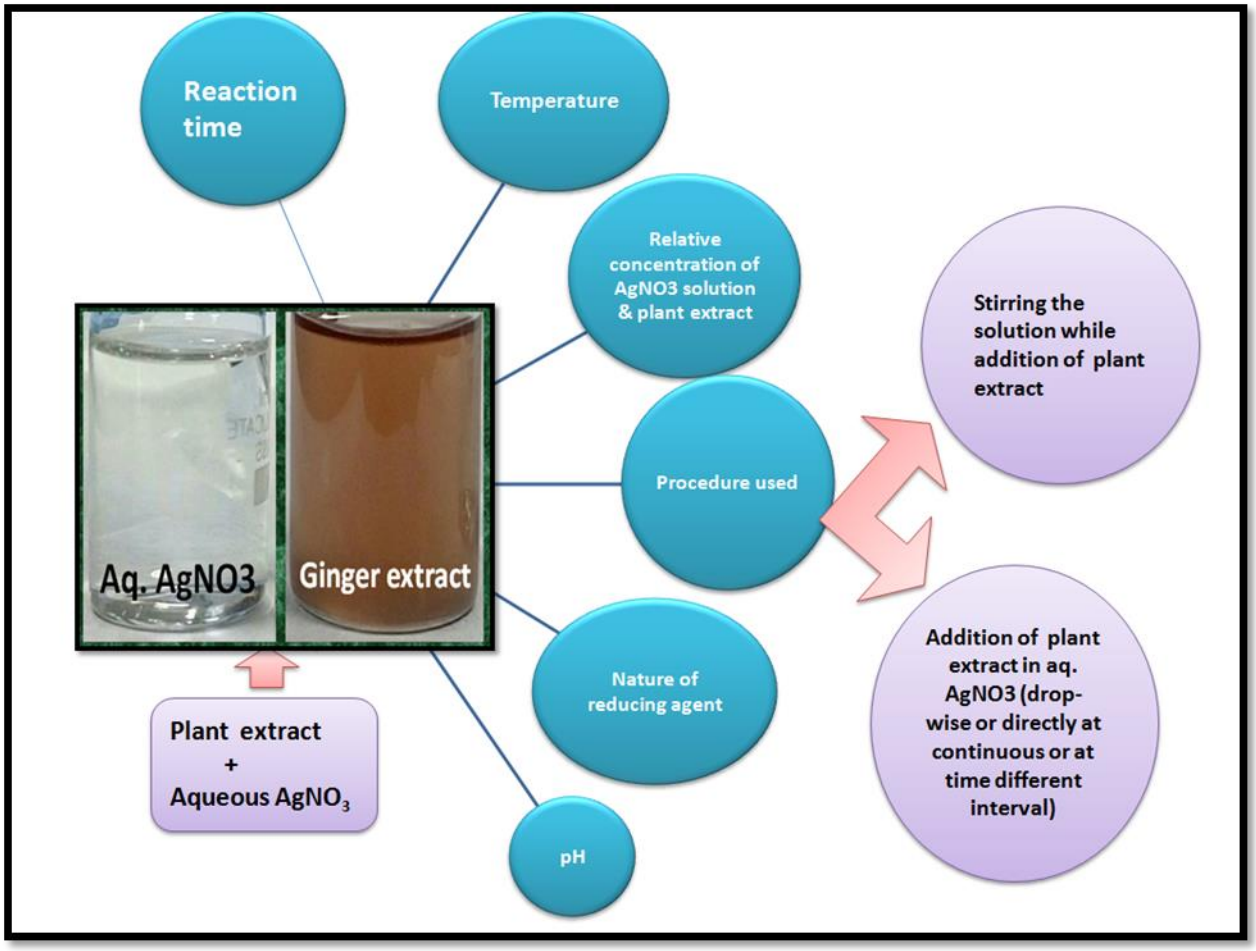


Fig:1.7 Diagrammatic representation of depending factors for AgNPs synthesis.

1.2.8.2. Mechanism:

There is no exact explanation in the literature about the mechanism of nanoparticles synthesis mediated through plant exact. A hypothetical mechanism for the green synthesis of silver nanoparticles are involving in four steps and shown in figure: 1.8.

1. Formation of ion in aqueous solution,

2. Cluster formation,

3. Reducing of AgNPs through phytochemicals like flavonoids, quinones, terpenoids, glucose, fructose, etc present in plants extract and plant nectar.

4. Reduced nanoparticles are stabilized through enzyme present in plants parts like leaf, root, bark, stem, latex, etc.

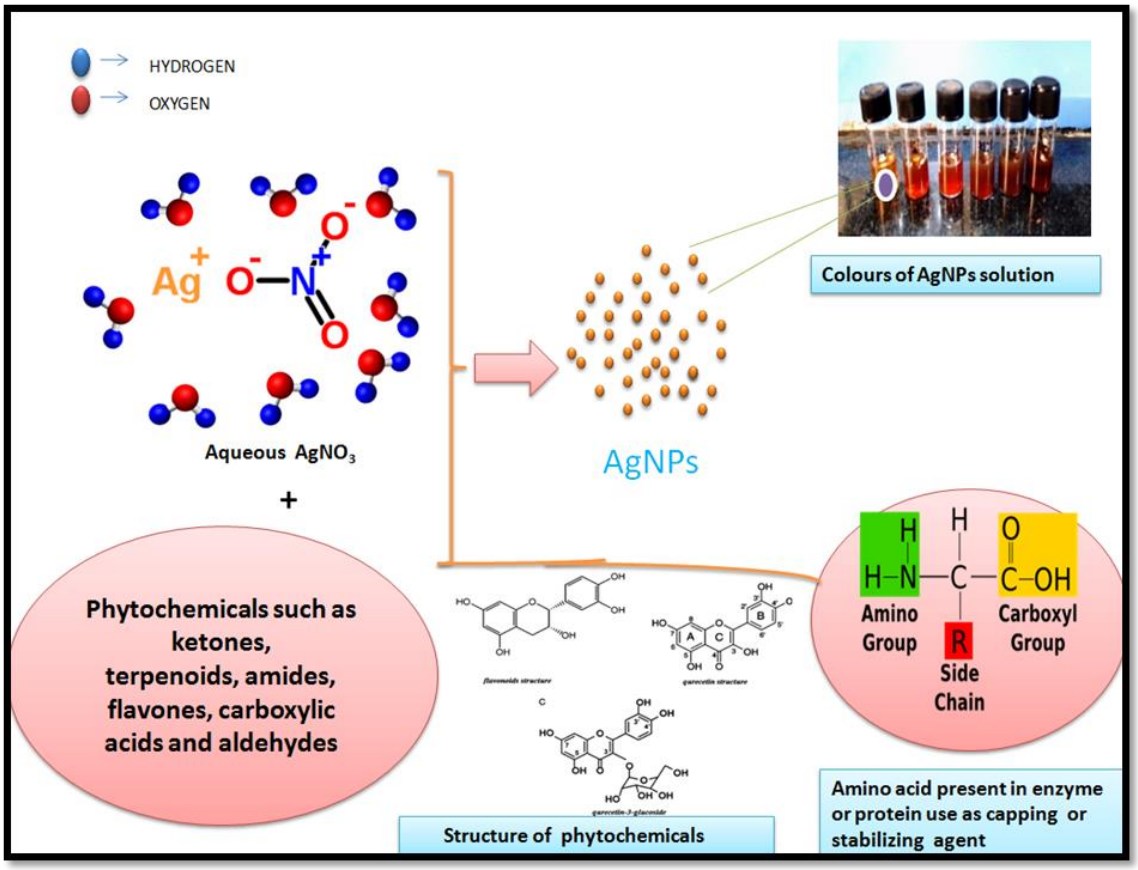


Fig:1.8 A hypothetical mechanism of plant parts mediated synthesis of AgNPs.

Reduction of AgNPs are possible due to tautomerization (changing in the keto-enol form) of an alcoholic group(-OH) present in phytochemicals and stabilized via the enzyme (protein) present carboxylic group(-COOH) and amine group(-NH_2) which are attached with Ag^+ and -COO-with electrostatic attraction. In protein the primary unit is amino acid (NH_2-RCH-COOH), which are present in zwitterion form means (+) ve and (-) ve charge in same molecule ($+NH_3$-RCH-COO^-) ,when increase the pH of solution it supports the stabilization of AgNPs for more without any stabilizer, which is illustrated in the following reaction [2], [27].

$$^+NH_3\text{-RCH-}COO^- + OH^- \longrightarrow NH_2\text{-RCH-}COO^- + H_2O$$

1.2.9. Applications of silver nanoparticles:

Silver nanoparticles offer wide range applications due to numerous properties such as high electrical and thermal conductivity, chemical stability, catalytically action, surface plasmonic behavior and antimicrobial action demonstrated in figure:1.9. The unique properties of AgNPs are arises to similar size and shape which are fabricated through plants part and microorganism like bacteria, fungi, yeast. AgNPs recently develop imaging technique for in vivo diagnosis, cell signaling, biomarkers for protein, tissues and various effective medical application with less side effect. AgNPs are also applicable in an agricultural field like preserve food packing nano sensor, biosensors which can plant virus, nano capsules containing herbicides, chemical, properties of plant and herbs. Silver nanoparticles also used for sensing for Hg^{2+}(mercury) present in tap water which is a major cause of Minamata disease, colorimetric sensor, cancer treatment, antibacterial spray, cosmetics, nano silver embedded in sports cloth, dietary supplement, detergent, ointment, and cream [28].

Fig:1.9. Schematic representation of the Applications of silver nanoparticles.

1.2.9. Antimicrobial action of silver nanoparticles:

Silver nanoparticles are the nanostructure ranging from 1-100nm used as the antimicrobial medium because of their large surface area- to- volume ratio at nano range. As small as the particles size around 1-10nm their antimicrobial action increase. Silver nanoparticles have still reported strong effect against several microbes, comprising gram-negative bacteria (Escherichia Coli, Salmonella typhimurium, and Pseudomonas aeruginosa), gram-positive bacteria (Staphylococcus aureus and Bacillus subtillis) and fungi (Aspergillus niger and Candida albicans). The proper mechanism of silver nanoparticles against microbes is still not known exactly. According to more researcher when silver nanoparticles in contact with reactive oxygen species(ROS) such as hydrogen peroxide(H_2O_2), oxide ion(O_2^{--}),superoxide(O_2^{-}), free radicals($O_2^{\cdot-}$) convert into silver ion(Ag^+) these silver ion interact with group(-SH) of bacterial enzyme and protein, disrupt the peptidoglycan layer of bacterial cell wall and interfere the respiration mechanism, causing the apoptosis (bacterial death), this mechanism was described in figure: 1.10. Small AgNPs(5nm) released more Ag^+ than larger (11nm) under aerobic environment through increased surface area to volume ratio as size decreases. Agnihotri et al investigate from disk -diffusion test of E. coli, the antibacterial action depends on different size and shape of AgNPs: triangular AgNPs > spherical AgNPs > rod-shaped AgNPs [26].

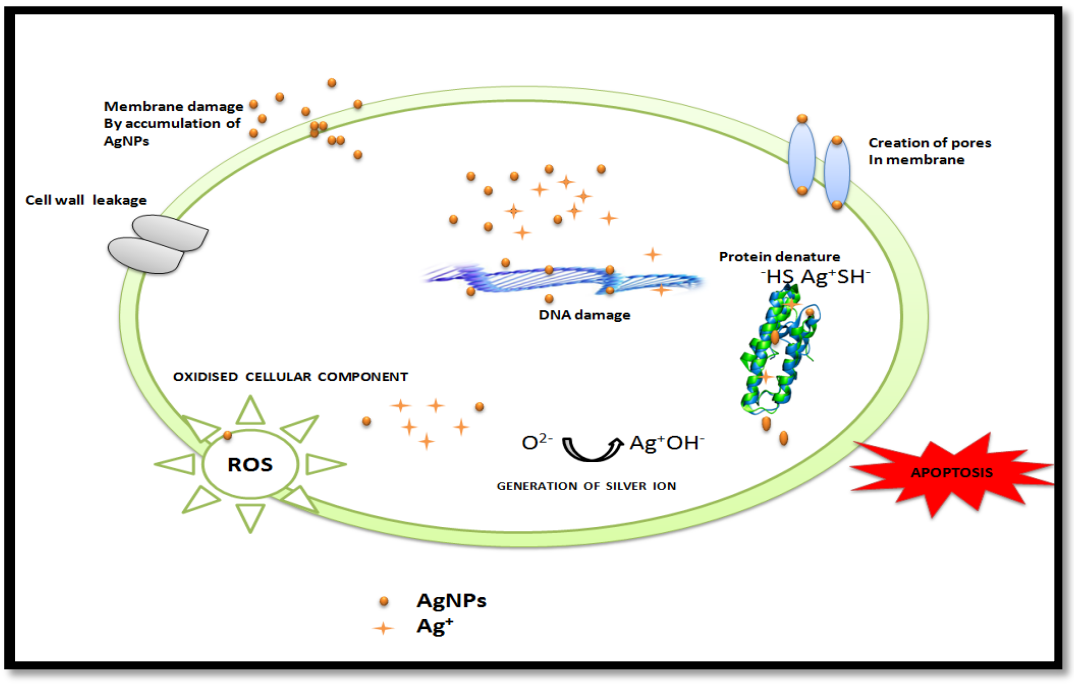


Fig:1.10. Schematic representation of the antimicrobial mechanism of AgNPs.

1.2.11. Toxicological issues of silver nanoparticles:

Although, approximately fifty-five years after Richard Feynman's prominent speak a remarkable improvement has been attained in the expanse of nanoscience & nanotechnology. But, still, some toxicological issues in this field because nanoparticles are not only toxic for microbe it is also toxic for living animals. AgNPs can be cytotoxic effects on animals, cytotoxicity depends upon the size shape and dose of silver nanoparticles. According to some research report silver nanoparticles accumulate in a target cell, tissues through various ways and toxic effects like cell wall break, swelling, DNA destruction, and animal death. Mostly silver nanoparticles accumulate in the liver and causing the generation of reactive oxygen species (ROS). smaller nanoparticles approx 20nm size AgNPs are easily translocated through the bloodstream and reached in liver, lungs, kidney, and brains of an animal-like rat. (R) silver nanoparticles distributed in various organs more to less: lung >spleen > kidney > thymus > heart. More exposure of silver salt ($AgNO_3$, AgCl) can cause of the skin disease like argyria (causing the color of skin bluish grey) and argyrosis (affected eye). AgNPs can also accumulate in skin and nail and through respiratory system enter into alveolar space [26], [29].

Silver nanoparticles also disrupt the nitrogen fixation process which leads to disturbing the eco-system. Bacteria like rhizobia and associative bacteria which are supporting the changing of nitrogen gas into ammonium compound and symbiotic relation with legumes plants but nano silver exposure affects these bacteria and harm the soil microbial colony [29].

1.2.12. Catalytic properties:

In recent year, the catalytic action of silver nanoparticles (AgNPs) has gained great attraction by large surface area -to- volume ratio. Organic pollutants have a major cause of environmental pollution. In many organic pollutants, it is necessary to identify, the obstacle of organic dye pollution caused by the development of industries waste such as plastic, paint, textile, and paper. The discharge of water waste, which carries plenty of organic dyes, can impede with sunlight penetration and with the photosynthesis of plants. Furthermore, many synthetic dyes can cause a serious menace to the human body. To overcome that obstacle, a variety of methods has been used, such as catalytic degradation, fabric filtrations, chemical oxidation, and adsorption. Amongst such methods, catalytic degradation of perilous dyes with metal nanoparticles is a convenient degradation method

because of their novel properties like physical, chemical, and electronic, which are not present in bulk counterpart. Silver nanoparticles are the first choice because they're a unique shape, size, and strong catalytic action. Although, it is critical to separate dye from water because of their aromatic structural stability. Catalytic degradation of dyes using silver nanoparticles is an assuring agent [12], [49].

1.3. Characterization Technique:

1.3.1. Spectrophotometer:

UV- visible spectroscopy indicate the absorption and emission spectroscopy in the region of an ultraviolet and visible region. the tool used for UV-visible spectroscopy is called UV-visible spectrophotometer. It used for measuring an intensity of light passing through the sample, sample absorbs, transmits or scattered these lights in a specific spectral region, ultraviolet(190-400nm) and visible (400-700nm). In nature, each chemical compound absorbs, transmits a specific colour range, that depends upon the electronic transition of the electromagnetic spectrum, atoms, and molecules. The spectrophotometer is shown in figure:1.11.

Fig:1.11. UV-VIS/IR spectrophotometer (Model: Perkin Elmer Lambda-750).

A molecule containing bonding and non-bonding electrons which can absorb energy in the UV-Vis region and excited these electrons to anti-bonding molecular orbital, and

some allowed and some forbidden transitions possible during this process like σ–σ *, n–σ*, π–π *, n–π*[52].

1.3.1.1. Devices and Mechanism:

In spectrometer contain a light source (UV and visible), monochromator, slit (wavelength selector), two cuvettes holder for sample and references solution, photomultiplier tubes (PMTs), detector and a computer for display. This basic arrangement of double beam spectrophotometer was illustrated in figure 1.12.

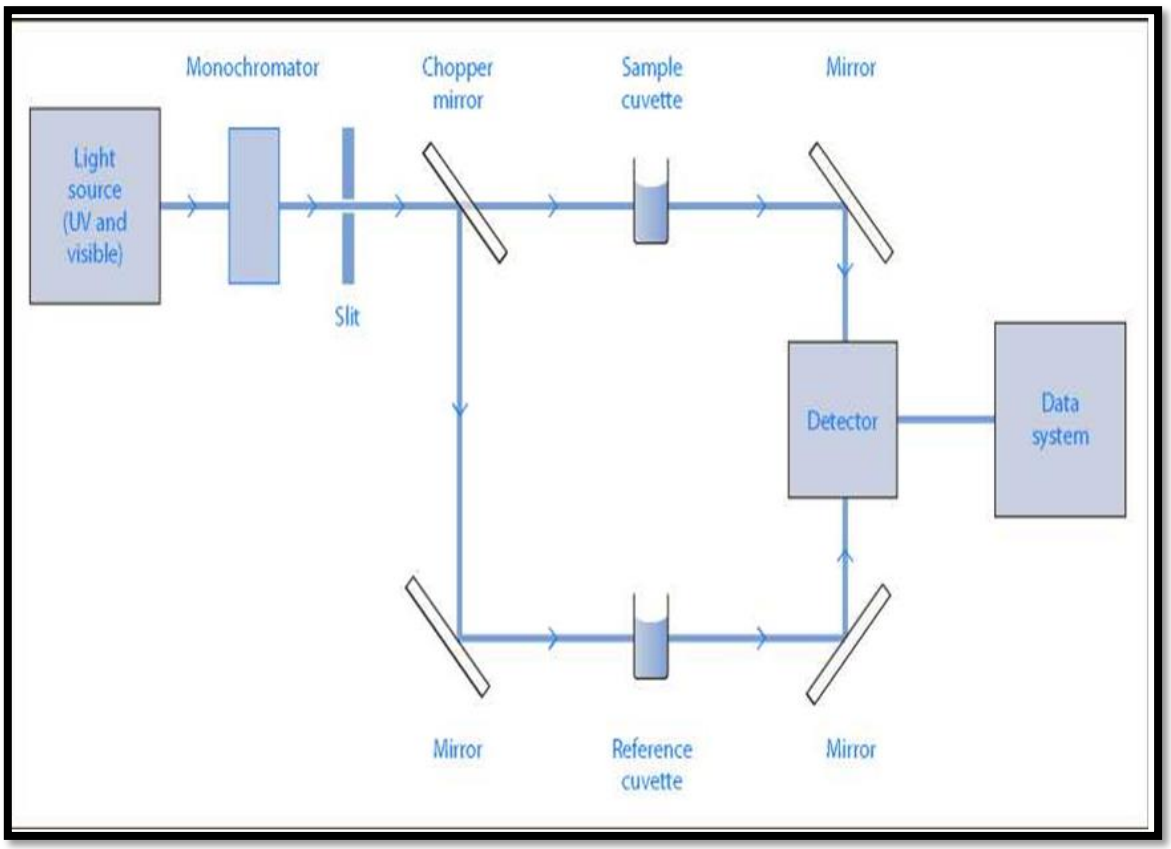


Fig:1.12. Diagrammatic representation of double beam spectrometer.

In common, a spectrophotometer containing two devices: a spectrometer and a photometer.

1. Spectrometer: It generates light of desired field wavelength. First, a light beam (photons) travel through a monochromator (prism) that separate into many components of wavelength (spectrum). The wavelength selector (slit) transmit only the desired wavelength of light.

2. Photometer: After the desired wavelength of light travels through the sample and reference solution present in different cuvettes, the photometer encounters the number of photons that are absorbed and then transmits a signal to a computer system in the above figure.

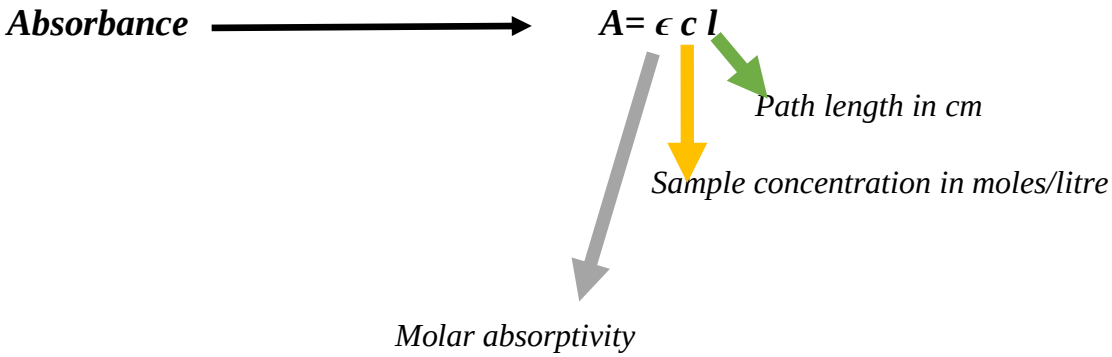
A lamp capitulates the source of light. The beam of light collided with the diffraction grating, which proceeds like a prism and splits the light into constituent wavelengths. Although if the sample absorbed light of a given wavelength, the intensity of transmitted light (I) is less than the intensity of absorbed light (I^0). Transmittance is represented by "T" and can be calculated using them.

$$T = \frac{I}{I_o}$$

Where 'I' is the intensity of light after the light beam passing through the cuvette and I^0 is the intensity of light before the light beam passing through the cuvette. Absorbance is compared with transmittance by this expression:

$$\text{Absorbance (A)} = \log(I_o/I) = \log(1/T)$$

Where absorbance means the quantity of absorbed photon. When T=1.0 then A=0, means absorbance has not occurred. To resolve the unrecognized concentration of the sample by using Beer-Lambert law.



Molar absorptivity may be large or small depending upon the strong absorbing compound (ϵ>10,000) or weak absorbing compound (ϵ=10 to100) [38].

Absorbance is a progression of light that is absorbed by the sample, the detector feels the light traveling through the sample and produce this information into the computer system. The particular sample absorbs at a particular wavelength; hence a spectrometer is used to

generate various wavelengths. For example, silver nanoparticles have the highest absorbance peak near 415nm and gold nanoparticles have the highest absorbance peak near 520nm, as shown in figure 1.13.

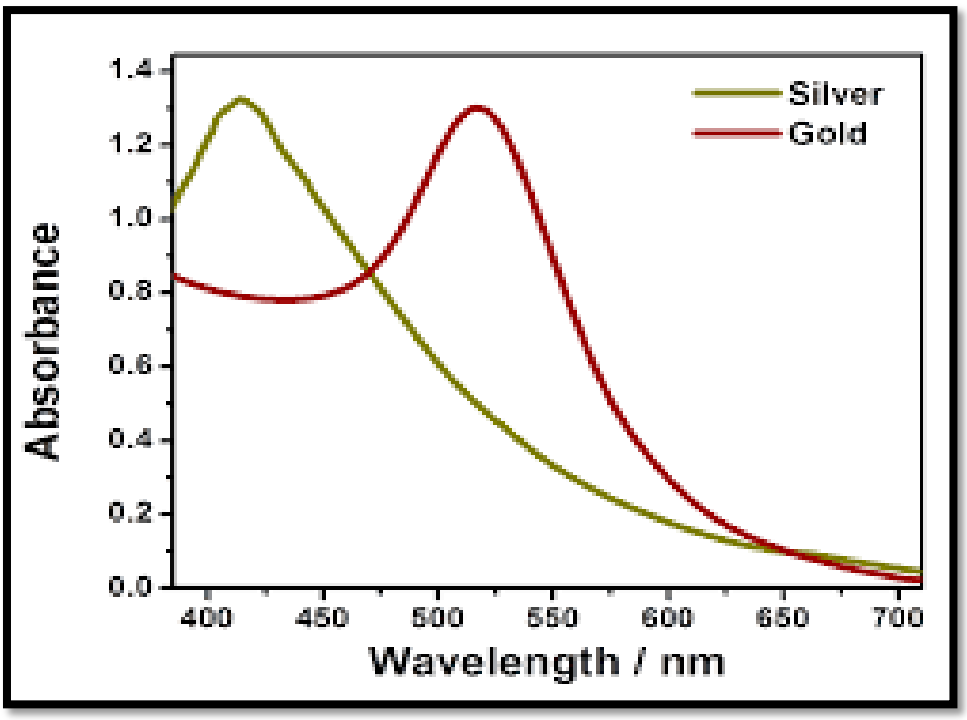


Fig: 1.13. Absorbance of two different nanoparticles [35]

1.3.2 Spectrofluorometer:

A spectrofluorometer is a device which takes an offer of fluorescents properties of few compounds to give information concerning their concentration and chemical atmosphere in a sample. Some excitation wavelength is accumulated, and emission is identified either as an individual wavelength, or scan is completed to note the intensity versus wavelength, means emission spectra. With the most spectrophotometer, it is feasible to observe both emission and excitation spectra. An excitation spectrum depends on the emission intensity because it estimated at a single emission wavelength. Conversely, and emission spectrum depends on the excitation wavelength. Here we used the precisely recorded spectra would show power emitted at each wavelength or the photon emission rate, across an interval of wavelength resolved by the slit breadth and dispersion on the emission monochromator. Moreover, at each excitation wavelength, the excitation spectrum shows the relative of the fluorophore [39]. For most fluorophores, the emission/PL spectra and

quantum yields are separated from the excitation wavelength. Emission spectra require recorded on different instruments are wavelength sensitivities.

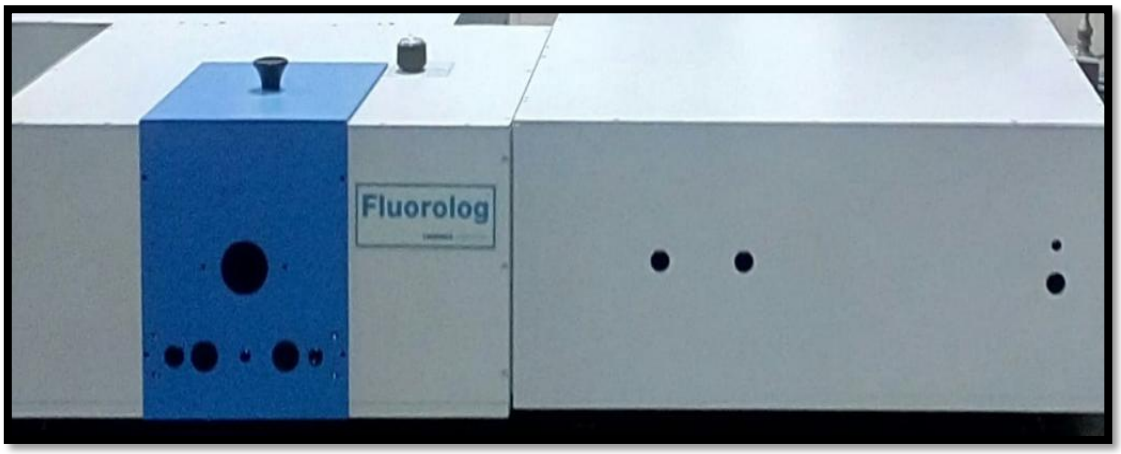


Fig:1.14. Spectrofluorometer Fluorolog-3.

The Horiba spectrofluorometer consisting of xenon arc lamp as a light source of 50W commonly effective through large intensity for entire wavelength range starts from 200nm, a duel monochromator to best both the excitation and emission wavelength .Also, concave gratings are used by these monochromators, generate by holographic means to diminishing stray light (light with different wavelengths from the one chosen). That a simple section with a cuvette holder and a photomultiplier tube (PMT) for the detection of fluorescence and then measured it by the suitable devices via spectrofluorometer Fluorolog-3 shown in figure:1.14. The outcome is generally represented in the form of graphic. A probe of a fiber-optic can be connected to the sample segment such that spectroscopy measurements can be made casually. Through spectrofluorometer fluorescence spectroscopy fluorescence (emission or excitation spectrum) also reflectance spectra (in synchronous scan mode) can be measured. the flexible variables are emission wavelength and excitation wavelength, excitation and emission and emission slit breadth, sampling advancement and assimilation time.

1.3.2.1. Fluoroscene Phenomena

Often, spectrofluorometers use light sources of high intensity to blitz a sample of as many as photons possible. This allows a large number of molecules to be excited at any one bit in time. light is either passed to a monochromator or filter, which allow us to select a wavelength of interest for use as a simulating light. The emission is collected at 90˚ to the stimulating light. Emission is either going through a filter or monochromator before

being observed by a PMT, or a charged couple-device detector. The signal can either be treated as an analog or digital output.

1.3.3. X-ray diffraction:

X-Ray Diffraction commonly applied for a surface recognized of the materials and can provide information of crystal lattice. In1912, Max von Laue, detected the crystalline materials performed as 3-D diffraction gratings for X-ray wavelengths associated with the spacing of planes in a lattice. X-ray diffraction is currently a universal system for the search of crystal structures and atomic spacing [40]. X-Ray Diffraction Bruker's Model D8 ADVANCE is illustrated in figure 1.15.

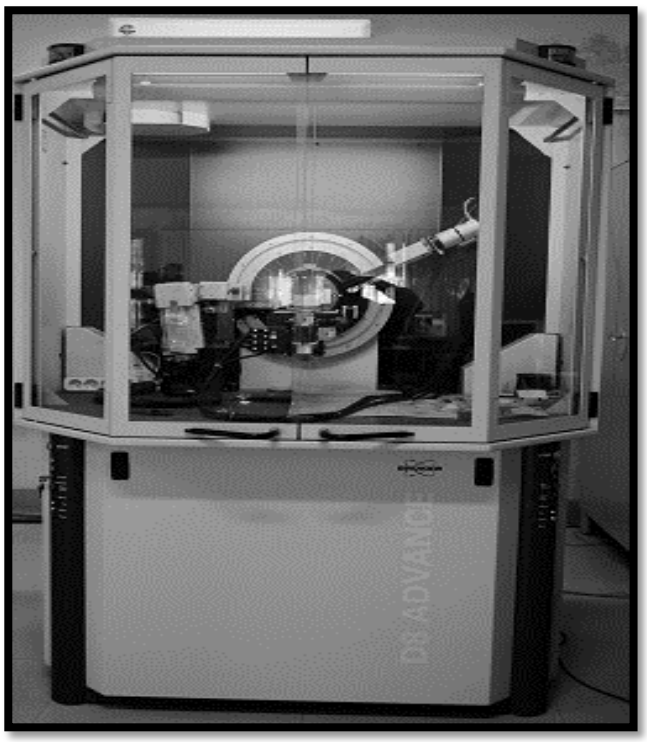


Fig:1.15 Bruker's X-Ray Diffraction [Model: D8 ADVANCED]

The main components of X-Ray Diffraction an X-Ray source, detector, sample holder and goniometer. Sample rotate within the path of diffracted beam collimator at angle θ and detector is on arm and rotate an angle 2θ. The function of goniometer is to maintain the angle and rotating sample. In general, the angle range 10˚ to 90˚ for XRD of sample detection, detector detect the sample and results are display on computer. A perfect crystal contains single plain, an imperfect crystal will show broadened peak and liquid or amorphous material will give a continuous function. The main components of XRD are

shown in figure:1.16. When sample interact with incident ray and generate constructive interference and satisfied the conditions of Bragg's Law.

$$n\lambda = 2dSin\theta$$

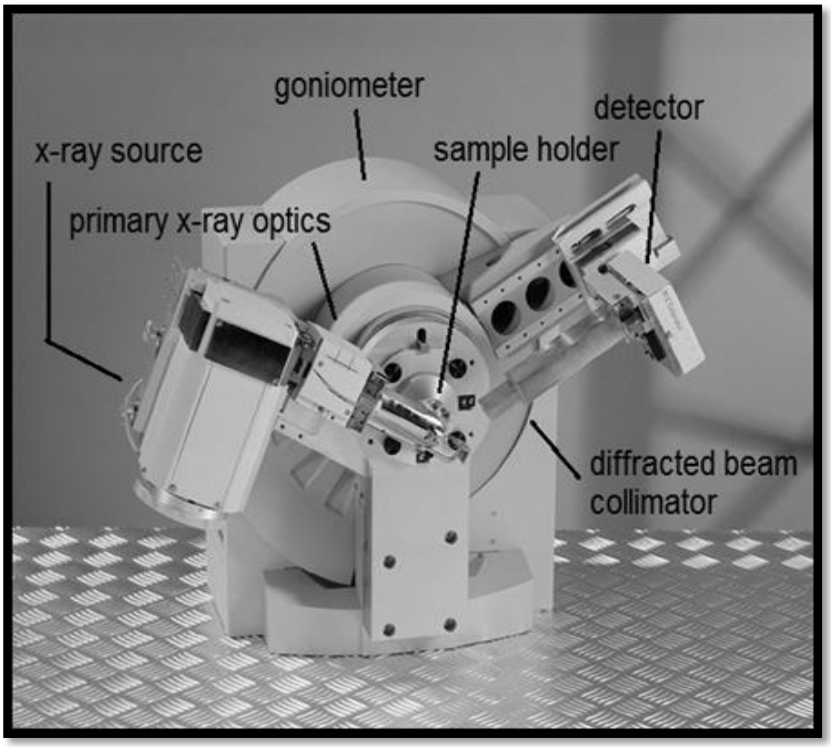


Fig:1.16. Main components of XRD .

The crystallite smaller than 100nm create broadening of peak, the peak broadening are used to calculate the crystalline size of nanomaterial using the Scherreer equation. Thus XRD is a fundamental technique provides high precision and accuracy in the measurement. The ability to analyze multiphase materials also allows analysis of how materials interact in particular matrix**.**

1.3.4. Fourier Transformation- Infrared Spectroscopy:

FT-IR spectroscopy is applicable to find out the infrared spectrum with emission or absorption of a liquid, solid or gas [36]. This spectrometer synchronously gains high-resolution spectral information over a large spectral range. This converse a remarkable improvement over a dispersive spectrometer, which evaluates intensity over an attenuated range of wavelength at a time. The FT-IR spectrophotometer shown in figure:1.17.

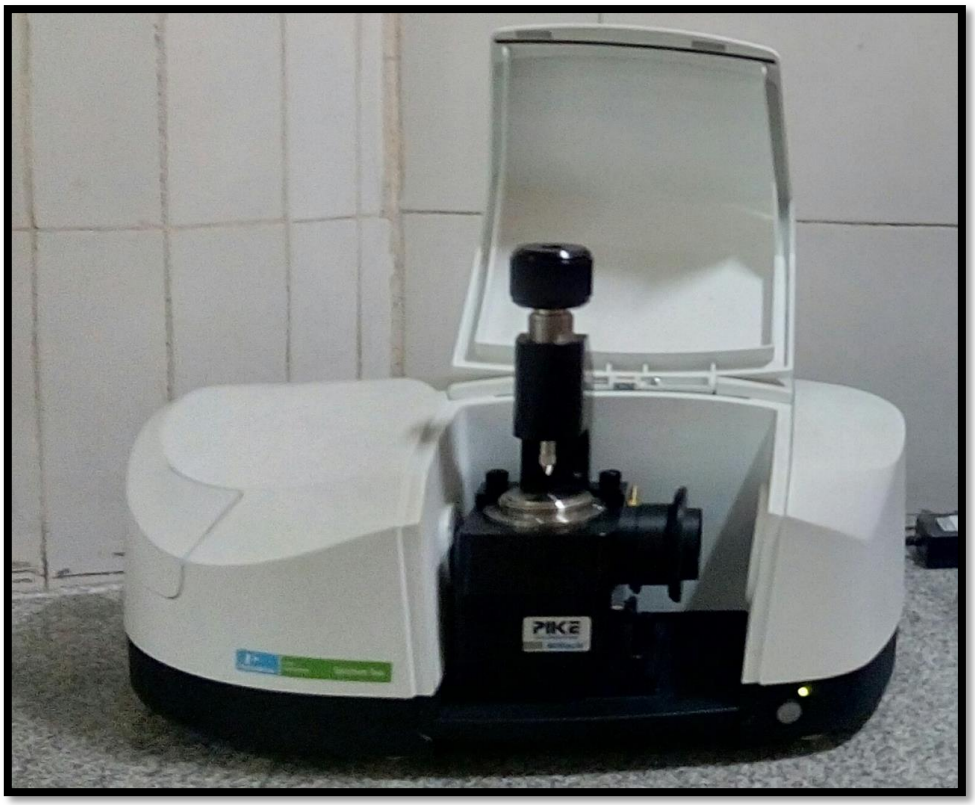
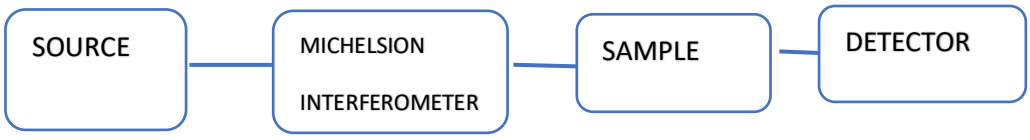


Fig: 1.17 FT-IR spectrophotometer (Perkin Elmer)

1.3.4.1. Instrumentation:

- **Source:** Usually consist of solid heated between 1500-2000K to give equal intensity source.
- **Nernst glower:** It is composed of rare earth oxide.
- **Detectors:** All detector of IR spectrophotometers depends on heating effect associated with IR radiation. Most popular detector is pyroelectic detector, which is made up of deuterated triglycine sulphate.
- **Window material/Sample holder:** Glass, quartz and metal cann't be used as window material because, this marerials have high tendency to absorb IR radiation. In stead of these material KBr is most popular window material for IR spectrophotometer. The block diagram illustrated below of FT-IR .



Michelsion interferometer is coposed of fixed mirror, movable mirror and, beam splitter, IR radiation from source riches to the beam splitter then36 beam splitter, splits beam into two equal half. One beam goes to the fixed mirror and after reflaction riches to the detector another beam goes to the moving mirror and after reflection riches to the sample. These two reflected beam superimposes before riching to the sample and creates constructive and distructive interference of sample. This mechanism are shown in figure: 1.18.

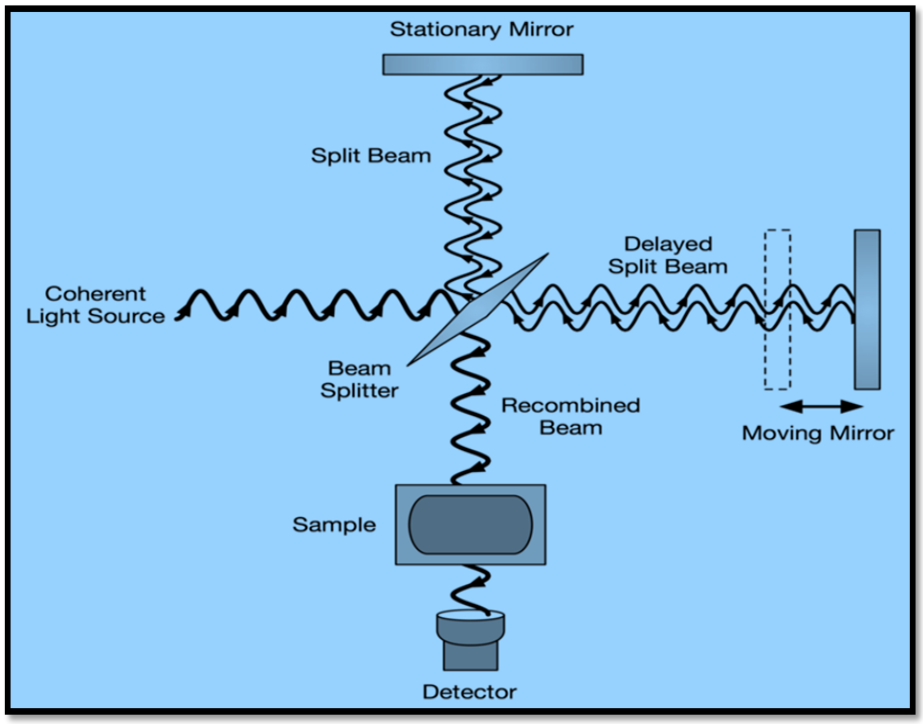


Fig:1.18 Michelson Interferometer[36]

Table ii) IR Regions

Serial no.	Region	Range cm^{-1}	Vibrational/Rotational Information
1	Near IR	14000-4000	Changes in vibrational and rotational level, electronic transition.
2	Mid-IR	4000-400	Changes in fundamental vibration levels of most molcule.
3	Far IR	400-20	Rotational energy level change.

Mostly analytical applications are confined to the mid- IR region because of absorption of the organic molecule are high in this region. There are two types of vibrational modes are observed in the IR spectrum: stretching mode and bending mode. The stretching band are towards longer wavelength or lower frequencies and bending vibration shift towards shorter wavelength or higher frequencies. Molecules are formed with atoms connected by chemical bonds, the movement of atoms and the chemical bonds like balls and spring (vibration) [50], [51].

The characteristic vibration is termed as natural frequency vibration. When the energy in the form of IR radiation is applied then it causes the vibration between the atoms of the molecules and when applied IR match to the natural frequency of vibration then absorption of IR radiation takes place and the peak is observed. Distinct functional group absorbs characteristic peak value. Consequently, the IR spectrum of a chemical species is a finger of a molecule for its reorganization. Organic group involved in three regions of the spectrum:

1. 4000 and 1300cm-1_ alcohols and amines

2. 1300 and 909 cm-1_complex interaction

3.909 and 650 cm-1_ benzene rings

All frequencies are examined simultaneously in FTIR rather than an individual. since different molecules with a different combination of atoms produce their unique spectra, FT-IR can be used to qualitative identification of the substances and performed on computer.

1.3.5. Transmission Electron Microscope (TEM):

TEM is a distinctive, great technique for material science. A high energy beam of the electron is passed through a sample, and interactions between the electron and the atoms will be used to observe features like the crystal structure and features within the structure such as dislocations and grain boundaries. Qualitative analysis may be performed. TEM will be used to analyse the shape, size, expansion of layers, defect in semiconductors and composition. High resolution will be used to study the standard shape, size, and density of quantum dots, wires, and wells [37]. The TEM was the first type of electron microscope to be developed and patterned exactly based on a light microscope. TEM uses

high energy electron approximately the speed of light. The electron beams are about a million times shorter than the light waves. Developed by Max Koll and Ernst Ruska Germany 1931 resolution about 1000 times and magnification approx. 500 times greater than the optical microscope. TEM Technai image shown in figure: 1.19.

Fig:1.19 Transmission Electron Microscope (Tecnai) [37]

1.3.5.1. Working Principle of TEM:

Transmission electron microscope works on the basic principles of spectrophotometer but uses electron instead of light shown in figure: 1.20. When an electron beam passes through the very thin- section specimen of a material, electrons are scattered. A sophisticated system of the electromagnetic lens focuses the scattered electrons into an image or a diffraction pattern, or a nanoanalytical specimen depending on the mode of operation.

1.3.5.2.1. Imaging:

The electron beam of the electron gun is converged toward a small, thin, coherent beam by the use of the condenser lens. The beam is then hitting the specimen and portions of it

are transmitted depending against the depth and electron clarity of the specimen. The transmitted portion is focused by an objective lens into an image on a phosphor screen or charge coupled device (CCD) camera. The image then passed down the column through the intermediate and projector lens.

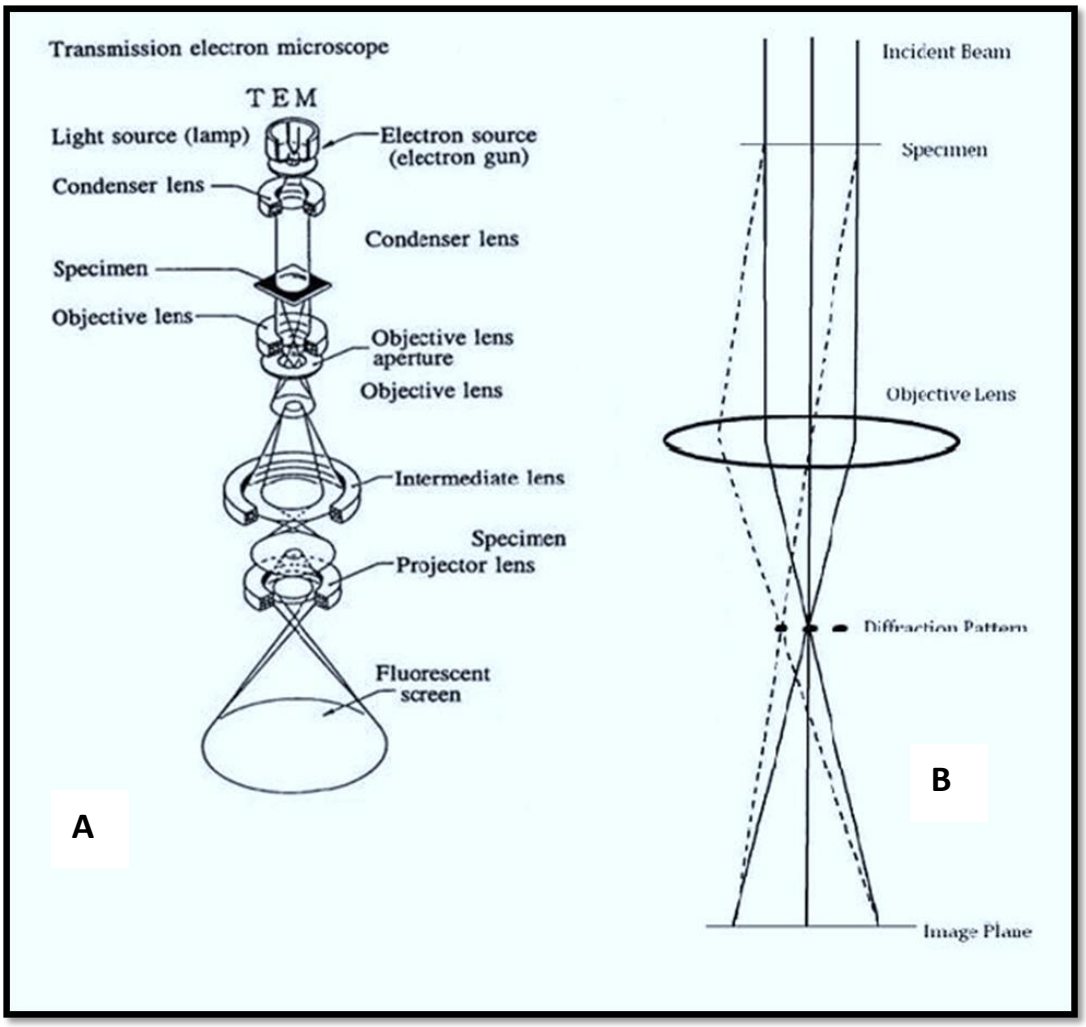


Fig:1.20 A. Schematic diagram of a TEM defining the path length of electron beam, B. TEM diffraction mechanism illustrated via ray diagram.

1.3.5.2.1. Diffraction:

The figure: 20 shows a straightforward representation of the route of an electron beam in a TEM, when beam passing through the specimen, they have gone through the electromagnetic objective lens that focuses all the electrons scattered from one point of the specimen into one point within the image plane. Also as represented in the figure: 1.20(B) a dashed line where the electrons scattered in the same direction by the specimen are collected into a single point.

CHAPTER-2

EXPERIMENTAL

2.1 Chemical and instrument used:

Chemicals used in this experimental project work were of scientific grade and used as received. Silver nitrate ($AgNO_3$) salt (99%) was obtained from Sigma- Aldrich chemical co, sodium hydroxide (NaOH), fructose, citric acid, and all experimental process were completed in aqueous media, distilled water used throughout this process. All glass wares were properly clean and dried before used. The ginger extract and other plant extracts such as neem leaf, pomegranate peel, honey (plant nectar) and fructose used as a precursor (reducing and stabilizing agent). First of all, we screened the various plant part and use the chemicals present in honey like fructose and citric acid and systematic comparative study was carried out to investigate their efficiency to reduced silver ion and formation of silver nanoparticles.

The aim is to identify those compound and mechanism involved in this process and comparative study with various parts of plant and at least one method mediated through chemical route for understanding the stability and reduction ability. As a preliminary confirmation about the silver nanoparticles formation will be observed through UV-Vis absorption spectra obtained with Perkin Elmer Lambda-750 UV-Visible-NIR spectrometer.

2.2. Preparation of 1mM silver nitrate solution:

All the glass wares were properly cleaned before used. Silver nitrate ($AgNO_3$) salt (99% purity) were obtained from Sigma-Aldrich Chemical Co. and were used without further refinement. For preparing 1 mM taken 0.0085g of silver nitrate (AgNO3) salt added in 50 mL double distilled water in 250 mL flask and stirring magnetically at room temperature shown in fig:2.1.

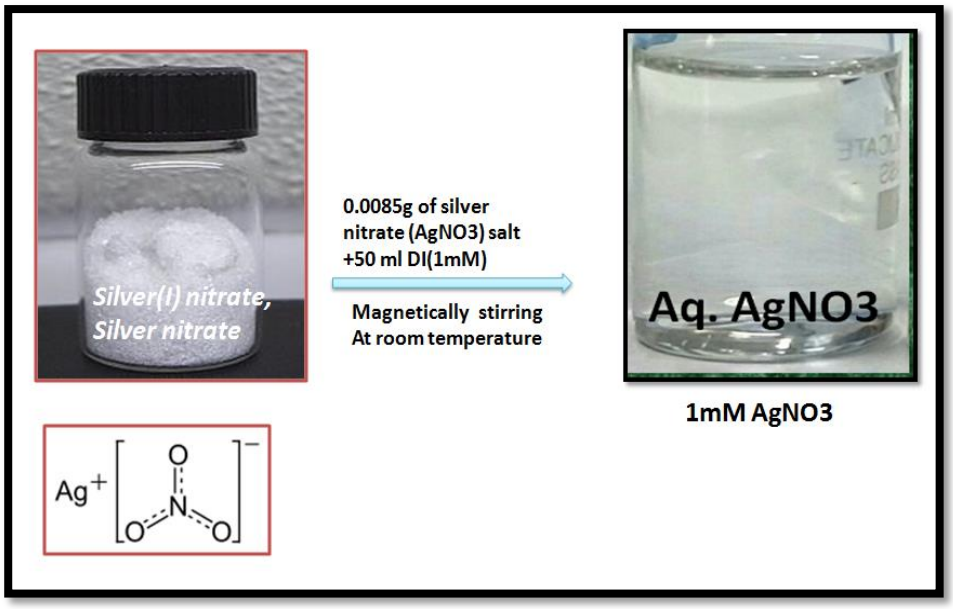


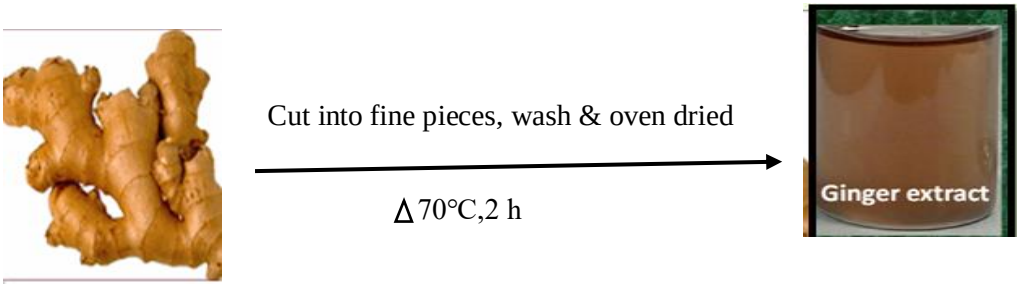
Fig:2.1. Diagrammatic Representation Of 1mM $AgNO_3$ Preparation.

2.3. Ginger (Zingiber officinale) extract mediated synthesis of AgNPs:

The synthesis process was improved from one report and completed in various steps [16].

2. 3.1. Preparation of Ginger (Zingiber officinale) extract:

Ginger was collected from Delhi market washed properly with DI water, after cleaning fresh ginger cut into fine pieces and oven dried. 5gm ginger was weighed and added 50 ml DI water in a 200ml flask, heating about 2hours at the 70°C temperature. After cooling of extract filtered with Whatman filter paper. The extract was sonicated about 30 minutes at 40KHz. The ginger extract shown in figure: 2.2.



Zingiber officinale

Fig:2.2 Preparation of extract from Zingiber officinale.

2.3.2. Synthesis procedure:

5ml of the extract was added to 25ml of 1mM $AgNO_3$ solution and heated at 80°C, the color of reaction mixture turn transparent to sparkling yellow after 10 minute and then change to sparkling brown after 20 minutes mixing, which was the first confirmation about AgNPs formation and absorption spectra found a peak at 408nm but after maintaining the pH-10 the peak was shifted at 404nm and very sharp, which is shown in figure: 2.3.

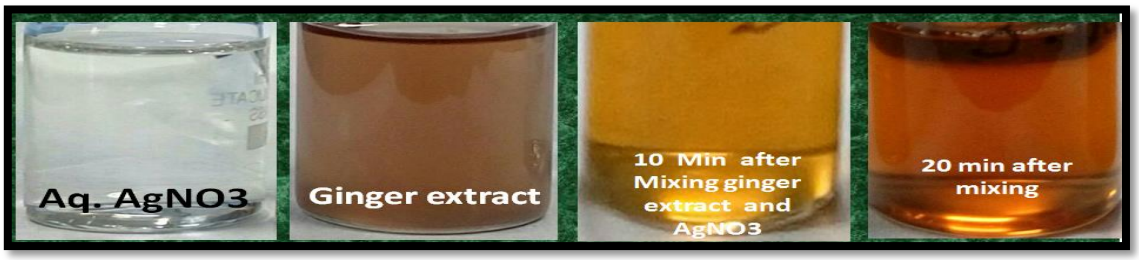


Fig: 2.3 Change in the color after mixing of ginger extract and aq. AgNO3.

The effect of pH on ginger-capped Silver nanoparticles was analyzed by maintaining the pH in the range of 7 to 12. The impact of ginger extract on the fabrication of silver nanoparticles was observed by varying the concentration of ginger extract 0.5ml, 1ml, 1.5ml and 2ml with 1mM silver salt. The temperature effect on silver nanoparticles formation was observed by changing the temperature of the reaction mixture from room temperature (40°C) to 90ºC and the growth of nanoparticles was observed by varying the time from 15minutes to 75 minutes. For all investigation using absorption spectrophotometer, an equivalent amount of colloidal nanoparticles (0.5ml) was diluted in a constant volume of de-ionized water and then it's absorption spectra were measured at room temperature.

2.4. Synthesis of Silver Nanoparticles Mediated through Local Honey:

The synthesis process was improved from one report [10] ,The step involved in this process-

2.4.1. Preparation of solution (honey precursor):

The precursor solution was prepared in a 100ml beaker.10 ml of honey diluted with 20 ml DI (de-ionized) water, diluted honey moved magnetically stirred at room temperature.

The pH of honey approximately 3.93 which was maintained 10 by adding 1mM of NaOH solution drop-wise.

2.4.2. Synthesis procedure:

1mM as prepared silver nitrate solution of 20ml and 15ml diluted honey mixed drop-wise and stirred well for a one hour at room temperature, the color of the solution changed light yellow to dark yellow and after 24 hours later changed to colloidal brown. As preliminary confirmation about silver nanoparticles growth was observed through UV-VIS absorption spectra, which was found the strong peak at 408 to 413nm.

2.5. Fructose mediated synthesis of AgNPs:

The synthesis process was improved from one report and completed in various steps [15]

2.5.1. Chemicals:

All chemicals were pure and used without further cleaning. silver nitrate ($AgNO_3$) 99% pure and citric acid (98%) were purchased from Sigma- Aldric, D-fructose (>98%) and sodium nitrate (NaOH) purchased from Rankem.

2.5.2. Preparation of precursors:

1mM silver nitrate was prepared in an aqueous medium. 12.5 gm of D-fructose was dissolved in 50 ml of DI water and stirred magnetically. 0.5gm of citric acid was dissolved in 10ml DI water and stirred well.

2.5.3. Synthesis procedure:

5ml of 1mM $AgNO_3$ solution was mixed with 5ml of fructose solution drop-wise and magnetically stirred at room temperature, fructose was behaved as reducing agent. After 15 minutes later added 2ml citric acid solution used as the stabilizer with the help of a syringe drop-wise and maintain the pH-10 via NaOH added. The color of the reacting mixture was turned transparently to yellow after 45 minutes later. The preliminary confirmation of AgNPs formation observed through UV-VIS absorption spectra and the peak was observed at 393nm.

2.6. Pomegranate fruit peel mediated synthesis of AgNPs

The synthesis process was improved from one report and completed in various steps [41]-

2.6.1. Preparation of pomegranate peel extract:

Pomegranate peel was washed for removed impurity, and dust particles, after normal water washing, washed with DI water and air dried. 20gm pomegranate fruit peel was weighted and added 100ml DI water in 250 ml flask and heating about 1hour at the 50℃ temperature and filtered with Whatman filter paper and after cooling use for synthesis.

2.6.2. Synthesis procedure:

In 50ml of 1mM $AgNO_3$ solution added 10ml of pomegranate peel extract drop-wise with magnetically stirring at room temperature. After 15 minutes passes the color of the solution was light orange which pH 4.48 and peak observed in UV-VIS absorption spectra was 374nm. after some drop of NaOH added (pH-5.58) in the reaction mixture the color of the reaction changed to ruby red and absorption peak at 372nm.

2.7. Aqueous Neem (Azadirachta indica) leaf extract mediated synthesis of AgNPs:

The synthesis process was optimized of one report and completed in various steps [8]-

2.7.1. Preparation of Neem (Azadirachta indica) leaf extract:

The plant extract was prepared from Fresh leaves of Azadirachta indica (Neem) were collected from D.T.U. campus, India, the healthy leaves cleaned properly by de-ionized water, and oven dried for 45 minutes at 90ºC. Measure the 5g leaf and boiled with 50 mL double distilled water in 250 mL flask at 50˚C for 25 minutes. After cooling the extract, filtered by Whatman filter paper. The filtrate was stored at 5º C for again experiments. The neem extract preparation are shown in figure : 2.2.

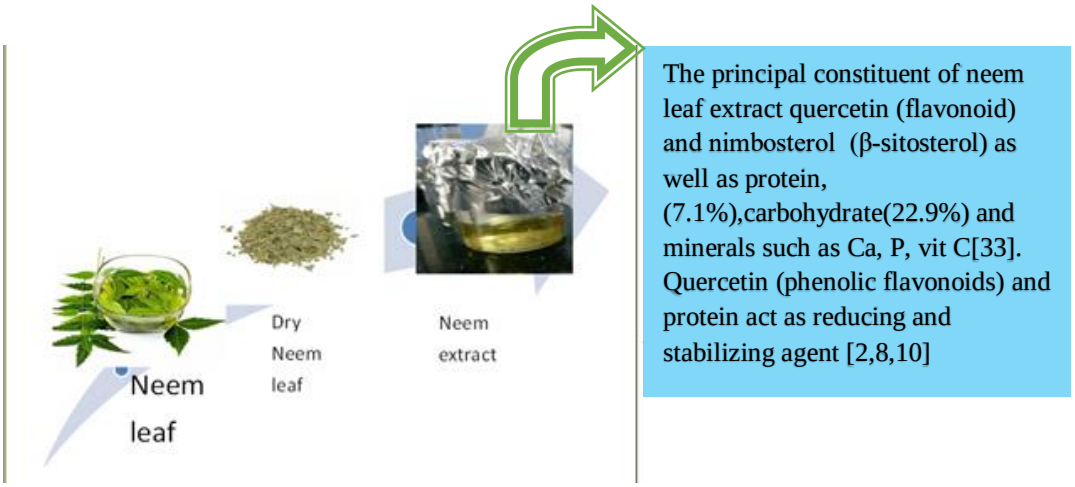


Fig:2.4 Diagrammatic Representation of Neem Extract Preparation.

2.7. 2. Synthesis procedure:

In a reaction process, 10 mL of Azadirachta indica (Neem) leaf extract was mixed to 50 mL of as prepared aqueous silver nitrate solution, with stirring magnetically at room temperature. The yellowish-brown colour of the solution of aqueous silver nitrate and Neem leaf extract at 2 min of reaction time, changed very fast at room temperature and after 5 min to 15 min colour changed colloidal- brown, that shows the development of silver nanoparticles (fig:2.5). The synthesized AgNPs are purified by ultrasonic treatment (ultrasonic bath, 40KHz) [14]. For preliminary conformation observed via UV-VIS absorption spectra and, the peak found at 440nm-445nm.

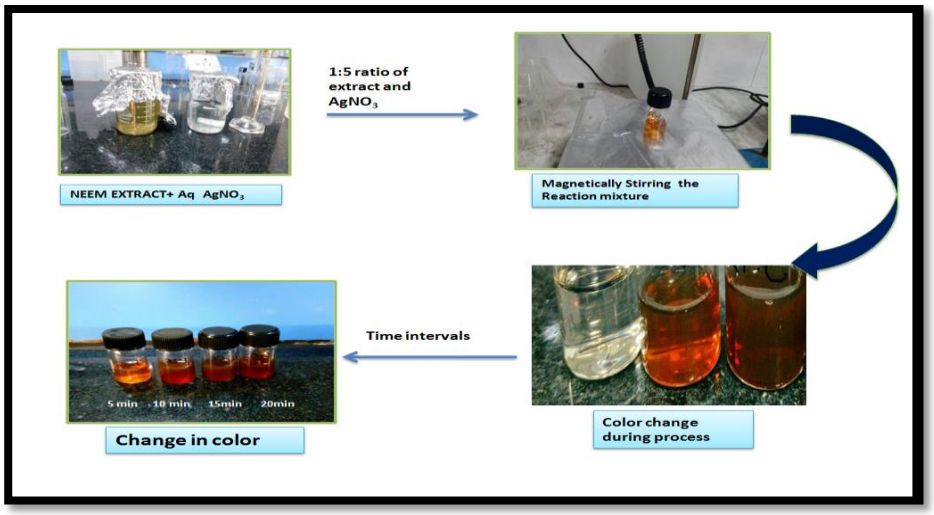


Fig: **2.5.** Diagrammatic Representation of Fabrication Process of Neem Capped AgNPs

This above synthesize AgNPs mediated through several plants' extracts were applicable in a various application and stabilized about six months without the use of any stabilizer.

2.8. Homogeneous Catalytic reduction of Methylene Blue (MB):

Catalytically degraded MB to leuco MB by ginger -capped silver nanoparticles was explained by the reaction with sodium borohydride ($NaBH_4$), which was use as reducing agent in this reaction. This reaction was explained by following flow chart

50ml(10mg/l) aqueous solution of methylene blue at room temperature.

2ml of freshly prepared $NaBH_4$ (O.2M).

1ml ginger -coated silver nanoparticles as well as an only ginger extract in another beaker for the comperative study were added and reactant mixture quickly.

At regular time interval, 0.5 ml of the reaction was to withdraw and diluted in 2.5 ml DI for UV observation and the same process apply with uncatalyzed reaction mixture and ginger extract mixed reactant mixture.

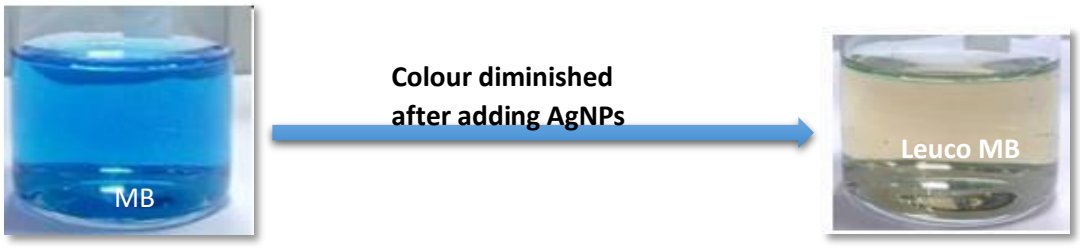


Fig: 2.6. MB Colour diminished after adding as- synthesized AgNPs.

2.8.1 Photocatalytic Degradation Efficiency Silver Nanoparticles on MB Dye:

After adding as- synthesized AgNPs in methylene blue in presence of NaBH4, the colour of MB diminished in four minutes shown in figure 2.6.. Degradation capacity of methylene blue by ginger coated AgNPs was estimated via the following equation [12].

$$R = \left(\frac{\mathrm{A_o} - \mathrm{At}}{A_o}\right) * 100$$

Where A_0 and A_t are the absorbance of initial time and 't' time at 664 nm for methylene blue. During reaction without catalysed reaction mixture are used for reference. AgNPs assist the electron of BH^{4-} (donor) to methylene blue (acceptor). Where the AgNPs acquire electrons from BH^{4-} ions and transfer them to the MB. The reduction of methylene blue with sodium borohydride was observed to be stimulated in the appearance of AgNPs as well as fast decrease in the absorption intensity of the MB solution.

CHAPTER - 3

Results & Discussion

3.1. Analysis of the capacity of ginger-extract during green synthesis of silver nanoparticles:

Usually, phenolic compounds and phytochemicals present in aqueous extract of plant metabolites can prevent the aggregation of silver nanoparticles due to binding and chelation with the metal ion [51]. Here, we used the extract of ginger, as a reactant (behaved as a reducing as well as a stabilizing agent), in the fabrication of silver nanoparticles, other chemicals like stabilizer is not required during the process. The method was completely pure, environment-friendly and non-toxic. The ginger Rhizomes extract contained approximately 45 chemical compound, more quantity of phenolic compounds such as 6- gingerol (27%) and 6-shogaol (20%)) are found in a higher amount than others. Besides these, amino acids, aromatic compound zingiberene, vitamins, protein, and minerals are also present [48].

3.2 Optical analysis:

The absorption spectrum of the ginger extract (Fig.25) shows absorption peak at 277nm due to the π- π^* transition. No other band were observed in 280-700 spectral range except hump at 380nm from the ginger extract and aqueous $AgNO_3$. While the ginger extract mixed with 1mM $AgNO_3$ solution, colour change from transparent to sparkling yellow and then sparkling light brown was seen later 20-minute heating. The figure:3.1 and 3.2 shown the change in color and absorbance peak at 406, which was the preliminary confirmation of AgNPs growth. AgNPs shows strong surface plasmon resonance in aqueous media [41]. The band (400-415nm) were observed after mixing of the substrate ($AgNO_3$) and reactant (ginger extract), which is shown in absorption spectra of figure 3.2.

Fig:3.1. Change in colour after mixing of ginger extract and aq. $AgNO_3$.

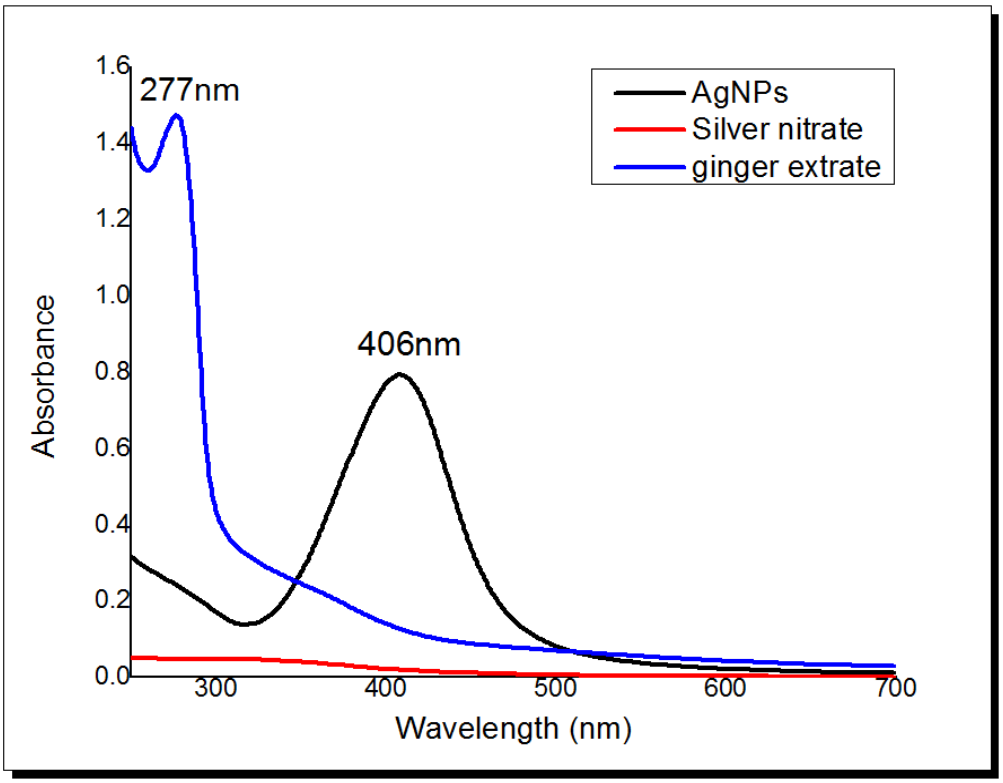


Fig:3.2 Absorption spectra of silver nanoparticles observed after mixing of the substrate (aq. $AgNO_3$) and reactant (extract of Ginger rhizome).

3.2.1. Impact of the various parameter on the growth of silver nanoparticles:

Several parameters such as pH, time intervals, temperature, ginger extract concentration significantly affect the dimension, appearance, and morphology of silver nanoparticles. To illustrate the change of the optical properties of synthesized NPs by adjusting the period of reaction, we kept all another experimental variable constant. A change in absorbance with changing the reaction time (15 - 75 minutes) were recorded in the range of 250-700nm. The figure:3.3 shown that as the time passes, the absorbance intensity increases as well as blue shifting of absorbance spectra.

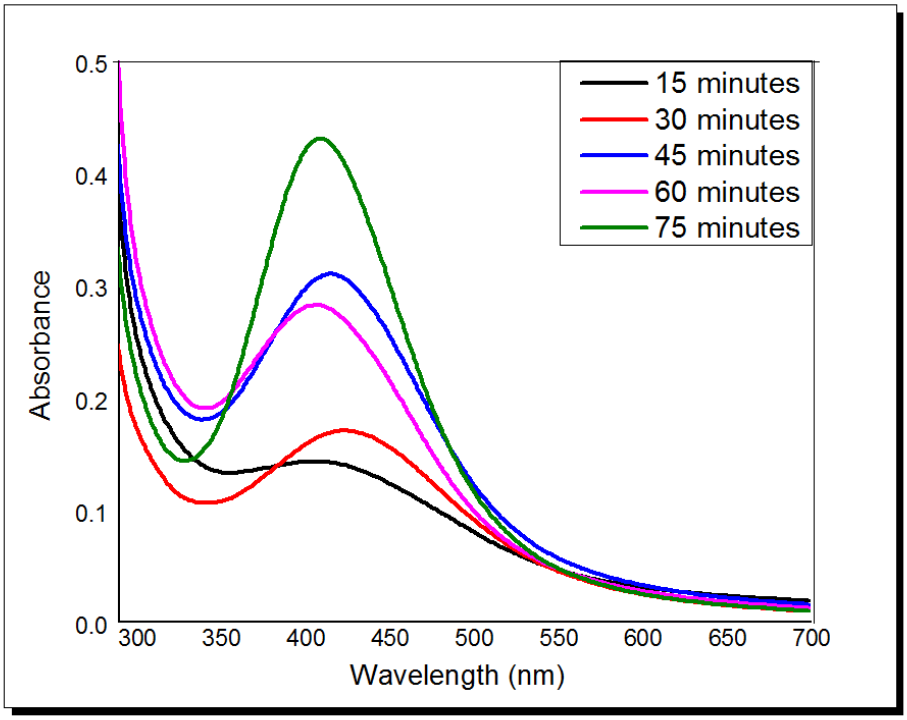


Fig:3.3 Absorption spectra of silver nanoparticles observed after mixing of the substrate (aq. $AgNO_3$) and reactant (Ginger extract) at time intervals 15-75 minutes.

3.2.2 Impact of extract concentration on the formation of AgNPs:

The ginger extract plays a vital role in the formation of the silver nanoparticles. Changing the extract concentration from (0.5ml, 1ml, 1.5ml and, 2ml) and kept the other variables constant. On increasing the concentration of ginger extract into 1mM AgNO3 solution the peak of abruption shift towards shorter wavelength as shown in figure: 3.4. The ginger extract concentration changes 0.5ml to 1ml significantly change in peak intensity as well as blue shifting and then change to 1ml, 1.5ml and, 2ml slightly change in intensity, meaning that the particle size decrease with increasing the concentration of ginger extract in the reaction process.

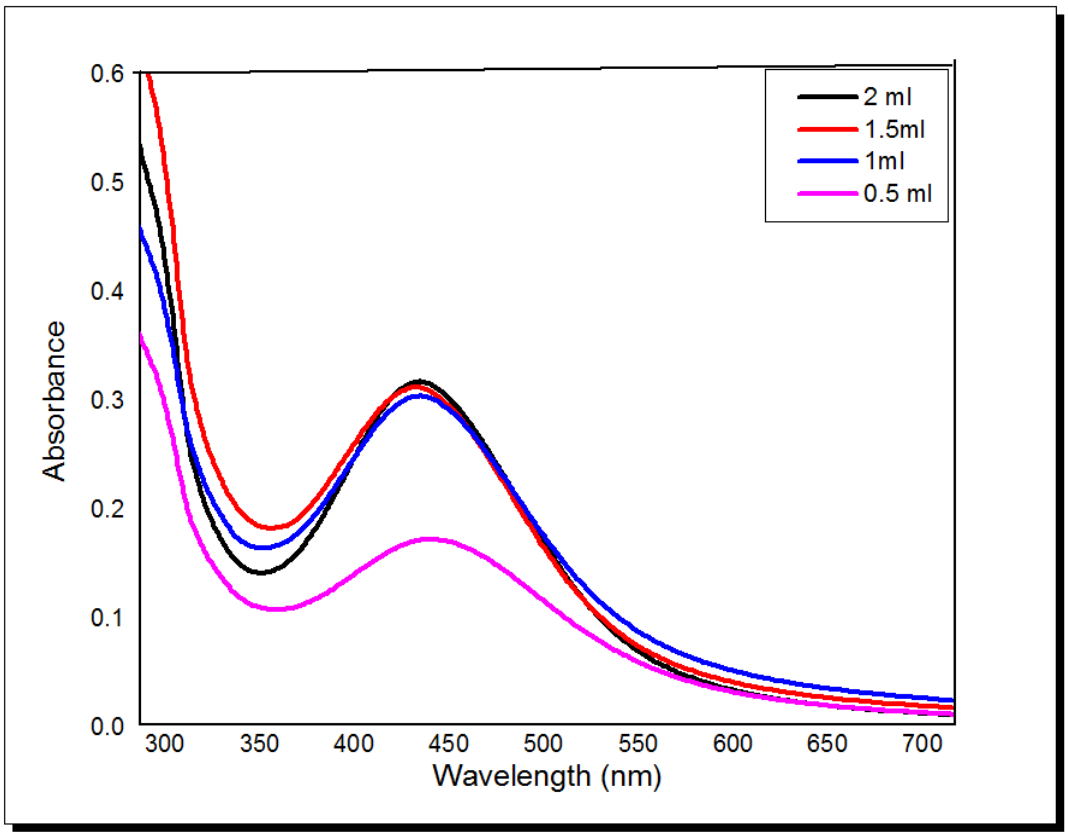


Fig: 3.4. Absorption spectra of silver nanoparticles observed by changing the extract concentration and remain constant the other variables.

3.2.3. Impact of temperature on the formation of AgNPs:

Temperature is an important factor for the fabrication of silver nanoparticles. Varying the temperature range from room temperature to 90°C. After increasing the temperature room temperature, 50°C, 60°C, 70°C, 80°C, and 90°C, the peak of spectral band shifted towards lower wavelength. While increasing the temperature, intensity of peak increases. In figure:3.5, we saw that at room temperature peak was not observed as increasing temperature, peak intensity significantly high. Indicating that the temperature proceeds to the nucleation and growth of silver nanoparticles.

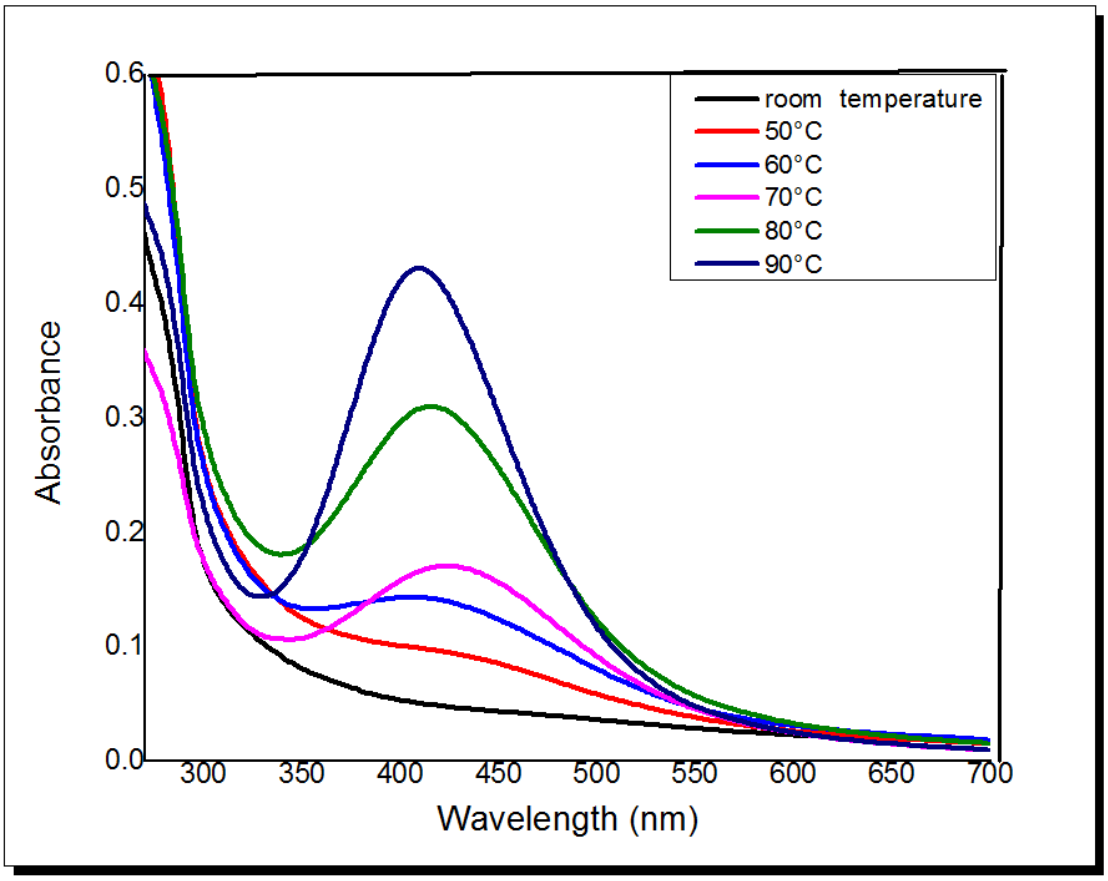


Fig: 3.5. Absorption spectra of silver nanoparticles observed after mixing of the substrate (aq. $AgNO_3$) and reactant (Ginger extract) by changing the temperature range room temperature to 90°C

3.2.4. Impact of pH on the formation of the AgNPs:

pH plays a significant role in the formation of silver nanoparticles. While increasing the pH neutral to alkaline: 7-12 the peak intensity increases till 7-10 and between 11- 12, the peak intensity decreasing. Which is clearly visualize in figure 3.6. Some aggregation was observed after increasing pH range from 11 to 12.

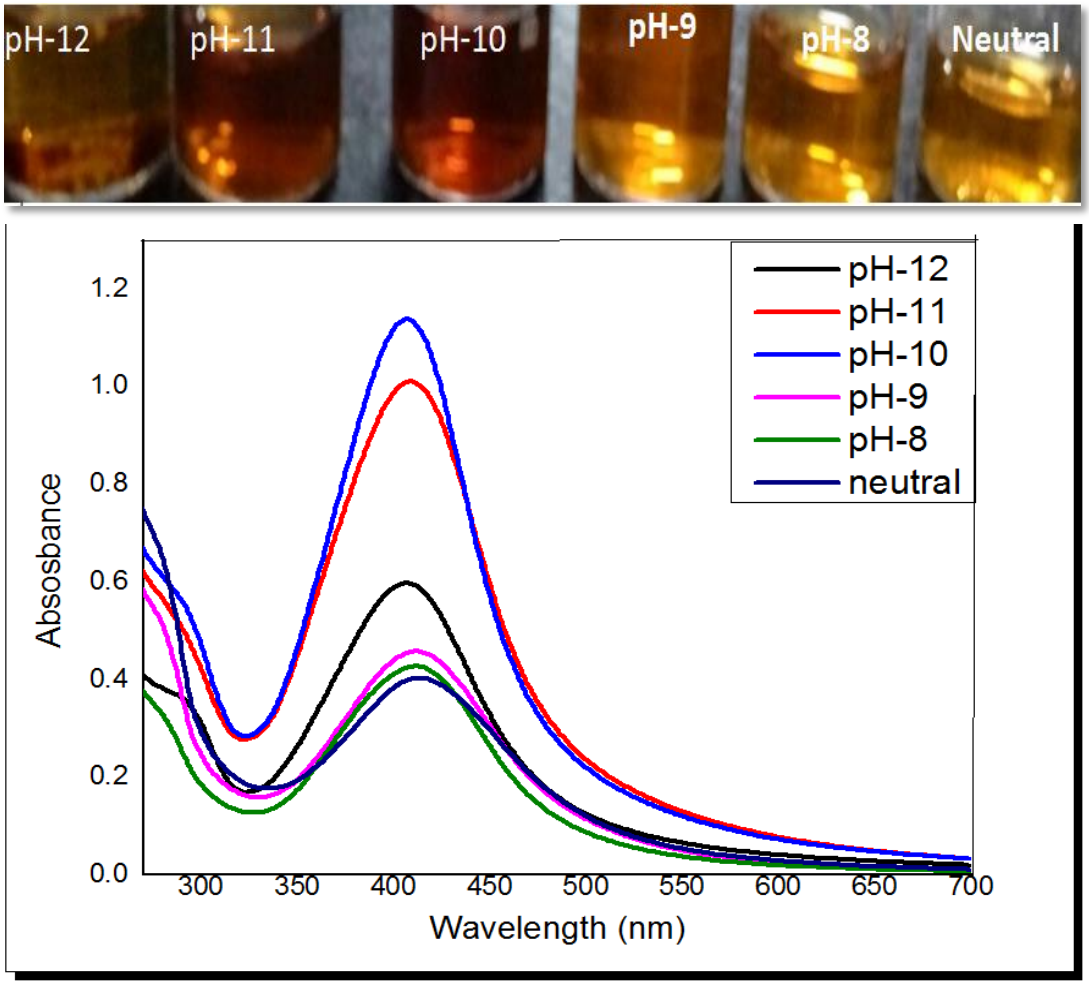


Fig: 3.6 Absorption spectra of silver nanoparticles observed after mixing of the substrate (aq. $AgNO_3$) and reactant (Ginger extract) at various pH range.

3.2.5. Comparative study of AgNPs synthesis mediated through different parts of plants and white sugar (fructose):

The current study was the analysis of several methods using various parts of plant extractS and fructose in an aqueous medium. Analyze the reaction time and stability of AgNPs through absorption spectroscopy. For fabrication of NPs using different parts plants like neem leaf extract, plant nectar(honey), pomegranate peel extract, ginger extract and, fructose. Also, search most applicable, non-toxic and safe methods. In all fabrication route, the ginger extract mediated method is the best method and then plant nectar mediated. Honey mediated synthesis is time taking (4-24hours) and required more concentration of honey and pH-10 for better result. Neem mediated synthesized nanoparticles had a broad peak at the longer wavelength (440-460nm) and honey mediated peak about 406-415nm intense and sharp. In fructose mediate synthesis other chemicals are required as the stabilizing agent (citric acid) and peak intensity very low at 393nm and stability approximate 5 days. In pomegranate peel mediated synthesis, the peak observed at 372 -374nm and similar peak observed in pomegranate peel extract, thus exactly conformation about AgNPs formation in a dilemma, all absorption peaks of AgNPs mediated through several methods are shown in figure: 3.7(B) . In other precursors, the absorption peak of silver nanoparticles does not observe, shown in figure: 3.7(A). In all methods ginger extract mediated route is the best because of the very intense and sharp peak at 402-408nm, fast formation NPs, four-month stability and more applicability. Hence other characterization like PL, XRD, TEM and, catalytic activity completed with ginger -capped silver nanoparticles.

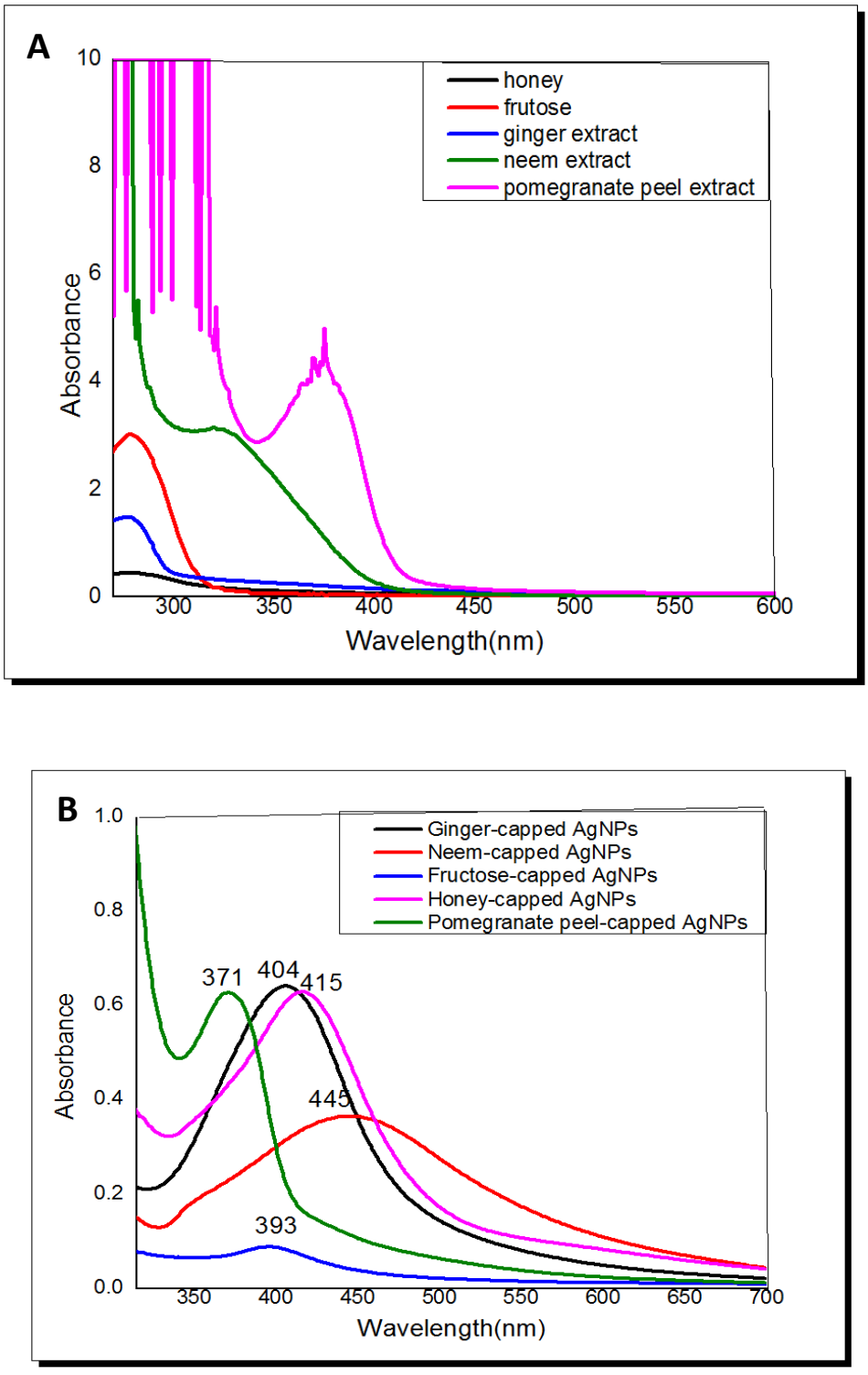


Fig: 3.7 The Uv-Vis absorption spectra of (A)different plant extract, honey and, fructose (B) AgNPs synthesized from different plant extract, honey and, fructose.

3.2.6. Photoluminescence (PL) spectra of silver nanoparticles containing ginger extract:

Photoluminescence (PL) observation of silver nanoparticles containing ginger extract, the AgNPs were excited at 330 nm, and the emission peak was observed at 420 nm as the figure: 3.8 shown. The stabilization of AgNPs through ginger extract with the emission band at 420 nm is observed upon excitation at 330nm at pH-10 and also 420 nm observed at pH-7 but peak intensity is high in case of pH-10. So, it can be concluded that after increasing the pH, the size decrease and intensity increase. Confirmation for such a PL mechanism in noble metal NPs has been conferred in earlier studies [45], [46].

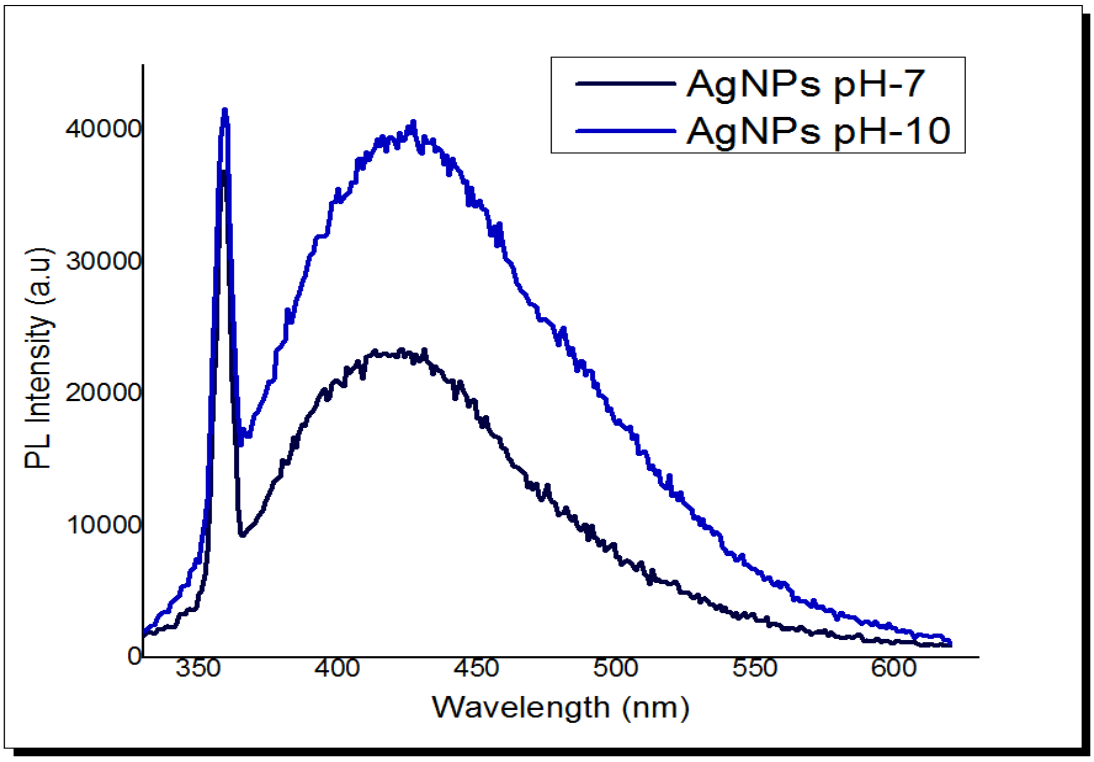


Fig: 3.8 The Photoluminescence (PL) spectra of AgNPs at different pH

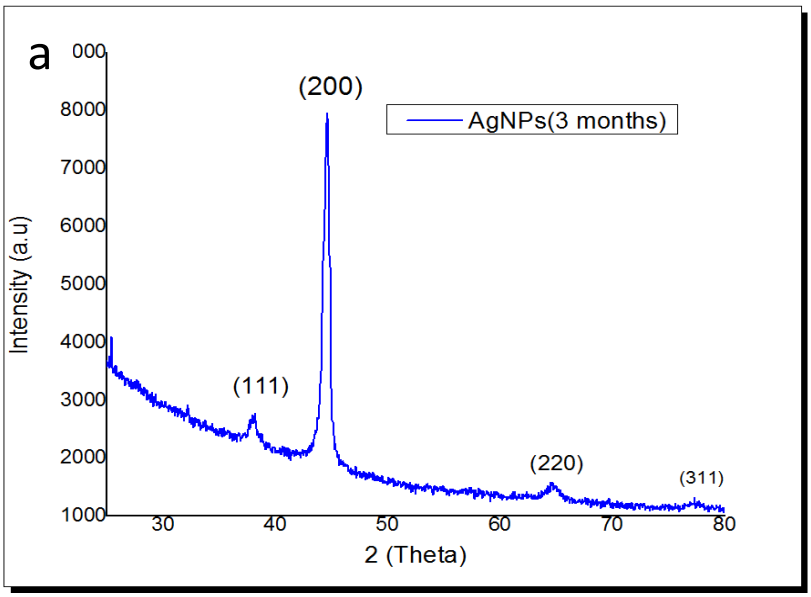
3.3. XRD Analysis:

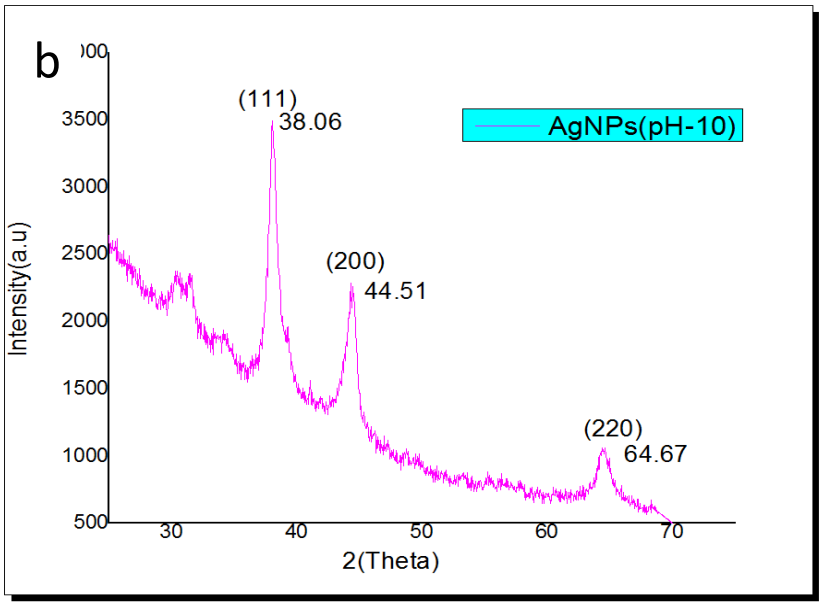
X-ray diffraction of ginger capped silver nanoparticles is used to analyze the crystalline size in the range of 20^{o} to 80^{o} at 2θ angles. Figure 3.9 (a, b,c) represents the XRD peaks of as-synthesized AgNPs . The intense peaks of ginger-coated AgNPs were observed at 38.03^{o}, 44.51^{o}, 64.67^{o} and, 77.28^{o} relative to (111), (200), (220) and (311) F.C.C silver,

which shown the crystalline behavior of silver nanoparticles. The crystalline size of silver nanoparticles is calculated through Scherer's formula.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where λ is X-ray w avelength (1.54 Å), β is the full-width half maxima (FWMS) of diffraction line. Based on the FWHM of the reflection from (111) plane in FCC structure and average crystallite size of AgNPs ~~ 10nm.





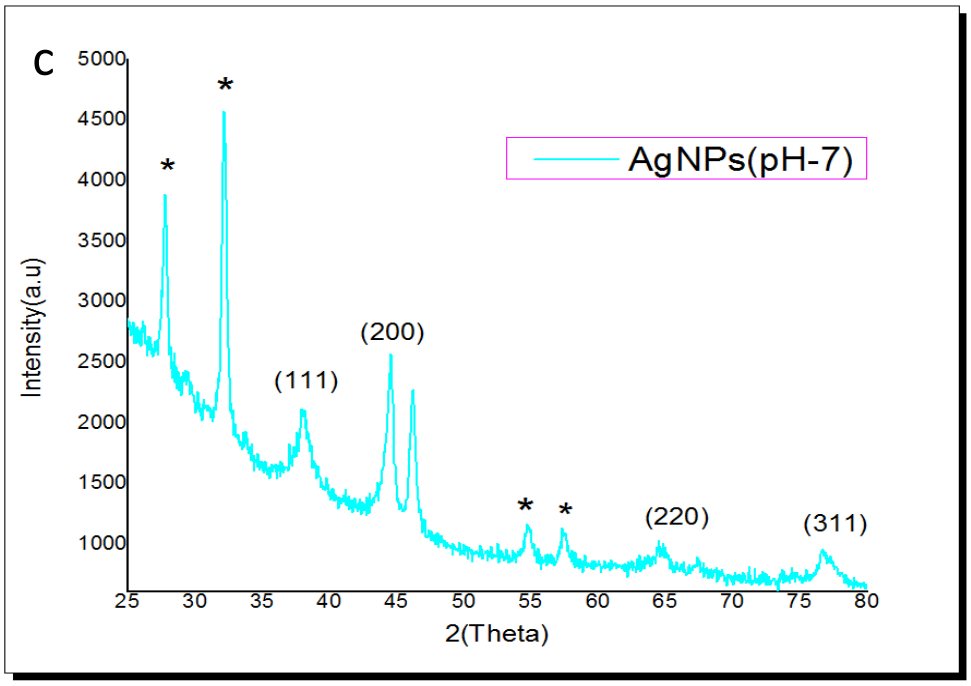


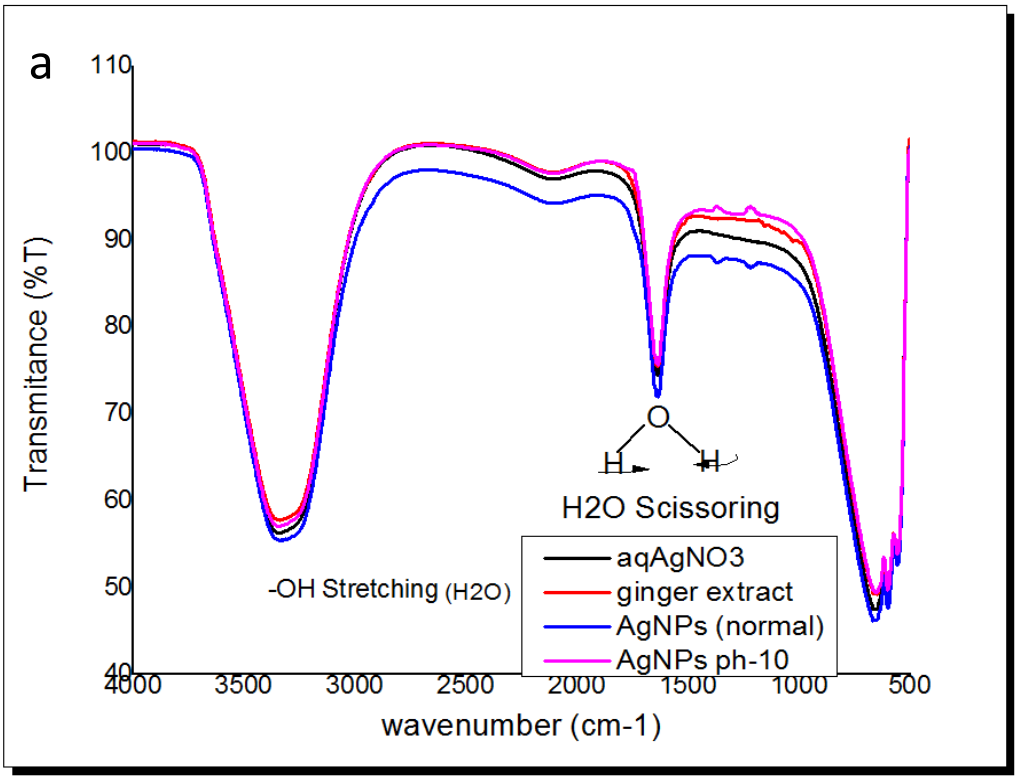
Figure: 3.9 XRD pattern of AgNPs. (a) (synthesized before) three months, (b) pH-10, (c) pH -7

Table-iii) Crystalline size of ginger-capped AgNPs

Serial no.	AgNPs	2θ	Θ	FWHM (radian)	Crystalline Size(nm)
1	Normal pH(7)	38.06	19.03	0.0128	10.71
2	pH-10	38.04	19.02	0.0147	9.78
3	3 months	38.16	19.08	0.0105	22.16

3.4. FT-IR analysis:

The FT-IR frequency help to understand the functional group transformation during the formation of NPs. In figure: 3.10 (a) clearly, indicate some peak are common in $AgNO_3$, plant extract and, synthesized silver nanoparticles such as -OH stretching, H2O scissoring and combined bond at the range of (3340-3335 cm^{-1}), (2122-2114cm^{-1}) and (1641-1635cm^{-1})[54]. In figure: 3.10 (b) Some small peaks are also observed in ginger extract the range of 1200-1000 cm^{-1}, these frequencies range are found due to the presence of flavonoids and enzyme functional group (alcohol, amine, ester, carboxylic acid, etc) after the formation of AgNPs some frequencies peaks (1200-1000 cm^{-1}) are disappearing and two new frequency peaks (1367cm^{-1} and 1230-1200 cm^{-1}) appearing, which clarify the AgNPs growth shown in figure . The frequencies range 4000-450cm^{-1} for FT-IR analysis [51],[52].



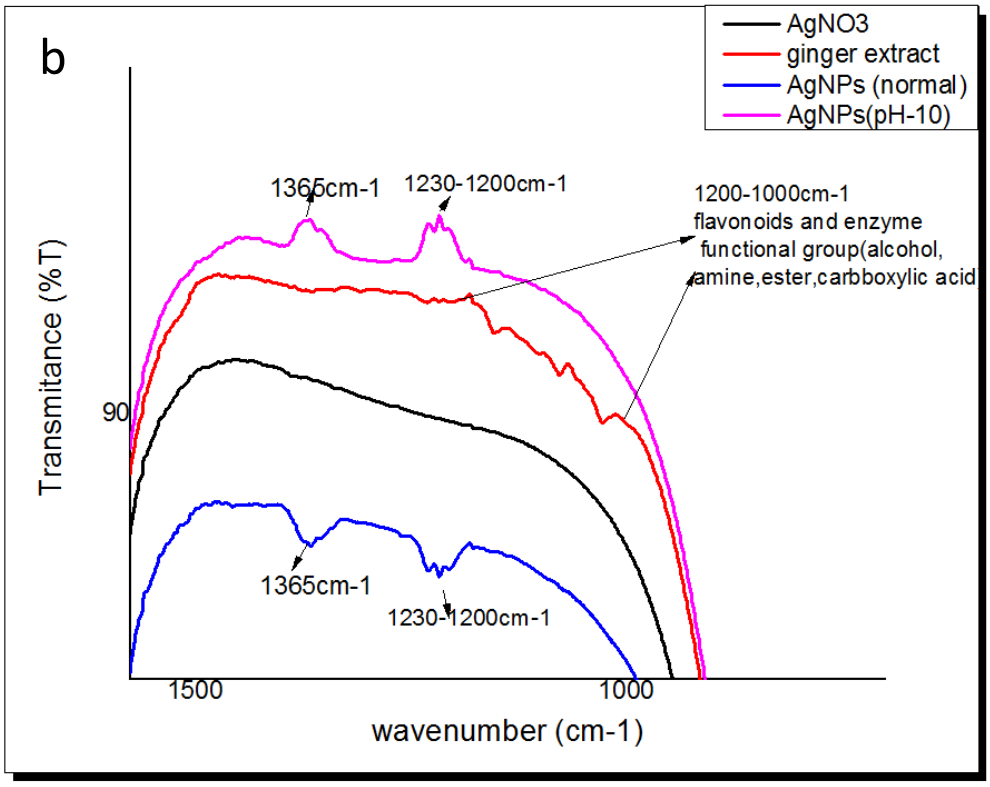


Fig:3.10. FT-IR spectra of ginger-coated AgNPs pH-10, ginger extract, aqueous $AgNO_3$, ginger-coated AgNPs pH-7 (a) frequency range 4000-450cm^{-1}, (b) frequency range 1600-900cm^{-1}

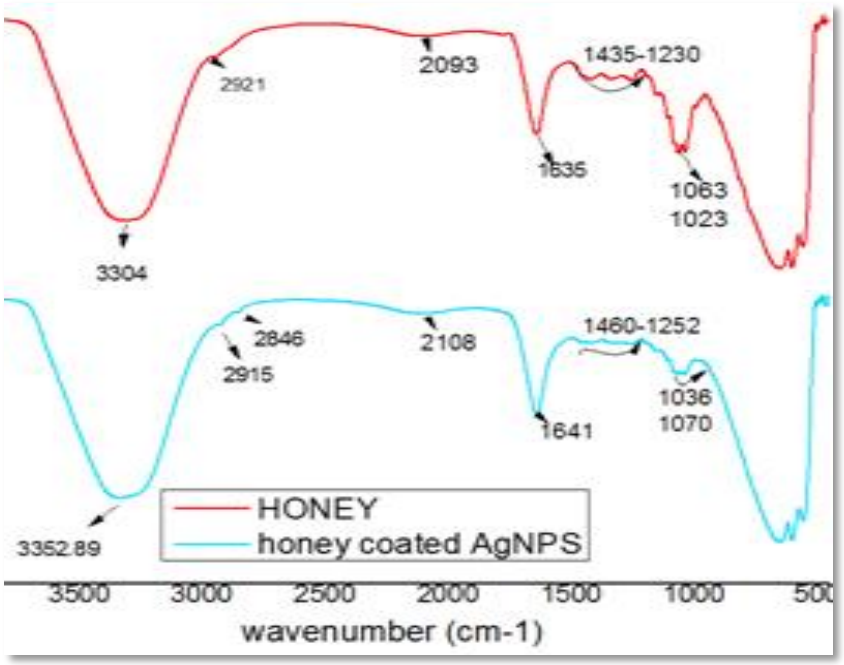


Fig:3.11 FT-IR spectra of honey and honey-coated AgNPs

In figure 3.11, we analyzed the FT-IR spectra of honey and honey-capped AgNPs and the frequencies variation due to the nucleation and growth of AgNPs. According to FT-IR, we can conclude that the formation of silver nanoparticles is due to the presence of phenolic compounds, carbohydrate, starch, terpenoids, enzyme, etc and their functional group.

3.5. TEM analysis:

Ginger- capped AgNPs was characterized by transmission electron microscope for morphology and size description. Here, in figure: 3.12 the TEM image of a different dimensions (100nm, 50nm and 20nm) of as-synthesized AgNPs at pH-7 and pH -10 are well-distributed and almost spherical in shape and variation in size about 5-25nm and an the average size of NPs is 10nm. In the image of both pH range the silver nanoparticles are almost spherical but in respect of pH-7, pH-10 NPs are some small (approx. 3-5nm) and more variation in size.

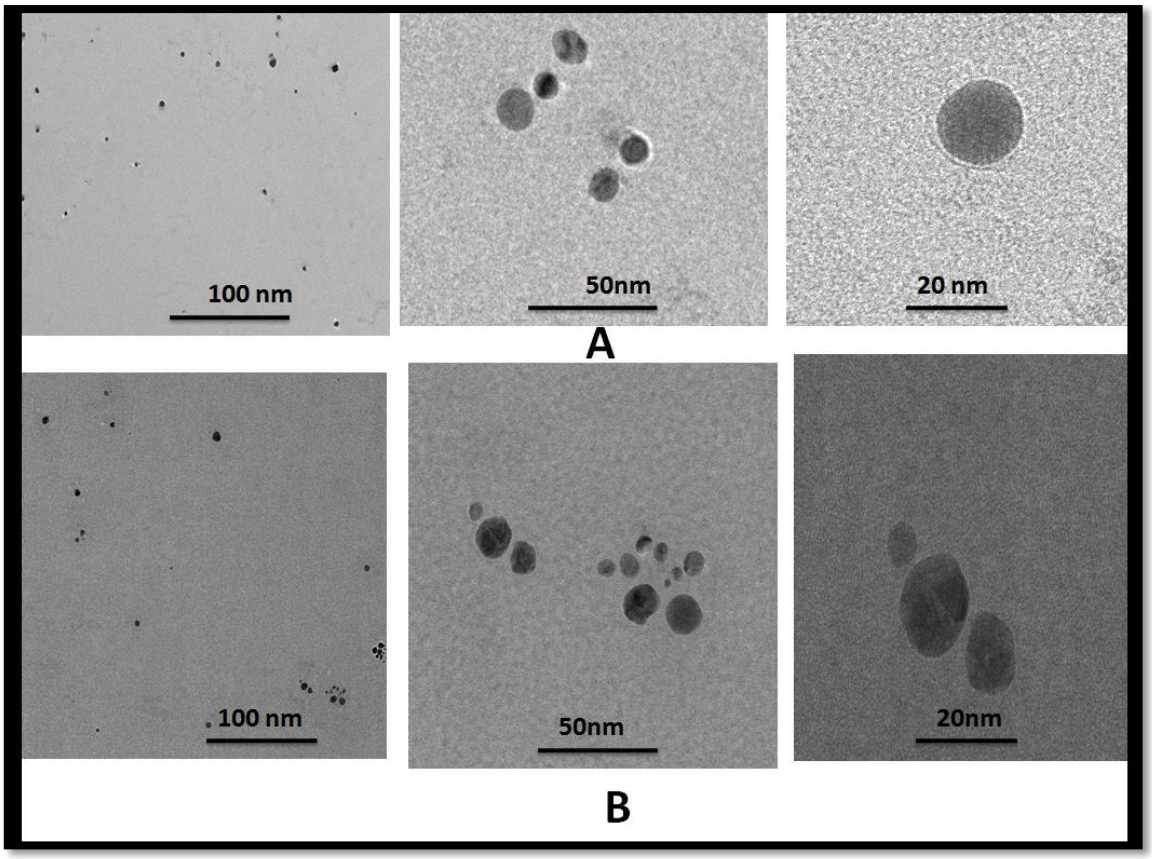


Fig: 3.12 TEM images of ginger-coated AgNPs at (A) pH-7, (B) pH-10.

3.6. Photocatalytic Observation:

Homogeneous photocatalytic reduction of MB to Leuco MB via NaBH4 as a reducing agent and ginger-capped AgNPs as a photocatalyst is shown in figure: 3.13. Figure: 3.14 (a,b and, c) are the absorption graph of MB reduction at different time intervals of MB+$NaBH_4$, MB+$NaBH_4$+AgNPs, MB+$NaBH_4$+ginger extract respectively. The absorption graph clearly, shows that the AgNPs catalyzed MB degraded 98.99% in 10 minutes and ginger extract catalyzed and without catalyzed was not significantly degraded in the time.

Hence, the reduction efficiency of ginger-coated silver nanoparticles is quick and, continuously decreases with time. So that biosynthesized silver nanoparticles are efficient for the reduction of deleterious methylene blue dye. As an observation, it is meritorious to regard that the homogeneous photocatalytic reduction of MB dyes with $NaBH_4$ in the presence of ginger-capped AgNPs is remarkable than that of some other generally fabricated AgNPs. Usually, absorption spectrum of MB is characterized by an absorption band at high energy (π-π* of benzene ring) and a band at low energy around 660-670 nm (moving according to the pH of the solution) and corresponding to n-π* transitions [49].

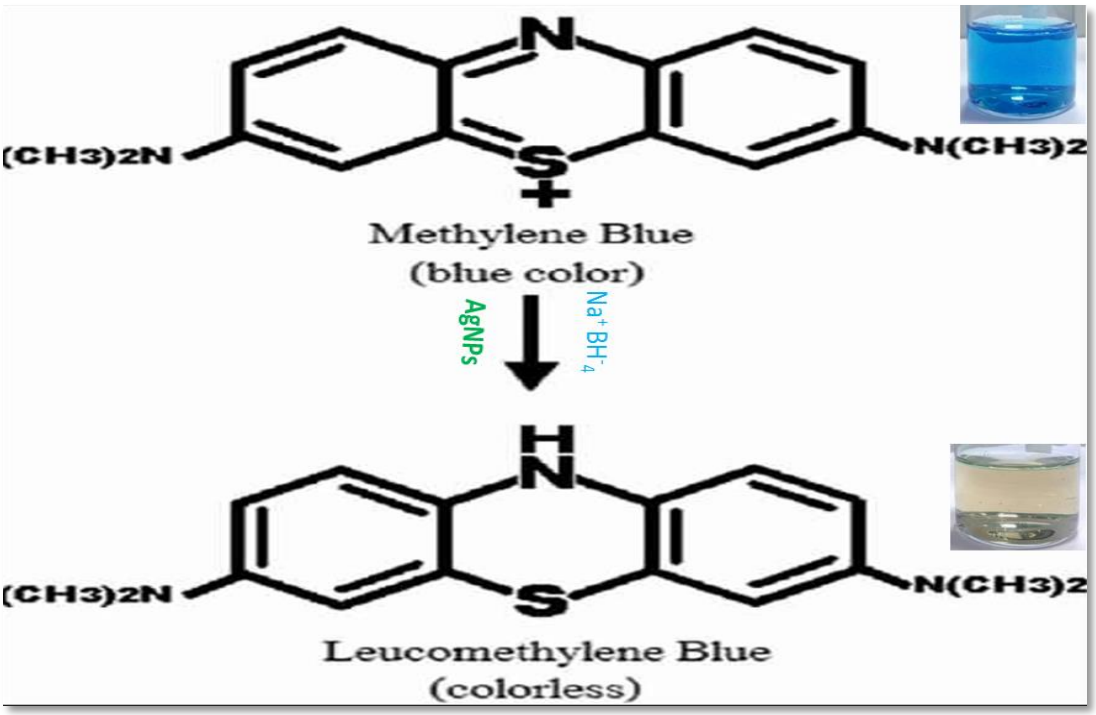
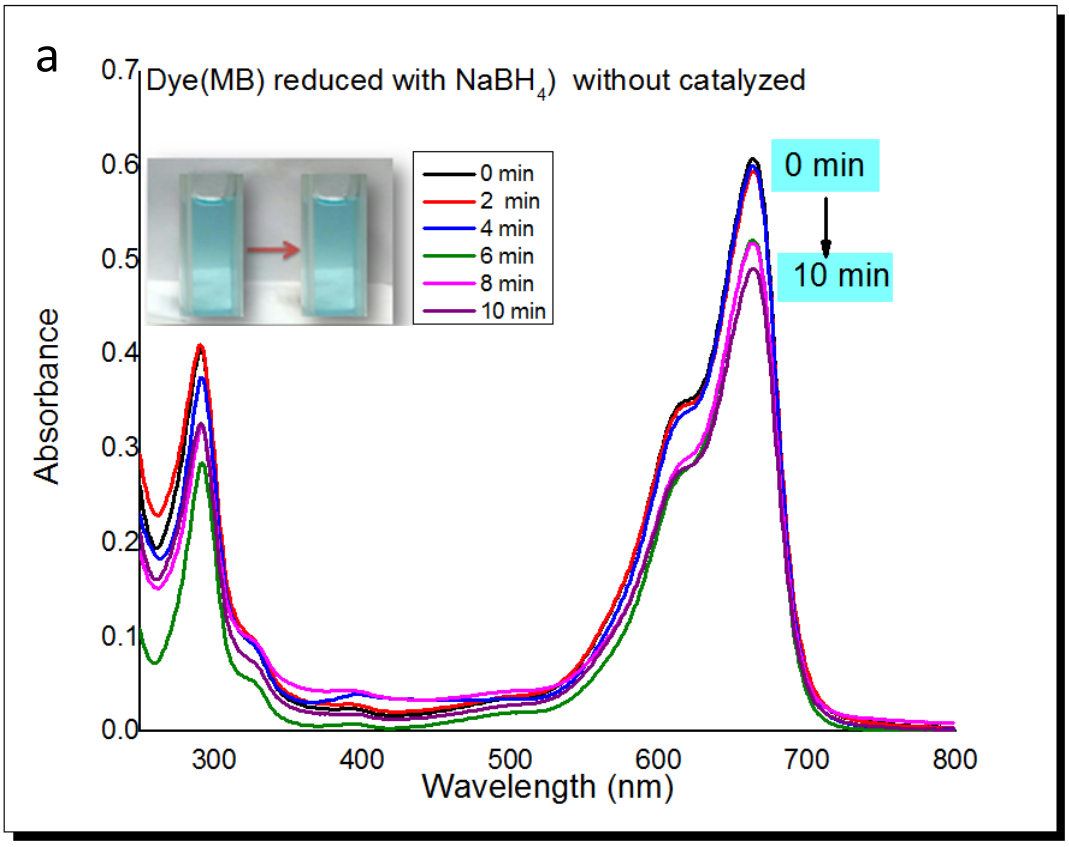
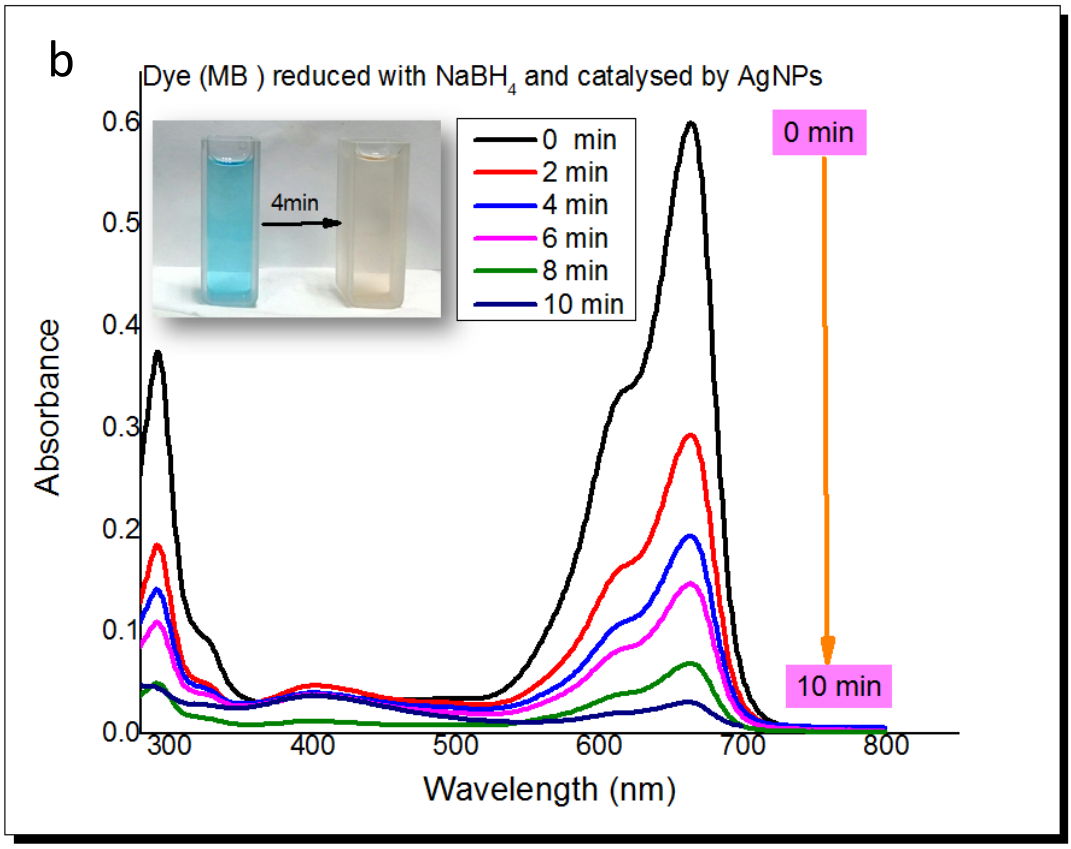


Fig:3.13 Schematic representation of the catalytic reduction of MB to leuco MB.


a
Dye(MB) reduced with NaBH4) without catalyzed
0 min
2 min
4 min
6 min
8 min
10 min
0 min
10 min
Absorbance
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
300
400
500
600
700
800


b
Dye (MB) reduced with NaBH4 and catalysed by AgNPs
4min
0 min
2 min
4 min
6 min
8 min
10 min
0 min
10 min
Absorbance
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
300
400
500
600
700
800

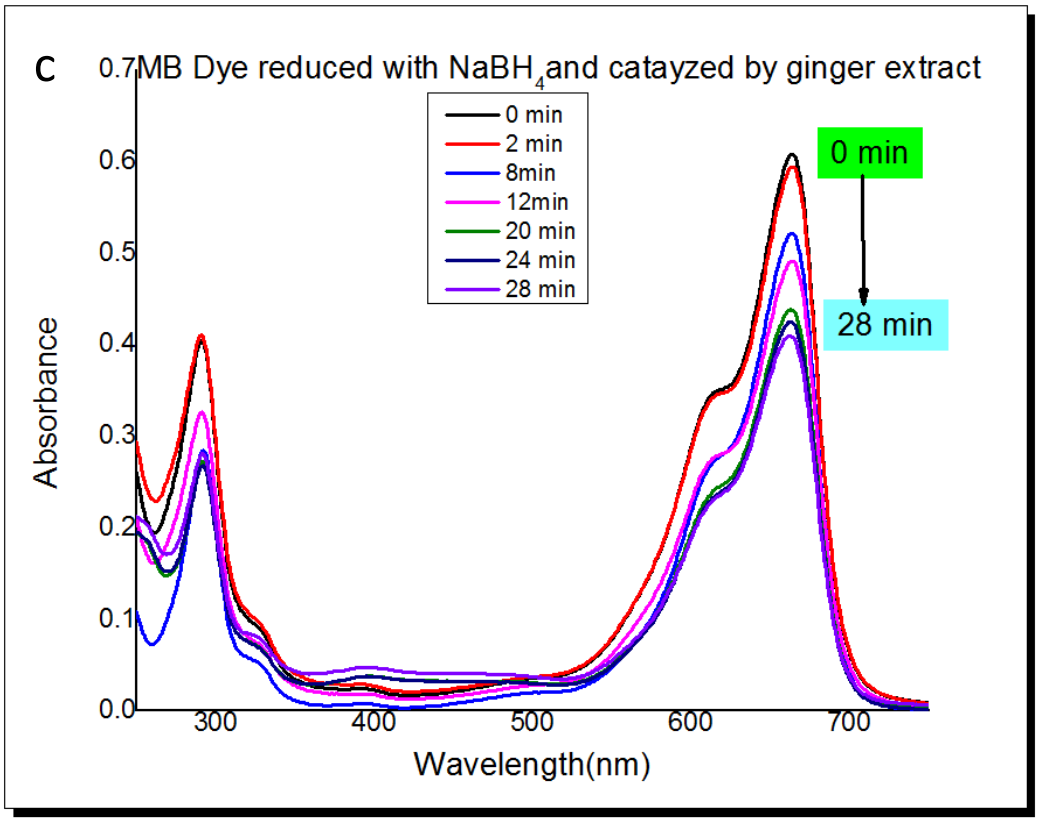


Fig:3.14 Absorption spectra of the Degradation of Methylene Blue (MB) Dye with $NaBH_4$ as reducing agent(a) catalyzed with as-synthesized AgNPs, (b) without catalyzed, (c) catalyzed with ginger extract.

Table-iv) Percentage degradation of MB dye

Serial no.	**Time[minutes]**	**Without catalyzed [MB+$NaBH_4$]**	**With catalysed [MB+$NaBH_4$+A_gNPs]**
1	**0**	***0%***	***0%***
2	**2**	***1.67%***	***50%***
3	**4**	***3.33%***	***66.67%***
4	**6**	***3.50%***	***75%***
5	**8**	***13.37%***	***91.67%***
6	***10***	***20%***	***98.99 %***

CONCLUSION

We have successfully synthesized the silver nanoparticles mediated through aqueous plant extract (Neem leaf, pomegranate peel, ginger rhizome), honey and, white sugar (fructose). Plant extract containing phenolic, ketonic organic macromolecules and enzymatic compounds act as a precursor (reducing and stabilizing agent) in the synthesis of silver nanoparticles. Here we performed the various parameter changes during the fabrication AgNPs such as reaction time, temperature, pH and, plant extract concentrations. By changing the different parameters, we have controlling the shape and size of synthesized nanoparticles. We have successfully compared the various method and concluded that the ginger extract mediated synthesis is the best method because of the formation of very small size, well-distributed and spherical shape of AgNPs and average size around 10nm observed in TEM. Absorption spectra of ginger- capped nanoparticles are around 405nm. All methods for fabrication of AgNPs are natural and most efficient to control the shape and size rather than fructose because fructose capped nanoparticles are not stable. All these methods are cost-effective, non-toxic and eco-friendly for a living being. Ginger capped AgNPs is successfully applicable for homogeneous catalytic degradation of MB, without further any purification procedure. As we know that dyes are the major cause of pollution throughout textile work. In all methods used for the AgNPs synthesis, the absorption peak in range 372-415nm, and size range approximately 5-45nm. These synthesized silver nanoparticles can be widely used in various application such as antioxidant, microbe killing, bio-imaging, drugs delivery, etc.

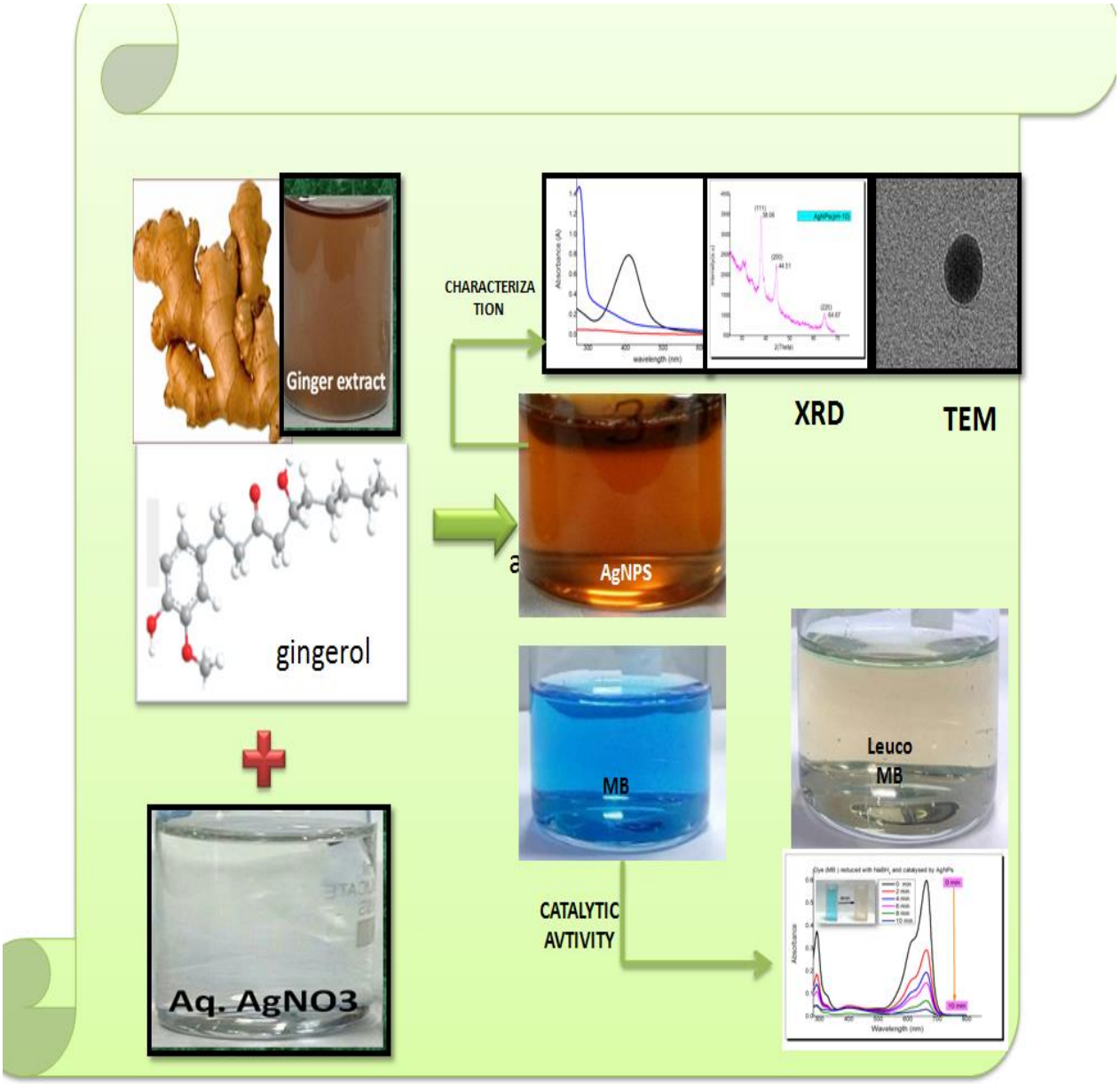


Fig:3.15 Schematic representation of the synthesis ginger-capped AgNPs, characterization and catalytic activity.

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