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Green Synthesis of Silver Nanoparticles by using Fruit and Vegetable Waste: a Review

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ABSTRACT
Nanoparticles have unique properties from their bulk counterparts; as a result of that nanosize particles are presently developing consideration for the ample area of applications. Among all the metals silver is gaining attention because of its unique properties specially its antimicrobial property. Silver nanoparticles synthesized using conventional methods have many drawbacks to overcome those drawbacks green method is coming up. Green synthesis using biological molecules derived from fruit and vegetable waste sources in the form of extracts provide stable, uniform silver nanoparticles. The present review focuses the different fruit and vegetable waste utilized for synthesis of silver nanoparticles. This review presents synthesis methods of silver nanoparticles, characterization techniques of silver nanoparticles, factors affecting silver reduction, antimicrobial property of silver nanoparticles and various applications of silver nanoparticles.
Keywords: Antimicrobial activity, Applications, Green synthesis, Fruit and vegetable waste, Silver nanoparticles

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I. INTRODUCTION

In Greek, word Nano is a synonymous to extremely small which is indication of 10^{-9} or one billionth a meter [1]. Rising and vibrating field of research on the particle having the size of human hair called Nanotechnology, is a rapid growing field with relevance in science and technology aim to manufacture new materials at the Nano level [2,3]. It is new and emerging field having enormous impact on mankind by helping their major challenge in context to health and energy [4]. Nanotechnology is a significant modern research field going to deal with morphology, synthesis and design of particle size ranging from 1 to 100 nm approximately [5]. Nanometer sized metal particles show rare and quite changed properties including physical, chemical and biological in comparison with their macro scale, due to their high surface to volume ratio which leads to rise in the surface reactivity [6].

Nanoparticles have unique optical, catalytic, magnetic as well as biological properties it has application in catalysis, biosensing, biomedical sciences, drug delivery, photo-electrochemical, food, health and cosmetics [3, 7]. Nanomaterials may have important availability than macro units, ensuring in utilization of individual cells, tissues and organs [8]. Nanoparticles have functional platforms that can be prepared from various materials including organic and inorganic. Due to its easy modification, high drug loading capacity and stability, the inorganic platforms are very prominent [9].

Metal nanoparticles are holder of small number of atoms to many metal atoms. Nanoparticles plays an important role in catalysis as they increase activation of metal surface and increase the efficiency to heterogeneous catalysis as well as homogeneous catalysis [8]. Silver is a metal which is soft, white, lustrous element having high electrical and thermal conductivity. It is used in many forms as coin, solution oil and vessels [8]. Silver is the precious metal among all the noble metal due to different properties especially catalytic nature, antimicrobial, antifungal, anti-inflammatory and antiviral activity [8, 10]. As an antimicrobial agent it is capable to killing 650 types of diseases causing bacteria [11]. Silver products are known for strong inhibitory and bacterial effects. It has been developed for biological, physical and pharmaceutical purpose as it is known as nontoxic [8, 10]. Silver nanoparticles plays important role in the study of biology and medicine because of its unique physiochemical, electrical, optical and biological properties thus it has various field application [8, 11]. AgNPs also exhibit catalytic activity with anticoagulant applications [12].

Silver nano particles has application in a various field such as use in cosmetics, electronics , textiles industries, medical, coatings of various surgical medical devices as well as in formulation of dental resin composites and ion exchange fibers. In food industry, it has been used as a component of food packaging materials which can resist the entry of moisture, O_2 & CO_2 from reaching to fresh vegetables and fruits, meats and other processed food products. Excess generation of free radical in human body results many degenerative diseases such as cardiovascular and cancer. And silver as a inorganic nano particles found effective against them [13].

As reported in the literature, physical and chemical methods are not reliable but biological can be used as eco-friendly alternative for synthesis of silver nanoparticles [7]. Chemical synthesis of NP considers using of toxic chemicals and has adverse effects on the environment and also resists its application in medical field. Physical methods include thermal decomposition, evaporation-condensation and chemical methods includes photochemical reaction and etc. As these methods utilized environmentally toxic chemicals, required high energy and tedious purification, and many more issues arise while processing mainly regarding stabilization and agglomeration of nanoparticles [7]. Green synthesis has been proven advantageous in comparison to the other methods. It is economical and does not need any of temperature, pressure, energy or the use of toxic chemicals [7]. Mainly plant and fruit extracts, microbes, fungi and enzymes have been used as a source [7]. AgNPs from the plants extract have more stability then synthesized from the microbial sources [7]. Recently research is focused towards green technology, natural elements including carbohydrates, plant extracts and microbe and it is a safer alternative, reducing agent, capping agent and stabilizing agent for synthesis of nanoparticles [7]. The product which got from biosynthesis includes metal, metal oxides and any metal nanoparticles are pure, safer, cleaner, and non-toxic and environment friendly for large scale synthesis [8, 14].

Various beneficial natural compounds are present in outer peels of fruits which usually discarded as a waste; therefore use of that waste as resource for synthesis of nanoparticles can be significant step towards effective solid waste management [13]. As per green technology strategy, the material which are being used should renewable and non-toxic and here we utilized a totally environmentally benign method to achieve silver nanoparticles from the fruit waste i.e. peel [7]. As an alternative of conventional methods, silver nanoparticles synthesized from various fruit waste are cost efficient and more preferable as it has a full range of pharmacological activities. The fruit peel extract itself used as a bio-reductant, stabilizing and capping agent [7]. It also having substantial amount of secondary metabolites [15]. Polyphenols and alkaloids primarily presents in fruit extract [5]. Ellagic acid is a main constituent that appears in several fruit and nuts responsible for multiple health benefits and it's naturally occurring phenolic compound [5]. These phenolic compounds possess carboxyl and hydroxyl groups which is able to bind heavy metals which may inactive ions by chelating. When metal salts come in touch with ellagic acid which present in fruit peel extract the ester oxygen atom and ortho-phenolic hydroxyl of ellagic acid makes p track conjugation effects. Esterification of above two make loose hydrogen much easily and forming steadier structure. Ellagic acid has ability to reduces size of silver nanoparticles also it is water soluble, having high bioavailability, major anti-oxidant component and have free radical scavenging capacity [5]. For reduction of the $AgNO_3$ into silver nanoparticles, phytochemicals which is present in vegetable waste were responsible [16].

II. SYNTHESIS METHODS OF SILVER NANOPARTICLES

Silver nanoparticles can be synthesized by two approaches: "Top to bottom" and "Bottom to top". In Top to bottom approach physical methods are used like grinding, milling, sputtering, thermal/laser ablation processes are used for breaking it bigger particles into the smaller particles. In Bottom to top approach, chemical and biological methods are used in which atoms goes under self-assembly from which nanoparticles grows. Chemical reduction, electrochemical and sono decomposition are generally used as chemical methods. Large quantities of nanoparticles are produces in short period of time in bottom-up approach while top-bottom approach have low yield. In "top to bottom" approach nanoparticles synthesized at atmospheric pressure with the help of tube furnace by evaporation condensation technique. The primary material is placed in centre of the furnace vaporized into carrier gas. Biggest disadvantage of this method is imperfect surface structure of the product and other physical properties which is highly dependent on the surface structure. Although these all methods are not environmental friendly so the alternative is green synthesis route [17].

In physical methods furnace is used for synthesis of nanoparticles which required several kilowatts. Various metal nanoparticles such as Au, Pbs have been synthesized through this technique but in case of silver nanoparticles, it has several drawbacks like required large space, consume more amount of energy which raises the temperature of materials and also take large span of time to get thermal stability as well as preheating are required [11].

Using organic and inorganic reducing agent, chemical reduction method is most common method for synthesis of silver nanoparticles. The confirmation of synthesized silver nano-particles is by generating a colored silver solution due to free charge electron on metal surface [18].

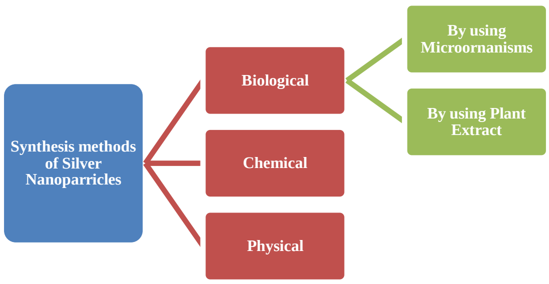

Fig 1: Different methods for synthesis of silver nanoparticles

As physical and chemical methods are giving low yield and also use of toxic chemicals and lots of energy only left an option of green synthesis in a eco-friendly way [18]. Wide variety of shapes ad different size range silver nanoparticles can be synthesized by using microbes, enzymes, fungi, fruit and its peel, plant and its extract which is a cheap, rapid and efficient method [13]. To overcome the problems like toxicity, non-environment friendly and expensive, the researchers gave a precious green route which includes naturally available sources. It is mainly categorized in 3 categories: 1.Microoragnisms 2. Plant and its extracts 3. Membranes [4].

For reduce metal ions bacteria and fungi are used by using bacteria ecological and profitable silver nano particles can be synthesized [18]. In comparison with bacteria, fungi have high potential for metal bioaccumulation capacity, high binding capacity and tolerance and easy to handle [4].

Plant extract works effectively then microorganisms for feasible synthesis of nano particle. Plants and plant extracts used as s reducing agent and capping agent for synthesis of silver nanoparticles [18].

III. GREEN SYNTHESIS OF SILVER NANOPARTICLES

Rapid, non pathogenic, single step process, eco friendly and economic synthesis of silver nano-particles using plants has gaining attention for the biosynthesis processes. Combination of biomolecules like enzymes, proteins, amino acids, terpenoids, phenolics, vitamins and polysaccharides present in the plant extracts are responsible for stabilization and reduction of silver ions [19]. For synthesis of different metal nano particles such as platinum, silver, titanium and platinum of different size and shapes, various parts are in use like bark, extracts, fruit, fruit peels and root [2]. Alternative of conventional process, silver nanoparticles synthesized from multiple fruit peel extract approach proved economically efficient, fast and eco-friendly [5]. Fruit peel extract itself performed a bioreductant; stabilizing agent and capping agent [7]. Usually peels are discarded as waste however the natural compounds presents in outer peels are making them useful in progress towards utilization of waste for synthesis of silver nano particles [13].
A large number of waste peels are reported to silver nanoparticles synthesis are mentioned in table and discussed briefly in the review. Various fruit peels are reported as used for synthesis of silver nano particles and discussed in table.

Table 1: Silver nanoparticles synthesize using Green technology with fruit and vegetable waste

Waste	Size range (nm)	Shape of nanoparticles	Reference
Banana Peel Extract	23.7	Spherical	[2]
Banana Peel Extract	10	Spherical	[3]
Satsuma peel Extract	5-20	Spherical	[18]
Citrus sinensis peel extract	15	Spherical	[15]
Orange Peel Extract	30.29	Spherical	[20]
Pomegranate peel Extract	5-50	Spherical	[1]
Dragon fruit peel extract	25-26	Spherical	[10]
Carica papaya peel extract	16-20	Spherical	[21]
Longon peel extract	38.6 +-7.0	Spherical	[14]
Fruit waste	9-46	Spherical	[7]

peel Extract			
Multiple fruit waste peel	25	Spherical	[5]
Waste vegetabl e peel	20	Spherical	[22]
Market vegetabl e waste	10-90	Spherical	[16]

Different factors are affecting on reduction of silver by using banana peels and also there were some optimum conditions such as silver nitrate (1.75 mM), Banana peel extract (20.4 mg dry), pH (4.5) and incubation time (72 h). Banana peel extract extremely fast reduces the silver ions within 5 min after heating showing reddish brown color. The characterization of silver nano particles done by x-ray diffraction, SEM (scanning electron microscope), field emission scanning electron microscope which shows spherical, crystalline and mono dispersed nanoparticles. Average size of nanoparticles is 23.7 nm. X-ray spectroscopy confirmed the pick of silver. FTIR confirmed the banana peel extract as a reducing agent as well as capping agent for silver ion. As well as silver nanoparticles show effective antimicrobial activity against yeast and bacteria [2].

Outer peels of sweet orange used for synthesis of silver nanoparticles. Color change from yellow to brown confirmed the synthesis of silver nanoparticles. Average size of nanoparticles is 23.81 nm by dynamic light scattering. Also all the characterization of nanoparticles was favouring the confirmation of silver nanoparticles [15].

Pomegranate was also used as capping and reducing agent and average size of these nano particles are 5-50 nm [34]. Another fruit peel used in these syntheses was dragon fruit and used as capping and reducing agent. TEM images are showed that size of silver nano particles reduced with increment in pH. The range of nanoparticles was 25-26 nm. Crystallized nanoparticles in face centred cubic symmetry indicated by XRD and EDX [10].

Papaya peel of various concentrations such as 5, 10, 15, 20 and 25 ml with silver nitrate was used for synthesis of Ag NP. Bands were shifted to higher wavelengths as papaya peels extract increases their concentration revealed by FTIR spectra. The average size for papaya peel extract observed around 16-20 nm in XRD spectral analysis confirmed by TEM analysis. Spherical structure showed by SEM analysis. Antibacterial activity showed by synthesized nano particles against human pathogens and it has many medical applications [21].

Longan peels extract also used for biosynthesis of silver nanoparticles and practical performed at room temperature. The silver nanoparticles from longan peel extract were irregular in shape with size of 38.6 nm. FTIR analysis showed the groups of phytochemical in synthesized silver NP. Other way of characterization of Ag NP by XRD and EDX indicate that NP was crystalline in nature and there was presence of silver ion. Zeta potential confirmed the stability of silver nano particle [14].

Formation of AgNPs from fruit waste extract was confirmed by color change and Extract itself acts as a capping agent. Size and shape of silver nanoparticles was determined by characterization. The range of size was found 9 to 46 nm [7].

Silver nanoparticles synthesized from fruit waste extract was showed high antimicrobial activity against plant, human and pathogens and against the human breast cancer cell so that it was suggested for further use in pharmacology field [5]. Vegetable peel extract of five different vegetables such as L.siceraria, S.melongena, L.cylindrica, C.sativus and S.lycopersicum was used as reducing agent and the AgNPs synthesized from that was having size of 20 nm. The characterization shows that certain protein and phytochemicals was present in the vegetable peel extract may be going to take part in synthesis, reduction and capping as well s stabilizing agent [22]. Silver nanoparticles synthesized from vegetable peel extract showed the antimicrobial activity against the clinical pathogens [16].

IV. CHARACTERIZATION OF SILVER NANOPARTICLES

To identify nanoparticles synthesis and for their applications characterization of nanoparticles is essential. Different microscopy such as scanning and transmission electron microscopy (SEM, TEM), Atomic force microscopy; Spectroscopy like X-ray photoelectron spectroscopy, UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR); and other techniques such as dynamic light scattering (DLS), powder X-ray diffractometry (XRD) are used for characterization of silver nanoparticles. All the techniques are used to characterise different parameters such as pore size, shape, particle size, crystalline, surface area and fractal dimensions. Also their dispersion, orientation and intercalation of nanoparticles could be determined by these various characterization techniques [23].

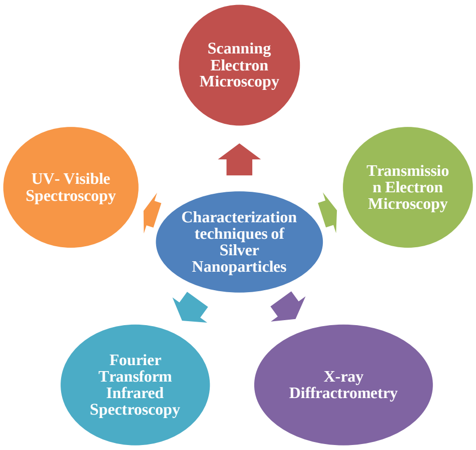

Fig 2: Characterization techniques of silver nanoparticles

In Scanning electron microscope cylindrical, copper made stub is used in which one side of stub covered with double sided carbon material and after putting sample with pipette in the stub it is fixed with holder [9]. Shape and morphology of nanoparticles are determined by SEM [11].

In Transmission Electron Microscopy technique, prepared nano particles were put on the copper girds coated with carbon. TEM instrument operated at accelerating voltage then micrographs of TEM generated for drop of nanoparticles. The image is formed from the interaction when the electrons transmitted through the specimen. Magnified and focused image on to imaging device showed the morphology and particle size for an accurate profile of the silver nano particles [9].

The absorbance was responsible for color of metal nanoparticles such as gold and silver. Due to oscillations, electromagnetic radiation and conduction electron are absorbed by incident light. The adjusted range for absorption is 0.5 and 0.7; distilled water is used to dilute silver nanoparticles solution. Particle size was indicated by wavelength of the absorption maximum in solvent. Silver nanoparticles produce 400 nm wavelength spectrums [9].

Functional group was determined by FTIR observed on silver nanoparticles [11]. Spectral ranges of 4000-400 cm were used for synthesized silver nanoparticles. A powder diffraction calculation was used for preparation of powder sample used in FTIR analysis. Two cells of NaCl on which prepared sample is placed, after containing the sample put it in the holder of KBr pellet cells. Detection of functional group occurs from the computer program to get signal [9].

The Crystalline nature of nanoparticles will confirm by the X-ray diffractometry analysis. Only small amount of sample is enough to obtain and confirm the structure and size of nanoparticles. Use of n-butyl alcohol for synthesis of silver nanoparticles shows a peak which confirms the hypothetical mono crystal. And the sharpness of peak also confirmed that it was in nano size. Data are also compared with pure silver nitrate [9].

V. FACTORS AFFECTING SILVER REDUCTION

Effect of Temperature

Smaller nanoparticles synthesised when temperature is increased considering reactants are consumed at high speed principal [11]. Absorbance peak decreases with increase temperature and reaction rate. Reaction time is also decreased as temperature increases considering temperature improve the rate of reduction. Kinetic energy of molecules increases at high temperature which increases the utilization of silver ions, as a result of this cause to remain minor liability for particle size produce and homogeneous size silver nanoparticles are assemble [24]. Ultra violet spectra show fine thin peaks at lesser wavelength region with increase in reaction temperature which express the formation of smaller nanoparticles [2].

Effect of Extract Concentration

Biological objective intermediate nanoparticles synthesis concentration is increased higher amount of biomolecules elaborate in the metal diminishing process are available concluding in a higher intense color [2].

Effect of pH

In the formation of silver nanoparticles pH plays a significant role. Charge present in the natural phytochemical of the extract may Change due to the Variation in to the pH value considering that change in the charge influenced the constancy of silver ions to biomolecules and affect the reduction of silver ions to silver nanoparticles. Size, production rate, Shape and stability of nanoparticles affect by the pH. Stability of silver nanoparticles explain by the zeta potential data considering that the low zeta potential at strongly acidic pH and high zeta potential at alkaline pH [24]. At highly acidic conditions biological nanoparticles synthesis from variety of biomolecules have possibility to be inactivated [2]. H^+ ions concentration is decrease as the pH value increases, concluding higher surface charge on the particle. Vast number of phenolic functional groups available for silver binding promote a higher number of silver ions to bind and form a more number of nanoparticles with smaller diameters at higher pH. Formation of silver nanoparticles not occur at acidic pH (pH<5) as they are instable at acidic pH [4].

Effect of Incubation Period

Relation between the intensity of the reddish brown color and incubation time of reaction mixture is directly proportional considering that the time during biosynthesis of metal nanoparticles using bacteria and fungi essential for complete the reaction is 24 to 124 h of the metal ions [11]. For synthesis of silver nanoparticles the exposure time of reducing agent to metal ions is responsible. It concludes that nanoparticles synthesis is expanded when the incubation time of silver with the reductant is increased. Considered that synthesis of silver nanoparticles are completed after resulting surface Plasmon peak of silver nanoparticles has been increased from zero to thirty and after that it become constant [24]. In one literature it is reported that maximum reduction of silver ions was obtained at 72 hour [2].

Effect of Silver Nitrate Concentration

Metal salt concentration and biological material variation considered in to the influence of nanoparticles synthesis [2]. In biosynthesis of silver nanoparticles silver ion concentration play significant role. One millilitre of extract is sufficient enough for reduction of 20 ml silver nitrate assuming that concentration of silver nitrate is increased then lower numbers of biomolecules are available as a reducing and capping agent considering that at the ratio of 1: 20 (extract and silver nitrate) best synthesize silver nanoparticles [24].

VI. ANTIMICROBIAL PROPERTY OF SILVER NANOPARTICLES

Among all the metal silver is known for its antimicrobial activity against a wide range over 650 microorganisms from different divisions such as fungi, gram-positive and gram-negative bacteria and viruses [19].

Silver nanoparticles synthesized using waste fruit and vegetable peel has antibacterial activities against gram positive and gram negative bacteria (Table-2).

Table 2: Antimicrobial activities of silver nanoparticles synthesized using waste peel

Biological waste	**Micro-organisms to be tested**	**Method used**	**Refe renc es**
Banana Peel Extract	B. substills, S. Aureus, P. Aeruginosa, E. Coli	MIC, MBC	[2]
Citrus Fruit Peel Extract	Salmonella Typhimuriu, Escherichia coli and Pseudomonas aeruginosa	-	[25]
Orange Peel Extract	Staphylococcus aureus, Salmomella typhi, Escherichia coli, Psuedomonas aeriginosa	MIC	[20]
Promogranate peel Extract	Staphylococcus aureus, Psuedomonas aeriginosa, Escherichia coli	Disc diffusion Method	[1]
Dragon Fruit peel Extract	Staphylococcus aureus, Psuedomonas aeriginosa, Escherichia coli	Disc diffusion Method	[10]
Carica papaya Peel Extract	Staphylococcus aureus, Escherichia coli	-	[21]
Longan peel Extract	Staphylococcus aureus, Escherichia coli	Agar Disc diffusion Method	[14]
Fruit peel Extract	Salmomella typhi, Escherichia coli, Psuedomonas aeriginosa	Agar well diffusion Method	[5]
Waste vegetable peel extract	Escherichia coli, K.pneumoniae	Disc diffusion Method	[22]

The antimicrobial properties of silver nanoparticles depend on environmental conditions, Size and capping agent used for synthesis [19]. When silver is in ionized form with positive charge implicate for antimicrobial activities it releases silver ions when comes in contact with moisture [19].Silver ions have ability to make complexes with nucleic acid, thus from any silver ion source antimicrobial activity has been observed in one or other form of silver based compound [19].Silver ions released with the time slowly and gradually from the substance containing it or it will obtain from ionized surface of solid silver piece as silver nanoparticles [19]. Gram positive bacteria have more peptidoglycan molecules then gram negative bacteria hence gram negative bacteria are more influenced by silver ions. Gram positive bacteria have thick wall with negatively charged peptidoglycan so that positively charged silver ions may get stuck [19].

VII. APPLICATION OF SILVER NANOPARTICLES

Silver nanoparticles are well known for its unique properties in the field of nanotechnology [8]. Because of its unique properties like chemical stability, Catalytical effect and antimicrobial activity silver nanoparticles have number of applications. Silver nanoparticles used as electronic products in the industry, antibacterial agents in the health industry, food storage, textile coating and environmental applications [26]. Silver nanoparticles act as a good catalyst in industry which provides high surface energy and which promote the surface reactivity [6].

Among all the metallic nanoparticles silver gained attention because of its antimicrobial property [8].Due to antimicrobial property silver nanoparticles were applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment [23]. In the textile coating industry silver nanoparticles use in different textile fabrics. Fibers containing silver nanoparticles showed good antibacterial activity against Escherichia Coli [26]. As a antimicrobial agent silver nanoparticles used in a number of applications like air sanitizer, sprays, shampoo, soap, detergent, wet wipes, face masks, socks, slippers, pillows, toothpaste, coating of refrigerators, washing machines, vacuum cleaners, food storage containers, air filters and cellular phones [6].

Silver nanoparticles used as a antibacterial, antifungal and antiviral agents as a antibacterial agent which showed good bacterial activities against gram positive and gram negative bacteria. Silver nanoparticles are considered as a fast acting fungicide. As a antiviral agent silver nanoparticles can be used to prevent infection after surgery and acting as anti-HIV-1 agents [24].

Silver nanoparticles use in medical applications including wound dressing and catheters. This is use in ointments and creams which is used to prevent wounds, burns and infections [24]. Due to enhanced antimicrobial nature of silver nanoparticles it is use for purification in water filtering apparatus. As an antimicrobial agent silver nanoparticles prevent the growth of harmful microorganisms [24].

VIII. CONCLUSION

Conventional method use for synthesis of silver nanoparticles require high energy, temperature as well as toxic reagents which produce harmful by products so there is crucial requirement of green method for synthesis of silver nanoparticles. The process of synthesis using fruit and vegetable waste is considered economical, energy efficient, cost efficient and easily scaled up. The biomolecules present in waste act as a reducing agent which reduce silver ions into silver nanoparticles. Synthesis of silver nanoparticles using fruit and vegetable waste can be advantageous over other biological entities which eliminate the use of complicated process of culturing and maintaining of microbes. The varied biomolecules present in the fruit and vegetable waste act as a capping, stabilizing and reducing agent for synthesis of silver nanoparticles from silver ions and give unique property to them. Since the synthesis of silver nanoparticles is economical, environment friendly, rapid and single step process it can be used in wide range of application such as textile coating, food storage, biomedical field, water purification and many environmental applications.

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