REVIEW ARTICLE

SYNTHESIS OF SILVER NANOPARTICLES, MULTIFUNCTIONAL PROPERTIES AND APPLICATIONS IN BIOMEDICINE AND ENVIRONMENT

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ABSTRACT: Nanotechnology has the got the potential to develop a succession of procedures and tools which can revolutionize biomedical field. They are faster, cheaper, lighter and more energy efficient. The word nanotechnology refers to those materials having at least one of its dimension in the range 1-100nm and display entirely different properties when compared to bulk material due to difference in shape, size and morphology of particles. These properties called nanoparticles (NPs) include large surface area and increased chemical reactivity. Size dependent properties are observed such as, quantum confinement in semi conducting materials and supermagnetism in magnetic materials, etc. They can be synthesized by both ways, either chemically or biologically. Metallic nanoparticles find their enormous applications ranging from medical treatments, antibacterial activities to use in industries for various purposes. In this regard silver Nps have got immense significance in technology and especially to prevent bacterial infection in medicine. It's also used in hospital equipments including catheters, stents, bandages, and wound dressings. This article intends to present various synthetic techniques, like chemical, physical and biological synthesis of silver nanoparticles. Furthermore, unique properties of silver nanoparticles along with their applications are also reviewed.

Key words*:* synthesis, nano particles, silver, properties, antibacterial activity, bio medical application, photonics.

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INTRODUCTION

The prefix nano comes from "nanos" which is Greek word and indicates one billionth parts or 10^{-9} units. Nano technology is a fast growing field as it produces nano particles including nano products that can have wide range of properties differing from larger matter. It also includes synthesis and development of various nano materials. Nano particles refer those particles which size range from 1 to 100 nm. Particles in this range show properties which differ from the bulk materials both chemically and physically, mainly because of huge surface and volume ratio. One of the techniques to synthesize nano particles is top down where size of the material is made to decrease. The other one is bottom up which breaks up large sized particles to make nano materials. Nano technology is the science of very small and is used to manipulate matter at very small scale. This technique not only affects a specific area but it also simply means the production of extremely small products. With the help of this technology, new nano sized materials can be synthesized for their application at atomic and molecular scales. (Pal *et al.*, 2011)

The classification of nano particles requires its dimensions. 1D structure includes thin films that are widely used in engineering and electronics such as storage system, biological and chemicals sensors, and many optical devices. Carbon nano tubes are example of two dimensional nano particles that are one nano meter in diameter and length is abouy100 nm. Because of high current density of carbon nano tubes i.e., billion amperes /m^2, it behaves as a supper conductor. Due to this mechanical strength of CNT's, it is 60 times greater than other best steel. Fullerenes are example of three dimensional nano particles. They display remarkable physical properties .e.g. when extreme pressure is applied on them, the shape changes but as some of pressure is released they regain the original shape. They are also used in the production of solar cells. Synthesis of noble metal Nps is an area of immense attention, for the reason that their applications in the field of optics, electronics, biotechnology and environmental sciences. Gold and silver Nps are widely utilized for the production of steady dispersion of nano particles to be used in optoelectronic devices, such as, photography, and photonics and also in catalysis of biological systems.

Silver nano (Ag Nps) particles have got more attention because of remarkable anti microbial properties. Beside this they exhibit broad spectrum of fungical and bactericide activities. They are used in industry to produce soaps, food, paste, plastic and textiles. Other than this, they show exceptional thermal and optoelectronic properties to be employed in electronic components, photonics and catalysis. Due to this reason special attention is being paid in the fabrication of silver nano particles using different techniques (Song *et al.*, 2016).

Now a days, a huge research is going on in the field of nanocomposites, which are defined as the materials formed by the combination of more than one Nps in order to gain the finest properties of all components. In nanocomposites, nanoparticles (clay, metal, carbon nanotubes) act as fillers in a matrix, usually polymer matrix (Nguyen-Tri *et al.*, 2018).

At present, silver nano particles are synthesized using different approaches which include many physical, chemical and biological techniques. All techniques have their own limitations and delimitations that depend on the availability of resources and produce nano particles with different sizes (Natsuki *et al.*, 2015): All of these methods are discussed in detail below.

Methods used for the synthesis of silver nano particles

Chemical Methods: Chemical methods are mostly utilized for the synthesis of silver Nps and among them the most common approach is chemical reduction method by organic and inorganic compounds. It produces stable nano particles in water and organic solvents. Production of nano particles mainly depend on the temperature during the fabrication process. Some of them can be performed at room temperature however for high reaction ratio; most of them have elevated temperature (Jiang *et al.*, 2006).

Chemical Reduction Method: Mainly the chemical reduction process in solution involves three main components, (i) Metal precursor (ii) reducing agent (iii) capping agent. In order to produce nano particles with uniform size distribution, it is required that nuclei must be produced at the same time. Only in this way all nuclei will have similar size and same subsequence growth. Nucleation and nuclei growth can be controlled by the adjustment of different reaction factors, such as, pH to reduce the effect of stabilizing agent and reaction temperature (Evanoff and Chumanov, 2004).

Electrochemical method: It was observed that size of selective nano scale of transit on metal particle could be seen electrochemically using tetra alkyl ammonium sales stabilizer of metal cluster in a nano aqueous solution. Since then process of electrolysis has been used for the reduction of material ions. It is a heterogeneous process. There are two general types of electrochemical methods; Potentiometeric (no current, equilibrium potential) and voltametric (current measured as a function of application potential). Main function of this method is an electrode which provides an interface where process of change transfer occurs. These processes are reported to be better than other chemical methods to produce nano particles because of low cost, ease to handling, higher quality and modest equipments (Guzmán *et al.*, 2008)

Pyrolysis: One of useful methods for the synthesis of silver nano particles is spray pyrolysis. Although this method can produce silver nano particles successfully, yet, the requirement of the use of stabilizer for the protection of the synthesized nano particles from agglomeration is necessary. The drawback of pyrolysis method is that it is very expensive and not friendly to environment (Natsuki *et al.,* 2015).

Physical methods: These methods usually involve process of evaporation and condensation which is carried out in a tube furnace and certain atmospheric pressure. Various types of nano particles like, Au, Pb, Cu and fluorine (F) have been produced by using this technique. Although Ag Nps can be produced by the use of tube furnace, it has several draw backs e.g.; tube furnace occupies large spaces around the source material and require much larger time to become thermally stabilize and require power consumption of more than several kilowatts but many physical methods have advantages above chemical methods because that they do not make use chemicals which are toxic. The process of ions formation for nano particles is usually faster rather than other methods (Abbasi *et al.*, 2016;Panwar *et al.*, 2017)which includes laser ablation (Baiee *et al.*, 2018; Gellini *et al.*, 2018; Sportelli *et al.*, 2018).

Bio-based methods: Nano particles prepared by biological methods are better to those prepared by chemical and physical methods in several ways. Though chemical and physical methods produce larger quantities of nano particles with a well defined shape and size in a short time, yet they are costly, complicated and produce toxic base materials which are dangerous for environment and human wellbeing. With the help of biological methods, there is no need of using expensive chemicals. These methods are also supported in a way that the micro organisms used in the process inhabit ambient conditions of varying temperature, pressure and pH. The nanoparticles produced by this process has greater surface area and high catalytic reactivity.

Biosynthesis of nano particles take place when the micro organism capture ion from there surrounding environment and turn these metal ions into the required metal through enzyme which is generated by the cell activities. This process can be characterized into extra cellular and intra cellular synthesis regarding the location of the particles, that is, where they are formed the intra cellular process takes place and ions transport into the microbial cell to form nanoparticles (Vélez *et al.*, 2018).

Table 1: Chemical methods to synthesize Ag Nps.

Reducing agent	Capping agent	Size of nano particle (Shanmugasundaram and Balagurunathan)	Characterization techniques	Shape of nano particle	Colour of solution	References
Chemical reduction method						
Hydrazine hydrate	Sodium citrate, Sodium dodecyle sulphate(SDS)	9-30	UV-Visible, TEM, EDX,XRD	Spherical	Pale yellow to pale red	(Guzmán *et al.*, 2008)
Hydrazin, formalyne, ascorbic acid	SDS	Below 20 at 20-25^{o}C temperature	UV-Visible, SEM, DLS			(Szczepanowicz *et al.*, 2010)
Sodium citrate	Sodium citrate	30 at high tem.	FESEM,UV-Visible,DLS	Spherical		(Zhou and Wang, 2012)
Tri-sodium citrate	Sodium borohydride ($NaBH_4$)	25 At high tem.	UV-Visible, HRTEM, AFM	Spherical	Greenish brown	(Bonsak *et al.*, 2011)
Sodium borohydrade, trisodium citrate	$NaBH_4$	-	UV-Visible, SEM	Triangular		(Rashid *et al.*, 2013)
AgNO3, sodium citrate		3 and 100 nm	UV-vis spectrometry, dynamic light scattering (DLS	spherical and cylinder		(Gakiya-Teruya *et al.*, 2019)
Nano composite silver nitrate with Dithiocarbamate Ligand	sodium citrate ,hydrogen peroxide and sodium borohydride		UV-vis, DTC showed a plasmonic absorption band	nanocomposite (NC) of spherical Ag NPs and PA polymer NPs	bright yellow and blue colors	(Reynoso-García *et al.*, 2018)
of 1-vinyl-1,2,4-triazole and N-vinylpyrrolidone	radical-initiated polymerization	2 to 6 nm	TEM,SEM,FTIR,UV			(Reynoso-García *et al.*, 2018)
Trisodiumcitrate,AgNO3		68 nm	SEM ,TEM,EDX,XPS			(Ahari *et al.*)
Micro emulsion						
Hydrazine hydrate	2-ethyle hexyl, Sulfosuccinate	2-5 at room temprature	UV-Visible, TEM	Spherical		(Zhang *et al.*, 2007)
Photo chemical process(X-Ray radiolysis)						
X-Ray		28 at 1atm. pressure		Spherical		(Remita *et al.*, 2007)
UV light		4- 10 in 20 min at 1 atm. Pressure	UV-Visible, TEM	Spherical		(Bakar *et al.*, 2007)
Xe–Hg lamp		0.75 -1.12 in 60 sec.	UV-Visible,	Spherical		(Zaarour *et al.*, 2014)

Sol gel method						
Material	**Reducing agent**	**Stabilizer**	**Size of nano particle(Shanmugasundaram and Balagurunathan)**	**Characterization techniques**	**Shape of nano particle**	**References**
Silica powder at 300°C	Ethanol, distilled water, Nitric acid	Nitric acid (HNO_3)	20-40	XRD, TEM, FTIR	Spherical	(Duhan *et al.*, 2010)
Silica powder at 700°C	Tetra butyl ($C_{16}H_{36}O_4T_2$ TNBT), metallic tin powder		16 ± 0.6	UV-Visible, SEM, XRD, TEM	Spherical	(Farasat *et al.*, 2011)
Silica powder at 600°C	Water alcohol		12-20	SEM, XRD, TEM	Spherical	(Serezhkina *et al.*, 2003)
Nanocomposite titanium isopropoxide and silver nitrate 400°C	isopropyl alcohol,	acetic acid		(XRD), (EDS), TEM UV-Vis		(Mohallem *et al.*, 2018)

Table 2: Variation in color and pH value by changing PVP-Ag.

PVP-Ag	pH	Color	Reference
250 ppm	5.6	Green	
500 ppm	5.8	Light brown	(Zielińska *et al.*, 2009)
1000 ppm	5.7	Brown	

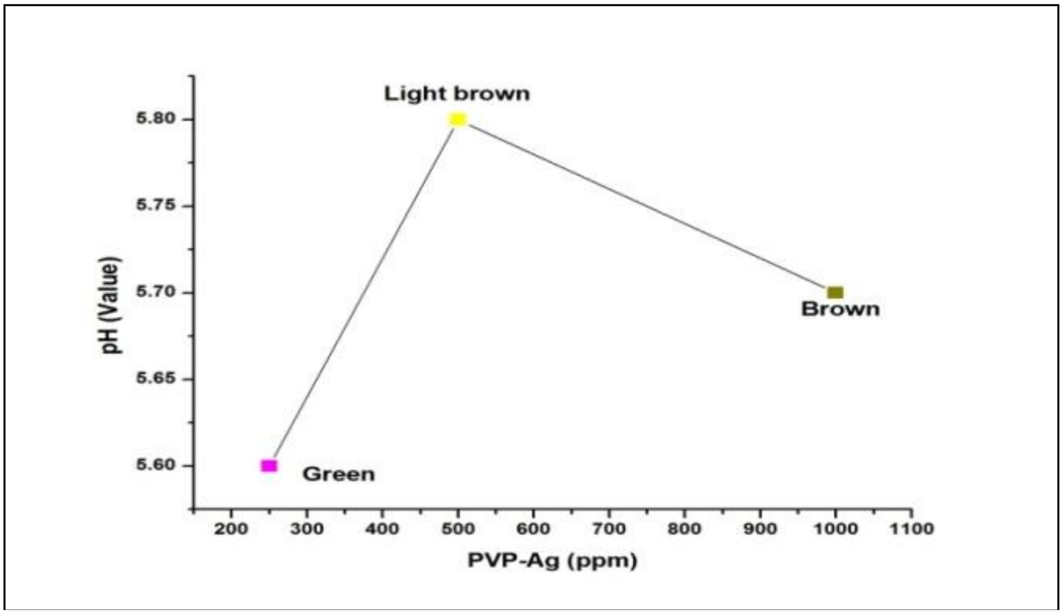

Figure 1: PVP-Ag Vs PH value at 250, 500 and 1000 ppm

Table 3: Variation in color and particle size by changing pH value.

PVP-Ag	Size	PH	Color	Reference
250 ppm	36 nm	5.3	Green	(Zielińska *et al.*, 2009)
250ppm	44 nm	5.6	Green	
250 ppm	140 nm	9.1	yellow	

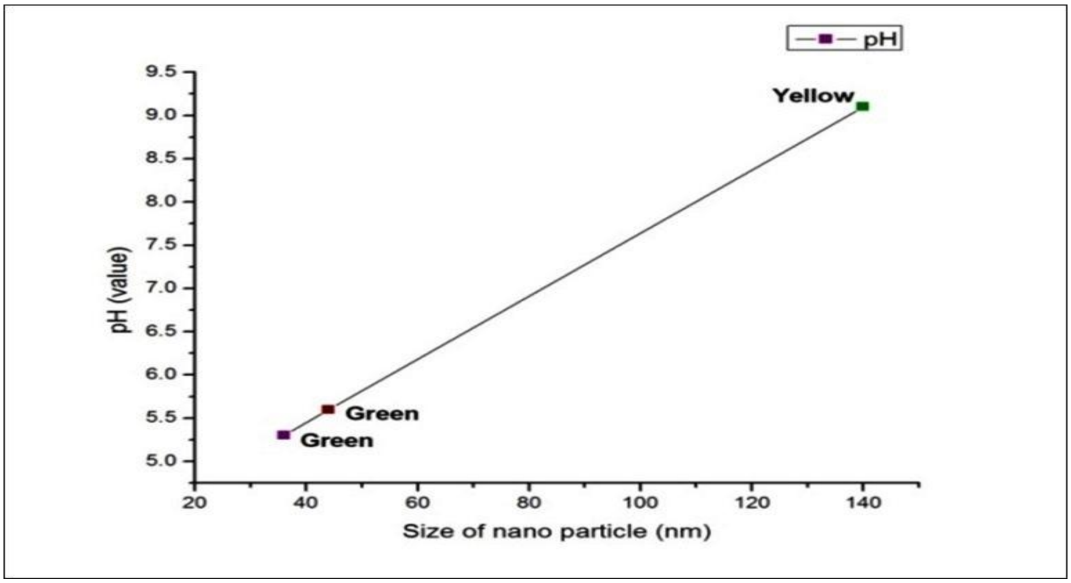

Figure 2: pH value vs particle size at 250 ppm.

Table4: Physical method to synthesize Ag Nps

Laser ablation (Nd:YAG Laser)

Wavelength (Shanmugasundaram and Balagurunathan)	Stabilizer	Size of nano particle (Shanmugasundaram and Balagurunathan)	Characterization techniques	Shape of nano particle	Reference
Second harmonic 532	Polyvinyl alcohol	5-45	UV-Visible, TEM	Spherical	(Hue, 2008)
1064	Sodium chloride	5-50	UV-Visible, TEM	Ellipsoidal	(Bae *et al.*, 2002)
1064	De-ionized water	34 at 50^{o}C	SEM, XRD	Spherical	(Tyurnina *et al.*, 2013)
Second harmonic 532	Chitosan, EG ethylene glycol and distilled water at 60∘C DW	10.5 for chitosan, 22.08 EG and DW (27.41 nm)	UV-Visible, TEM	Spherical	(Tajdidzadeh *et al.*, 2014)
1064 &Second harmonic 532	water, methanol, and isopropanol	12-33	UV-Visible, TEM	Irregular	(Jeon and Yeh, 1998)
1064 with 10ns pulse duration	Nitric acid	2-5nm	UV-Visible, TEM	Spherical with pale yellow color of solution	(Pyatenko *et al.*, 2004)

Precursor	Capping agent	Reducing agent	Size of nano particle (Shanmugasundaram and Balagurunathan)	Characterization techniques	Shape of nano particle	References
Sputtering process						
DC Magnetron	Ultra high purity argon 99.9%	7.5 cm	5×10^{-6} m bar at 50 mA	TEM	3.8-5.9 spherical	(Asanithi *et al.*, 2012)
Alpha CD	Carboxylic acid		.06 Mm bar for 20 s	XRD, IH-NMR	2-10	(Zhu *et al.*, 2013)

Table: 5 the particle size of silver nanoparticles and their corresponding volume fraction

Samples	Volume fraction	Particle size (Shanmugasundaram and Balagurunathan)	Standard deviation for particle size (Shanmugasundaram and Balagurunathan)	References
15 min	1.0×10^{-8}	6.33	1.93	(Zamiri *et al.*, 2011)
30 min	1.6×10^{-8}	5.18	1.65	
45 min	2.4×10^{-8}	4.84	1.09	

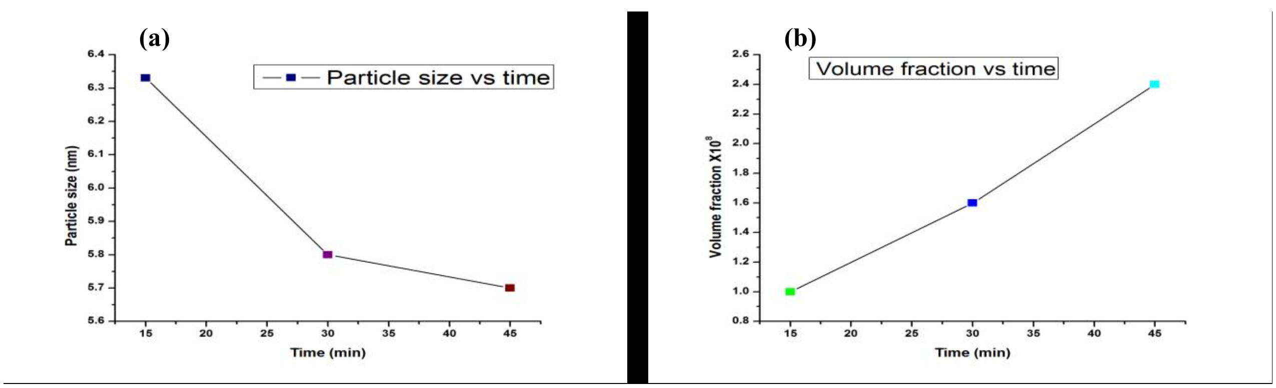

Figure 3: (a) particle size variation with time and (b) volume fraction variation with time

Chitosan-Based (Katas *et al.*, 2018, Rehan *et al.*, 2018) nanocomposites of silver are synthesized by bio based method and have many potential applications in bio medicine(Marques-Hueso *et al.*, 2018). Biogenic synthesis of platinum based (Pt/Ag, Pt/Au and Pt/Ag/Au) nanocomposites is formed by using biomass of *Streptomyces* (Shanmugasundaram and Balagurunathan, 2018).

Use of bacteria: For the first time in history silver particles were synthesized by using bacteria in 2000(Bhattacharya and Gupta, 2005). It was reported that stable silver NPs of size 40 nm could be produced by bio reduction of colloidal silver ions with a culture supernatant of nonpathogenic bacterium, *bacilluslicheniformis* (Joerger *et al.*, 2000; Kalimuthu *et al.*, 2008).

Fungi: In the list of microorganisms to synthesize nano particle, fungi is recent addition. Its use is encouraged as it secretes enzymes and is used in laboratory very easily. In 2001, by using *fungus* and *vetrrticillium* were used to synthesize Ag Nps. When fungus biomass was exposed to colloidal Ag^+ ions, it resulted in the reduction of metal ions to produce silver nano particles of size25 ± 12 nm (Mukherjee *et al.*, 2001).

Use of yeast: A few reports exist, in which silver nano particles are produced by yeast. Using yeast strain MKY_3 silver nano particles were synthesized with size range of 2-5 nm extracellularly (Kowshik *et al.*, 2002).

Use of plants: In biosynthesis plant or some important parts like stem and leaves are used to synthesize nano particles. Living plant(Ahmed *et al.*, 2016)like aloe vera (Logaranjan *et al.*, 2016; Tippayawat *et al.*, 2016)and Andean black berry fruit extract are not only used to produce Ag Nps, but also reduce toxic effect of silver(Kumar *et al.*, 2017).

In Situ Polymerization Method*:* This method was used to fabricate the nanocomposite coatings with organic matrices, which were conducting polymer (Asmussen and Vallo, 2016; Taormina *et al.*, 2018).

Nano polymer composite.

copolymer of 1-vinyl-1,2,4-triazole	*N*-vinylpyrrolidone as a stabilizer	metal nanoparticles	1 to 12 nm	Spheric form	powder X-ray diffraction, transmission electron microscopy	(Pozdnyakov *et al.*, 2017)
1-Vinyl-1,2,4-triazole and Acrylonitrile	ethyl alcohol	metal precursor.	17-125 nm		SEM, FTIR, X-ray diffractio	(Pozdnyakov *et al.*, 2019)

Table 6: Biological methods to synthesize Ag Nps.

Material	Temperature (°C)	Size of nano particle	Shape of particle/ color of solution	Location	Time (hour)	Characterization Technique	Reference
Bacteria							
Bacillus cereus	30-40	42-92	Pale yellow to brown	Extra/inter cellular	24	UV-Visible	(Das *et al.*, 2014)
Bacillus cereus		20-40	Spherical	Extra cellular	24	UV-Visible	(Sunkar and Nachiyar, 2012)
Fungi							
Fusariumoxysporum		20-50	Spherical	Extracellular	28	FTIR	(Durán *et al.*, 2005)
Verticillium		25 ± 12		intracellular		Electron microscopy analysis	(Mukherjee *et al.*, 2001)
Yeast							
yeast strain MKY3	30	2-5	Spherical	Extracellular	9-10	photoelectron spectroscopy, TEM ,XRD	(Kowshik *et al.*, 2002)
Plant							
Azadirachtaindica		34	brown color of soln.		15 min	UV-Visible, FTIR, DLS	(Ahmed *et al.*, 2016)
Solanumtricobatu,Syzygiumcumini, Centellaasiatica	35	41-53	Irregular shape, Orange color of soln.		48	UV-Visible, FTIR,XRD, AFM	(Logeswari *et al.*, 2015)

Applications: Silver nano particles show great area of interest owing to their exceptional properties, to be utilized into numerous antimicrobial applications, cosmetics industry, biosensors, electronic components, composite materials and many more(Caro *et al.*, 2010). Furthermore, they are also extensively used in fields like, drug delivery, medical imaging, (Joerger *et al.*, 2000) and low cost paper batteries (Hu *et al.*, 2009). Some of the properties and applications of Ag Nps are discussed below.

Optical Properties and Applications: When light falls on the metal surface of Ag Nps, a strong interaction occurs, which results in the oscillations of conduction electrons on the surface at specific wavelengths also known as Surface Plasmon Resonance (SPR). Due to this property, Ag NPs are very efficient in absorbing and scattering of light and exhibit a color that depends on the shape and size of these particles. Using SPR effect, Ag NPs gain very high sensitivity and measurements can be conducted in real time. With the help of Localized Surface Plasmon Resonance (LSPR), it is possible to monitor the quantity of chemical species and dynamical processes that occur inside a cell. The LSPR biosensors also provide a path to sensitive bio detection experiments with simple, light, small and low cost instrumentation (El-Nour *et al.*, 2010).

Biological Properties and Applications: Silver Nps are extensively used everywhere in industry including in food containers, detergents, cosmetics and in various other products to stop the increase of germs. It is because silver provides large surface area for contact with bacteria, to get attached with cell membrane and penetrate inside the bacteria at nanometer scale (Liau *et al.*, 1997; Rai *et al.*, 2009).

Once Ag Nps get inside cell of bacteria, release Ag+ which has lower pH and can create free radicals to increase antibacterial activity. As Ag Nps show evidence of immense toxicity to broad range of microorganisms, they along with their nano composites(Jaworski *et al.*, 2018; Song *et al.*, 2016) find numerous applications in the field of biology(Cheng *et al.*, 2016) such as, antibacterial agents and DNA sequencing.

Catalytic Properties and Applications: Use of metallic Nps and nanocomposites as catalysts (Mousavi *et al.*, 2016) is an emerging field and researches are going on to obtain basic insight to key features that control the activity, selectivity and life time of catalysts at nanoscale.

Metal Nps have a high surface area which increases catalytic activity because of occurring of more reactions at one time. Catalysts can be used in two different ways in catalytic process: either they can be the site of catalysis or they can act as a support for catalytic processes. Silver Nps/nano composite(Alshehri *et al.*, 2016; Mitsudome *et al.*, 2012) are used as catalysts in various chemical processes like, methanol oxidation to deformaldehyde and ethylene to ethylene oxide.

Medical Applications: Silver Nps find broad range of use in medicine and are incorporated for burn treatment coating stainless steel materials, medical devices, coating dental materials, and for personal health care. AgNps are constantly being used to improve today's therapies. It can also be used in purification of water, wound caring and drug delivery due to their antimicrobial behavior (Pal *et al.*, 2011).

On the other hand, these particles are also used in antibacterial cream, dressings, endotracheal tubes for the increment of efficiency. Silver compounds like silver proteinate and silver nitrate are being used to dilute solution of eye drops (Natsuki *et al.*, 2015; Nguyen-Tri *et al.*, 2018)

DISCUSSIONS

Invention of nanotechnology has changed our life altogether. The main focus is to produce Nps which show their enormous applications in variety of fields and are cheap and environment friendly at the same time. Although, noble metals have widely been used for a variety of purposes, silver Nps are under great attention in the way that they are antiviral, anti-inflammatory and anti-angiogenic and continuously been used in biomedical applications, such as, diagnosis of cancer and drug delivery, etc. That is why; they are produced using various physical, chemical and biological methods. Some of the methods and brief applications of these Nps have been discussed in this review article.

Conclusions: In this review, the synthesis routes of silver Nps, including chemical, physical and biological synthesis are discussed in detail along with tables. Then the unique properties and applications of silver Nps in different fields are discussed briefly. The main advantage of biological synthesis over other methods is that it avoids toxic reagents. Thus, Nps produced in this way are more stable than those produced chemically. However, the drawback is that the process of purification may result in pathogenic and potential bacteria which can cause contamination. That is why biological synthesis also needs caution while using in medical applications. Researchers are being done to synthesize Ag Nps using different reducing and capping agents such as protein, carbohydrates, bacteria, fungi and yeast as they are ecofriendly. The extensive utilization of Ag Nps in biological field is of great interest nowadays and is growing rapidly. Ag Nps provide large surface area for contact with these microorganisms, hence, increasing the anti-bactericidal activities. Due to this compatibility they are widely used in biomedical industry including drug delivery, diagnosis, sunscreen lotions and human health care.

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