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NANOSILVER - AN EFFECTIVE ANTIMICROBIAL AGENT FOR FINISHING OF TEXTILES

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ABSTRACT

This review presents an overview about antimicrobial activity of silver nanoparticles and then various synthesis approaches such as physical, chemical and biological methods. Silver has been in use since ancient time in the form of metallic silver, silver nitrate, silver sulfadiazine for the treatment of burns, wounds and several bacterial infections. Metallic silver in the form of silver nanoparticles has made a remarkable comeback as a potential antimicrobial agent. The use of silver nanoparticles is also important, as several pathogenic bacteria have developed resistance against various antibiotics. Hence, silver nanoparticles have emerged up with diverse medical applications.

KEYWORDS: *Antimicrobial Agent, Nanosilver, Nanotechnology, Textiles*

I. INTRODUCTION

The skin is a sensitive and protective organ. The skin surface represents a critical structure in the interaction of the human body with the environment. Other important protective functions of the skin are protection against infection and irradiation, in particular ultraviolet irradiation, thermoregulation and synthesis of hormones and other bioactive substances. The skin is associated with the protective system comprising of specific and non-specific defense mechanisms. The non-specific protective function of skin involved in antimicrobial resistance is of even greater importance, providing the base for resistance to microbial threat and may interact in several ways with the specific functions whenever necessary.

Among the different antimicrobial agents, silver has been most extensively studied and used since ancient times to fight infections and prevent spoilage. The antibacterial, antifungal and antiviral properties of silver ions, silver compounds and silver nanoparticles have been extensively studied. The microorganisms are unlikely to develop resistance against silver as compared to antibiotic as silver attacks a broad range of targets in the microbes.[1]

II. ANTIMICROBIAL FINISHING OF TEXTILES

2.1. Microorganisms

Microbes, bacteria, virus, fungi and yeast are present almost everywhere where as human beings have an immune system to protect against accumulation of microorganisms. Materials like textiles can easily be colonized by high number of microbes or even decomposed by them. Textiles are carriers of microorganisms such as pathogenic bacteria, odour generating bacteria, mould and fungi. These microorganisms can adhere to textile substrates. Additionally, the environmental conditions on textiles are favorable and thus support the bacterial growth. Indeed; microorganisms are invisible and extremely adaptable. If the environment is favorable, certain bacteria can grow in no time from single germ to millions. Given that sort of environment, these germs develop rapidly via cell division, dividing and multiplying at an alarming rate, following the simple progression. This happens three times an hour and a single bacteria can, theoretically, generate 4,800,000 per day. Human skin has

many surface bacteria present at any time; which is not a bad thing. Microorganisms can be found almost everywhere in the environment. NASA researchers have found microorganisms even at a height of 32 kms and to a depth of 11 kms in the sea. In the ground, microorganisms have been found during oil drilling to a depth of 400 m. It is estimated that the total mass of all microbes living on earth is approximately 25 times the mass of all animals. For microbes' growth and multiplication, the minimum nutritional requirements are water, a source of carbon, nitrogen, and some inorganic salts. These are normally present in the natural environment. All of which show why a measure of control is needed, particularly as our houses, working and leisure environments are becoming increasingly hermetic in terms of temperature and airflow.[3, 4, 5]

2.2 Necessity of Antimicrobials:

Microorganisms are nearly always present on human body even with clean skin, having typical population of between 100-1000 microbes/cm^2. At this level, number of microorganism such as bacteria, yeast and fungi cause possible infection to wearer. These microbial infections have several unpleasant consequences not only-foul odour but also stains are produced by discoloration of material. Thus, the growth of microorganisms on textiles inflicts a range of unwanted effects not only on the textile itself but also on the wearer.

Textiles, by virtue of their characteristics and proximity to the human body provide an excellent medium for the adherence, transfer, and propagation of infection causing microbial species to proliferate. [1, 2] Natural fibers are more susceptible to bacterial attack than synthetic fibers due to their porous and hydrophilic nature. The structure of natural fibers retains water and oxygen along with nutrients, thereby offering optimal enrichment culture for rapid multiplication of microorganisms. In addition to that, direct contact with human body supplies warmth, humidity and nutrients, thereby providing perfect environment and optimal conditions for bacterial growth. The most troublesome organisms are fungi and bacteria. Under very moist conditions algae can also grow on textiles. Fungi create multiple problems to textiles including discoloration, stains and fiber damage, unpleasant odour and a slick, slimy feel. Besides, structure of the substrate and the chemical processes may induce growth of microbes. Humid and warm environment further aggravates the problem. Although the synthetic fibers do not support the microbial growth but low molecular weight contaminated compounds that are used in finishing of textiles may provide sufficient nutrient for mildew growth of microorganism. This results into the generation of unpleasant odour, stains and discoloration in the fabric and reduction in fabric strength. For these reasons, it is highly desirable that the growth of microbes on textiles be minimised during their use and storage. Microorganisms, are small living forms of life, which we cannot see with the naked eye. Such as[3, 4]:

1. Bacteria rod/spiral/ball type
2. Fungi primitive plant
3. Algae single/multicellular plant
4. Dust mites.[5]

Bacteria, both pathogenic and odour-causing, interact with fibres in several phases including the initial adherence, subsequent growth and damage to the fibres. The attachment of bacteria to fabrics is dependent upon the type of bacteria and the physicochemical characteristics of the fabric substrate. Microbial adherence is also affected by the substrate and bacterial cell wall hydrophobicity, while the retention has been shown to depend on the duration of contact between the fabric and microbe.

Natural and synthetic fibers vary greatly in their response to microbial growth. Both may act as willing substrates but the mechanism in the both cases is very different. Natural fibers are easy targets for microbial attack because they retain water readily and microbial enzymes can readily hydrolyse their polymer linkages. Generally, most of the cellulosic and protein fibres are attacked by microbes. Cotton, wool, silk, jute, and flax are reported to be most susceptible to microbial attack.

Growth of microbes is slower on synthetic fibres as compared to their natural counterparts because their polymer backbone does not retain much water. However, these fibres encourage the holding of state perspiration in the interstices, wherein the microbes multiply rapidly. Foot infection, for example, has been found to be more pronounced with synthetic fibre socks than with natural fibre socks. It has been found that, the adherence of bacteria to the fabric increases as the content of polyester in the fabrics increases. Synthetic fibres also become susceptible to microbial degradation if

there are finishing agents such as polyethylene and polysiloxane emulsions on these fibres. These additives allow the microorganisms to degrade the polymer into 'chewable bites' by utilising the acidic or basic by-products of their metabolism, thus initiating the cycle of hydrolysis. In this way, even the tough polyurethanes can be broken down. Polypropylene, nylon, and polyester fibres have all been seen to be subject to microbial attack under conductive conditions.

A matter of greater concern, however, is that the textiles not only act as substrates for microbial growth, but may also act as active agents in the propagation of microbes. Viruses can persist on fabrics like cotton shirting, terry towel; washable wool suit, polyester/ cotton shirting, and nylon jersey for up to 16 hrs. Synthetic fibres allow a greater degree of viral persistence and transfer than cotton. When subjected to laundering, the virus gets physically removed from the fabric but is not inactivated, as it was found to be present in extracted water. Detergents that reduce the surface tension assist this physical removal. Thus, virus transfer can occur easily during normal cold laundering processes. Also, some bacteria actually continue to survive on laundered fabric as well. Textile products can meet all such requirements for bacterial growth, resulting in a range of undesirable side effects. The presence and growth of these microorganisms can cause health problems, odour, and finally fabric deterioration. As microbes often attack the additives applied to textiles, discolouration and loss of the textile's functional properties such as elasticity (brittleness) or tensile strength can also occur. Among the side effects, the formation of malodour is of particular importance. When microorganisms grow, they metabolise nutrients such as sweat and soiling present in it and produce odour-causing molecules; for example the metabolism of Gram-positive bacteria *S. aureus* is believed to generate 3-methyl-2, hexanoic acid, which causes the characteristic body odour[6].

The unpleasant odour develops when, among other things, bacteria convert human perspiration into smelling substances such as carboxylic acid, aldehydes and amines. The Gram-negative bacteria *P. Vulgaris* is known to be able to metabolise urea to form ammonia and is the cause of generation of odour in baby diapers. Several products can be used to tackle the odour problem in textiles. The first two approaches involve either trapping the odour-causing molecules by incorporating adsorbent materials into textiles or using perfumes to mask the malodour. Such measures, however, only tackle the odour problem that is already there. Another approach is to use antimicrobials to prevent the formation of odour-causing compounds by inhibiting the growth of bacteria. In many personal care products around the world, such as underarm deodorants, antimicrobial agents such as Triclosan have already been widely used with satisfactory results. It is observed that, occurrence of various bacteria on human skin and their persistence after one year in the same person. They found that normal skin supports resident microorganisms, and different microorganisms are predominant on different parts of the body and on people of different age groups. Bacteria isolated from clothing were similar to those isolated from normal skin flora.[6]

2.3 Origin of Antimicrobial Textiles:

During World War II, when cotton fabrics were used extensively for tent, tarpaulins and truck covers, these fabrics needed to be protected from rotting caused by microbial attack. This was particularly a problem in the South Pacific campaigns, where much of the fighting took place under tropical forest like conditions during the early 1940's, Cotton duck, webbing and other military fabrics were treated with mixtures of chlorinated waxes, copper and antimony salts that stiffened the fabrics and gave them a peculiar odour. After World War II, fungicides used on cotton fabrics were compounds such as 8-hydroxygiunoline salts, copper ammonium fluoride and chlorinated phenols. As the government and industrial firms became more aware of the environmental and workplace hazards these compounds caused, alternative products were sought. [5]

2.4 Functions of Antimicrobial Textiles:

1. To avoid cross infection by pathogenic microorganism.
2. To control the infestation by microbes.
3. To arrest metabolism in microbes in order to reduce the odour formation.
4. To safeguard the textile products from staining, discoloration and quality deterioration.[5]

2.5 Classification of Antimicrobial Finishes:

Antimicrobial textiles inhibit the growth of microorganism. It is convenient to sub divide this general type of finish into three main groups:

1. Rot proofing is an antimicrobial finish applied to give material protection either long term or short term against physical deterioration.
2. Hygiene finishes are concerned with the control of infection and unwanted bacteria, a specialized development is the prevention of dust mites.
3. Aesthetic finishes are used to control odour development and staining.[5]

2.6 Types of Antimicrobials:

Antimicrobials are of two types:

2.6. 1. Leaching Type:

- Diffuses from the garment to come in contact with microbe.
- Products migrate off the garments, forming a sphere of activity and any microbes coming into the sphere are destroyed. But in the course of time their strength decreases and thus, it just 'hurts' the microbes, giving them a chance to form a strain by mutation.
- The microbes consume the antimicrobials as it acts on them. The product is eventually used up by the bacteria and slowly loses its effectiveness.

2.6. 2. Non Leaching Type:

- Bound to the product, allowing control of the microorganisms.
- Products do not migrate off the garments and destroy the bacteria coming in contact with the surface of the garment.
- The microbes do not consume the antimicrobials; they destroy them by acting on the cell membrane.
- These products do not lose their effectiveness; the finishing effect will the permanent and remains functional through the life of the fabric. The finish can withstand more than 40 laundry washes.[5]

2.7 Examples of Antimicrobial Agents:

2.7.1. Natural Antimicrobial Agents:

Natural finishes are those in which various materials from plant or animal kingdom are used. In recent years, great attention has been devoted to biopolymers because of their biocompatibility and biological functions and consequently, they are used in textile, biomedical and pharmaceutical fields. Some marine animals such as prawns and fishes possess some compounds which exhibit antimicrobial activity. Chitosan is an effective natural antimicrobial agent derived from Chitin. Natural herbal products such as Neem, Tulsi, Pomegranate, Aloe Vera, Prickly Chaff Flower, Turmeric, Clove, etc. also exhibit antimicrobial activity. Studies reveal that some specific species of herbs having antimicrobial activity are suitable for textile application.

2.7.2. Synthetic Antimicrobial Agents:

The antimicrobial Dyes, Quaternary Ammonium Compounds, Polyhexamethylene Biguanides (PHMB), Triclosan (2, 4, 4'-trichloro-2'- hydroxydiphenyl ether), Regenerable N-halamine and peroxyacids and Metals and Metal salts such as Silver, Zinc, Copper. Their bactericidal activity goes on decreasing as they attach to the substrate. Furthermore, the biocide is gradually lost during the use and can be washed off the textile. For this purpose large amounts of these biocides are need to be applied to textiles for effectively control of bacterial growth and to sustain durability. [3, 4, 5]

III. SILVER AS AN ANTIMICROBIAL AGENT

3.1. The History of Silver as an Antimicrobial Agent:

The use of elemental silver as an antimicrobial agent is nearly as old as the history of mankind. The ancient Egyptians mention the medicinal use of silver in their writings. Romans stored wine in silver urns to prevent spoilage. The courts of the Chinese emperors ate with silver chopsticks for better health. Druids used silver to preserve food. American settlers put silver dollars in milk to stop spoilage. Silver leaf was used during World War I to combat infection in wounds.

3.2. Silver in Health Care:

Silver has a long and intriguing history as an antibiotic in human health care. It has been developed for use in water purification, wound care, bone prostheses, reconstructive orthopedic surgery, cardiac devices, catheters and surgical appliances. Advancing biotechnology has enabled incorporation of ionizable silver into fabrics for clinical use to reduce the risk of infections and for personal hygiene [2].

3.3. Biological Properties of Silver:

Silver is not a recognized trace metal but occurs in the human body at low concentrations (< 2.3 µg/l) due to ingestion with food or drinking water, inhalation and occupational exposures.[7, 14] Clearly, occupational exposure or medicinal use of silver as an antibiotic in wound dressings, indwelling catheters, cardiac devices and in orthopedic surgery will be associated with higher than normal blood levels and may be a safety concern [6].

3.4. Sustained Silver Release Wound Dressings:

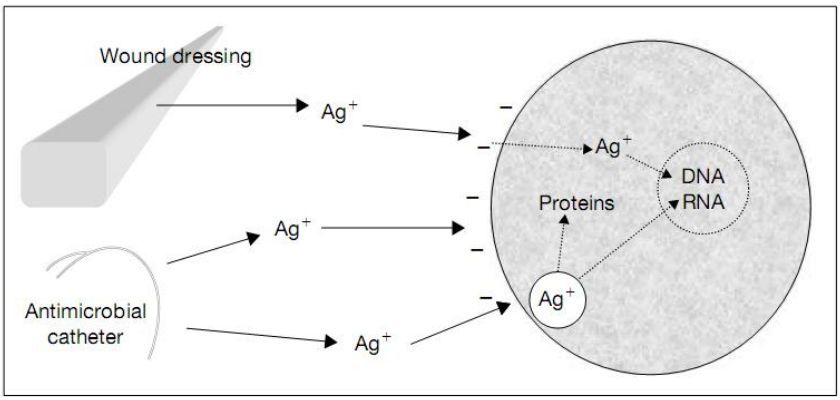
Silver ion release will be sustained for the expected life-span of the dressing (up to 7 days). Three main forms of dressing are currently available:
(1) Those releasing high levels of silver for rapid antimicrobial action.
(2) Dressings that absorb wound exudates and where silver ions released provide sustained antimicrobial action.
(3) Dressings that release silver sulphadiazine. [6]

3.5. Silver in Devices for Orthopedic Surgery:

Infection is a recurrent problem in association with external fixation pins and screws, prostheses, cements used in orthopedic surgery and dental cavity fillings [6].

3.6. Antibiotic Action of Silver:

Silver is inert and exhibits no biocidal action. However, it ionizes in the presence of water or tissue fluids to release silver or other biologically active ions. This ‘activated’ ion shows a strong affinity for sulphydryl groups and protein residues on cell membranes.



3.7. Antimicrobial Action of Silver:

(1) Attachment to the bacterial cell membrane;

(2) Absorption/diffusion into the cell;
(3) Coagulation with bacterial proteins/enzymes[6].
The mechanism of action of silver is linked with its interaction with thiol group compounds found in the respiratory enzymes of bacterial cells. Silver binds to the bacterial cell wall and cell membrane and inhibits the respiration process. In case of *E-coli*, silver acts by inhibiting the uptake of phosphate and releasing phosphate, succinate, proline and glutamine from *E. coli* cells.

3.8. Mechanism of Action of Silver Nanoparticles:

The silver nanoparticles shows efficient antimicrobial property compared to other salts due to their extremely large surface area, which provides better contact with microorganisms. The nanoparticles get attached to the cell membrane and also penetrate inside the bacteria. The bacterial membrane contains sulfur-containing proteins and the silver nanoparticles interact with these proteins in the cell as well as with the phosphorus containing compounds like DNA. When silver nanoparticles enter the bacterial cell it forms a low molecular weight region in the center of the bacteria to which the bacteria conglomerates thus, protecting the DNA from the silver ions. The nanoparticles preferably attack the respiratory chain, cell division finally leading to cell death. The nanoparticles release silver ions in the bacterial cells, which enhance their bactericidal activity.

3.9. Effect of Size and Shape on the Antimicrobial Activity of Nanoparticles:

The size of the nanoparticle implies that it has a large surface area to come in contact with the bacterial cells and hence, it will have a higher percentage of interaction than bigger particles. The nanoparticles smaller than 10 nm interact with bacteria and produce electronic effects, which enhance the reactivity of nanoparticles. Thus, it is confirmed that the bactericidal effect of silver nanoparticles is size dependent. The surface plasmon resonance plays a major role in the determination of optical absorption spectra of metal nanoparticles, which shifts to a longer wavelength with increase in particle size.
The application of nanoscale materials and structures, usually ranging from 1 to 100 nanometers (nm), is an emerging area of nanoscience and nanotechnology. Nanomaterials may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatment.[7,8] This increasing demand must be accompanied by green synthesis methods. In the global efforts to reduce generated hazardous waste, green chemistry and chemical processes are progressively integrating with modern developments in science and industry. Implementation of these sustainable processes should adopt the 12 fundamental principles of green chemistry[9-12]. These principles are geared to guide in minimizing the use of unsafe products and maximizing the efficiency of chemical processes. Hence, any synthetic route or chemical process should address these principles by using environmental friendly solvents and nontoxic chemicals[9].
In recent years, nanotechnology research is emerging as cutting edge technology interdisciplinary with physics, chemistry, biology, material science and medicine. The prex nano is derived from Greek word nanos meaning “dwarf” in Greek that refers to things of one billionth in size.
Nanoparticles are usually 0.1 to 1000 nm in each spatial dimension and are commonly synthesized using two strategies: top-down approach and bottom-up approach. [14] In top-down approach, the bulk materials are gradually broken down to nanosized materials whereas in bottom-up approach, atoms or molecules are assembled to molecular structures in nanometer range. Bottom-up approach is commonly used for chemical and biological synthesis of nanoparticles.
Unlike bulk materials, nanoparticles have characteristic physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties [15,16]. Decreasing the dimension of nanoparticles has pronounced effect on the physical properties that significantly differ from the bulk material. Nanomaterials often show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts [17]. Synthesis of noble metal nanoparticles for applications such as catalysis, electronics, optics, environmental, and biotechnology is an area of constant interest [18-24]. Gold, silver, and copper have been used mostly for the synthesis of stable dispersions of nanoparticles. Generally, metal nanoparticles can be prepared and stabilized by physical and chemical methods; the chemical approach, such as chemical

reduction, electrochemical techniques, and photochemical reduction is most widely used [25,26]. Studies have shown that the size, morphology, stability and properties (chemical and physical) of the metal nanoparticles are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents, and adsorption processes of stabilizing agent with metal nanoparticles [27,28]. Hence, the design of a synthesis method in which the size, morphology, stability and properties are controlled has become a major field of interest [26].

IV. NANOSILVER SYNTHESIS METHODS

4. 1. Polysaccharide Method:

The green synthesis of silver Nanoparticles involves three main steps, which must be evaluated based on green chemistry perspectives, including (1) selection of solvent medium, (2) selection of environmentally benign reducing agent, and (3) selection of nontoxic substances for the Silver Nanoparticles stability[13]. Based on this approach, has been reviewed the green-chemistry type Silver nanoparticle synthesis processes.

In this method, Silver Nanoparticles are prepared using water as an environmental friendly solvent and polysaccharides as a capping agent, or in some cases polysaccharides serve as both a reducing and a capping agent. For instance, synthesis of starch-Silver Nanoparticles was carried out with starch as a capping agent and β-D-glucose as a reducing agent in a gently heated system[13]. The starch in the solution mixture avoids use of relatively toxic organic solvents[50]. Additionally, the binding interactions between starch and Silver Nanoparticles are weak and can be reversible at higher temperatures, allowing separation of the synthesized particles.

4.2. Tollen's Method:

The Tollen's synthesis method gives Silver Nanoparticles with a controlled size in a one-step process[51-54]. The basic Tollen's reaction involves following reaction

$$Ag(NH_3)_2^+(aq) + RCHO(aq) \rightarrow Ag(s) + RCOOH(aq)$$

In the modified Tollen's procedure, Ag^+ ions are reduced by saccharides in the presence of ammonia, yielding Silver nanoparticle with particle sizes from 50–200 nm, silver hydrosols with particles in the order of 20–50 nm, and Silver Nanoparticles of different shapes.[52,53] $Ag\ (NH_3)^+_2$ is a stable complex ion resulting from ammonia's strong affinity for Ag^+, therefore the ammonia concentration and nature of the reductant must play a major role in controlling the Silver nanoparticle size.[53]

4.3. Irradiation Method:

Silver Nanoparticles can be successfully synthesized by using a variety of irradiation methods. For example, laser irradiation of an aqueous solution of Silver salt and surfactant can fabricate Silver Nanoparticles with a well defined shape and size distribution[55]. No reducing agent is required in this method. Additionally, laser was applied in a photo-sensitization technique for the synthesis of Silver Nanoparticles using benzophenone[56]. Here, low laser powers at short irradiation times gave Silver Nanoparticles of ~20 nm, while an increased irradiation power gave nanoparticles of ~5 nm. The formation of Silver Nanoparticles by this photo-sensitization technique was also achieved using a mercury lamp[56]. In the visible light irradiation studies, photo-sensitized growth of Silver Nanoparticles using thiophene as a sensitizing dye[57] and silver nanoparticles production by illumination of $Ag(NH_3)^+$ in ethanol has been carried out[58]. Synthesis procedures using microwave irradiation has also been employed. Microwave radiation of a sodium salt of carboxy methyl cellulose and silver nitrates solution produced uniform Silver Nanoparticles that were stable for two months at room temperature[59].

4.4. Polyoxometalates Method:

Polyoxometalates, POMs, have the potential of synthesizing Silver Nanoparticles because they are soluble in water and have the capability of undergoing stepwise, multielectron redox reactions without disturbing their structure. Silver Nanoparticles of different shape and size can be obtained using different POMs in which the POMs serve as a reductant and a stabilizer. [60-62]

4.5. Silver Nanoparticles and their Incorporation into Other Materials:

The unique properties of Silver Nanoparticles have been extended into a broader range of applications. Incorporation of Silver nanoparticles with other materials is an attractive method of increasing compatibility for specific applications.

4.5.1. Silver-Doped Hydroxyapatite:

There is interest in inorganic-inorganic hybrid nanocomposites materials because of their industrial and medical applications[63-66]. Recently, one-step synthesis of anisotropic Silver nanocrystals are achieved by reducing aqueous $Silver^{+}$ ion by the electron transfer from the surface of hydroxyapatite (HA) [67]. The hydroxyl group in this process acted both as a reducing and a binding agent to give highly oriented flat rod and needle-like Silver Nanoparticles[67]. A microwave process was also applied to synthesize nanosize Silver-substituted hydroxyapatite with a length of 60–70 nm and width of 15-20 nm[68].

4.5.2. Polymer-Silver Nanoparticles:

Nanocomposites material consisting of metallic Nanoparticles incorporated in or with polymers have attracted much attention because of their distinct optical, electrical and catalytic properties, which have potential applications in the fields of catalysis, bioengineering, photonics, and electronics.[44, 69-72] Polymers are considered a good host material for metal nanoparticles as well as other stabilizing agents such as citrates, organic solvents (THF or THF/ MeOH), long chain alcohols, surfactants, and organo-metallics[18, 25, 73]. The organic solvents are though not as environmental friendly.
Different chemical and physical methods exist to prepare metal polymer composites [40, 71, 74-82]. A successful preparation of nanoparticles is determined by the ability to produce particles with uniform distributions and long stability, given their tendency to rapidly agglomerate in aqueous solution[72,74]. The main fabrication approach is to disperse previously prepared particles in the polymer matrix[81, 82]. This method is often referred to as the evaporation method since the polymer solvent is evaporated from the reaction mixture after NP dispersion. However, this often leads to inhomogeneous distribution of the particles in the polymer. One solution is the in situ synthesis of metal particles in the polymer matrix, which involves the dissolution and reduction of metal salts or complexes into the matrix[78, 83]. Or, another approach is a system in which simultaneous polymerization and metal reduction occur. For example, the in situ reduction of Ag^{+} ions in poly(N-vinyl-2- pyrrolidone) (PVP) by microwave irradiation produced particles with narrow size distribution [84] and Silver Nanoparticles incorporated in acacia, a natural polymer, had been made under mild condition[85]. Or, a conventional heating method to polymerize acrylonitrile simultaneously reduces Ag^{+} ions resulting in homogeneous dispersal and narrow size distributions of the Silver Nanoparticles in the silver-polyacrylonitrile (Ag-PAN) composite powders[78]. Further, size-controlled synthesis of Silver nanocomplex was recently achieved in the reduction of $AgNO_3$ by a UV-irradiated argine-tungstonsilicate acid solution[86]. Other various metal-polymer nanocomposites have been prepared by these reduction methods, such as poly(vinyl alcohol)-Silver, Silver-polyacrylamide, Silver-acrylonitrile (Silver-PAN), Silver-polyimide, Au-polyaniline, and Cu-poly(acrylic acid)[83,87].

4.5.3. Silver Nanoparticles on TiO_2:

Ag/TiO_2 surfaces have advantageous properties such as visible light photocatalysis, biological compatibility, and antimicrobial activity.[88,94] Aqueous reduction, photochemical, liquid phase deposition, and sol–gel methods can be applied to synthesize Silver Nanoparticles on TiO_2 surfaces.[95-100] Silver Nanoparticles with a narrow size distribution were synthesized by simple aqueous reduction from silver ions in different molar ratios of TiO_2 suspensions and a reducing agent, $NaBH_4$. [96] One of the photochemical reduction methods involves loading Silver Nanoparticles with ~3–5 nm diameters onto the surface of TiO_2 nanotubes first using the liquid deposition approach followed by UV irradiation.[97]

4.6. Chemical Reduction Method:

Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles as stable, colloidal dispersions in water or organic solvents[29,30]. Commonly used reducing agents are borohydride, citrate, and elemental hydrogen[31-39]. The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers[27]. Initially, the reduction of various complexes with Ag^+ ions leads to the formation of silver atoms, which is followed by agglomeration into oligomeric clusters[37]. These clusters eventually lead to the formation of colloidal silver particles[40]. When the colloidal particles are much smaller than the wavelength of visible light, the solutions have a yellow color with an intense band in the 380–400 nm range and other less intense or smaller bands at longer wavelength in the absorption spectrum[41-43]. This band is attributed to collective excitation of the electron gas in the particles, with a periodic change in electron density at the surface (surface plasmon absorption) [44-46].

Previous studies showed that use of a strong reductant such as borohydride, resulted in small particles that were somewhat monodisperse, but the generation of larger particles was difficult to control[47,48]. Use of a weaker reductant such as citrate, resulted in a slower reduction rate, but the size distribution was far from narrow[31, 32,49]. Controlled synthesis of silver nanoparticles is based on a two-step reduction process[48]. In this technique a strong reducing agent is used to produce small Silver particles, which are enlarged in a secondary step by further reduction with a weaker reducing agent[31].

Nanosilver in the form of powders as well as suspensions, due to the high surface to volume ratios, has been used in most of applications as it enables the loading of small quantities of silver and thus makes the product cost effective. Synthesis of silver nanoparticles has been of considerable interest during the past decades[101]. A variety of methods have been reported for synthesis of metallic nano particles. These include thermal decomposition, laser ablation, microwave irradiation, reverse micelles, salt reduction, radiolysis, and electrochemical synthesize[102]. However controlling the particle size and production of particles by an industrial scale is an important task of all methods.

Chemical reduction of metal salts using various reducing agents in the presence of stabilizer is currently of interest for preparation of metal nanoparticles[103,104]. Reducing agents such as sodium Borohydride ($NaBH_4$), hydrazine (N_2H_4), formaldehyde, etc. can be used to reduce a silver containing salt to produce nanosilver particles. In an aqueous reaction medium, when a strong reducing agent such as sodium Borohydride ($NaBH_4$) or hydrazine (N_2H_4) is used, the fast reaction produces very small primary particles, and when the precursor (i.e. $AgNO_3$) concentration is relatively high, it becomes difficult for the protective agent, e.g. PVP molecules, to fully adsorb onto the silver colloidal surface in time due to the diffusion limit[105].

The reduction of $AgNO_3$ using mild reducing agents such as glucose or dextrose produce nanosilver with uniform size distribution and are capable of overcoming the above problems. Uniform silver nanoparticles are obtained by reduction of silver nitrate at 50-70°C under atmospheric pressure. Polyvinyl pyrrolidone (PVP) was used as stabilizer.[105, 106]

4.7. Biological Method:

Extracts from bio-organisms may act both as reducing and capping agents in Silver Nanoparticles synthesis. The reduction of Ag^+ ions by combinations of biomolecules found in these extracts such as enzymes/proteins, amino acids, polysaccharides, and vitamins[107,108] is environment friendly, yet chemically complex. An extensive volume of literature reports successful Silver Nanoparticles synthesis using bioorganic compounds. For example, the extract of unicellular green algae *Chlorella vulgaris* was used to synthesize single-crystalline Silver nanoplates at room temperature[109]. Proteins in the extract provide dual function of Ag^+ reduction and shape-control in the nanosilver synthesis. The carboxyl groups in aspartic and/or glutamine residues and the hydroxyl groups in tyrosine residues of the proteins were suggested to be responsible for the Ag^+ ion reduction[109]. The reduction process was carried out by a simple bifunctional tripeptide Asp-Asp-Tyr-OMe further identified the involvement of these residues. This method of synthesis gave small Silver nanoplates with low polydispersity and good yield (>55%) [109]. Plant extracts from live Alfalfa, the broths of Lemongrass, Geranium Leaves and others have served as green reactants in Silver Nanoparticles synthesis[110-112]. The reaction of aqueous $AgNO_3$ with an aqueous extract of leaves of a common ornamental geranium plant, Pelargonium grave lens, gave Silver Nanoparticles after 24 hrs[111]. The reaction time was reduced to 2

hrs by heating the reaction mixture just below the boiling point[113]. Secreted proteins in spent mushroom substrate reduced $Silver^{+}$ to give uniformly distributed Silver-protein (core–shell) Nanoparticles with an average size of 30.5 nm[114]. A vegetable, Capsicum annum L., was used to synthesize Silver Nanoparticles[115].

Studying the synthesis of Silver Nanoparticles with isolated/purified bioorganics may give better insight into the system mechanism. Glutathione (γ-Glu-Cys-Gly-) as a reducing/capping agent can produce water-soluble and size tunable Silver Nanoparticles that easily bind to model protein (bovine serum albumin) — attractive for medical applications[116]. Tryptophan residues of synthetic oligopeptides at the C-terminus were identified as reducing agents giving Silver Nanoparticles[117].

Recently, it was found that aqueous silver ions may be reduced extracellularily using the fungus *F. Oxysporum* to generate silver nanoparticles in water.[118-120] The mechanistic aspects were very recently described and this process occurs probably by conjugation of reductase action and by electron shuttle quinones. Different strains of *F. Oxysporum* have been used by different scientists to produce nanosilver particles. [121]

V. APPLICATION METHODOLOGIES

5. 1. By using Spun in Additives:

It is common practice to give the antibacterial properties to the synthetic fibres by incorporating bio active agents into melt and spinning dope solution. Various antibacterial agents can be incorporated in the polymer matrix during the fibre /yarn manufacturing process so that fibers have the permanent antimicrobial properties. This is the extremely important for the textile manufacturers who want to avoid difficult subsequent operations to treat their products with antibacterial finishes.

5. 2. Padding:

In this the fabric can be padded with the antimicrobial agent with expression nearly 70-80%. Along with antimicrobial agents certain cross-linkers, binders etc. can be used. Padding should be followed by the air drying or curing in stenter.

5. 3. Spraying:

The spraying of solutions of antimicrobial active agents is not normally recommended, due to the risk of production and subsequent inhalation of droplets of irrespirable size. Nevertheless, the treatment can be applied by spraying, provided suitable containment facilities are available. This method is particularly suitable for nonwoven fabrics.

5. 4. Polymer Modification:

This can be achieved by means of the copolymerization using monomers with, bio active functional groups. Advantage of this approach is that the bio active elements form an integral part of the fiber, resulting in durable effects. Disadvantage is that the technology is expensive due to the need of special polymerization plants. e. g. Modification of the acrylic polymer by means of copolymerization using monomers with bio active gives following functional groups

- Cationic amines or quaternary ammonium salts
- Carboxylic group in the polymer able to react with antibiotics

5. 5. Microencapsulation:

The regulated release of the antimicrobials form within the fibers seems to be proven and viable technology for achieving good antimicrobial durability for synthetic fibers, However this technique is not useful for the cotton So, new system that can be described as "fixation and controlled release" With this system the antimicrobials could remain on cotton fabrics after extensive launderings because the capsules that contain the antimicrobials are covalently fixed on the fibers. Even then it is a need to make sure that the particular capsule system should regulate the release of antimicrobial .Without release, the treated cotton surface would not show good antimicrobial efficacy. When the release is too fast there is the problem of washing durability. Furthermore, the capsules need to be

robust enough to withstand the processes that are commonly involved in treating fabrics and should be small enough so as not to cause any changes in the hand and other properties of the treated fabrics. Indeed cotton fabrics treated with this system show excellent antimicrobial properties even after 100 launderings. [5]

VI. CONCLUSIONS

From this it can be concluded that though silver has been in use since very old times, nanosilver has been more effective antimicrobial agent against various microorganisms. Several biological, physical and chemical methods are available for a synthesis of nanoparticles. The silver nanoparticles with their unique chemical and physical properties are proving as an alternative for the development of new antibacterial agents. The silver nanoparticles have also found diverse applications in the form of wound dressing, coating for medical devices, silver nanoparticles impregnated textile fabrics, etc. The advantage of using silver nanoparticles is that there is continuous release of silver ions and the devices can be coated by both the outer and inner side thereby, enhancing its antimicrobial efficacy.

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