Available online on 15.11.2024 at http://jddtonline.info

Journal of Drug Delivery and Therapeutics

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Review Article

Advances in Green Synthesis of Silver Nanoparticles: Sustainable Approaches and Applications

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Article Info:

Article History:

Received 04 Aug 2024
Reviewed 27 Sep 2024
Accepted 23 Oct 2024
Published 15 Nov 2024

Cite this article as:

Panwar MS, Pal P, Joshi D, Advances in Green Synthesis of Silver Nanoparticles: Sustainable Approaches and Applications, Journal of Drug Delivery and Therapeutics. 2024; 14(11):177-184 *DOI: http://dx.doi.org/10.22270/jddt.v14i11.6854*

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Abstract

In the rapidly evolving field of nanotechnology, the synthesis of silver nanoparticles (AgNPs) has shifted towards eco-friendly methodologies, aligning with the growing demand for sustainable practices. Biologically synthesized AgNPs, particularly noteworthy for their applications in medicine and materials science, exhibit exceptional efficacy against microorganisms. The unique physicochemical properties of AgNPs, including their small size and large surface area-to-volume ratio, contribute to their versatility in diverse sectors. The advantages of AgNPs, such as ease of production, low cost, and high carrier capacity, make them preferred for various applications, including drug delivery systems. Despite concerns about environmental hazards and toxicity, the benefits of AgNPs, such as controlled drug release and targeted delivery, position them as valuable contributors to advancements in nanotechnology. Green synthesis methods, emphasizing biological processes and natural compounds, gain prominence for their sustainability and reduced environmental impact. The regulatory oversight of nanoproducts ensures their safe use, balancing their advantages with environmental considerations. Ongoing research promises further innovations, solidifying AgNPs' role as key contributors to progress in nanotechnology and materials science.

Keywords: Silver nanoparticles, Green synthesis, Sustainable approaches, Characterization, Applications, Eco-friendly methods.

Introduction

In the rapidly evolving landscape of nanotechnology, the synthesis of nanoparticles has undergone a transformative shift towards eco-friendly methodologies, responding to the increasing demand for sustainable and environmentally conscious practices. The concept of "green synthesis" has emerged as a central paradigm, advocating for the use of natural, renewable resources and benign processes in nanoparticle production[1].

Various nanomaterials, including copper, zinc, titanium, magnesium, gold, alginate, and silver, have arisen. Among these, silver nanoparticles have demonstrated exceptional efficacy against bacteria, viruses, and other eukaryotic microorganisms. The ascendancy of biologically synthesized silver nanoparticles (SNPs) reflects a broader trend towards green synthesis, particularly noteworthy for AgNPs, given their extensive applications and growing concerns about the environmental impact of conventional synthetic methods[2-3].

The importance of silver nanoparticles (AgNPs) spans diverse applications due to their unique physicochemical properties. Their small size and large surface area-to-volume ratio contribute to exceptional reactivity, rendering them invaluable across various fields.

Throughout history, different metals have been harnessed for their antimicrobial properties, including silver (Ag), gold (Au), copper (Cu), aluminum (Al), titanium (Ti), iron (Fe), and zinc (Zn). Within the pharmaceutical sector, nanotechnology has garnered significant attention for its myriad advantages. Various metal nanoparticles and their derivatives have been explored for potential antimicrobial effects[4].

Among metallic nanoparticles, silver nanoparticles (AgNPs) have emerged as the most popular antibacterial agents. Silver, in all its forms, exhibits activity against bacteria, including drug-resistant strains, viruses, and spores. Notably, AgNPs have demonstrated higher efficacy compared to other forms of silver. This underscores their significance in ongoing efforts to develop innovative and sustainable solutions in nanotechnology and antimicrobial applications[5].

Importance of silver nanoparticles

The significance of silver nanoparticles spans across various industries, including cosmetics, medicine, and defence, owing to their distinctive chemical and physical attributes. At the nanoscale, these particles exhibit properties that differ significantly from their larger counterparts[6].

1. **Air Purification and Quality Management:** Silver nanoparticles find applications in air purification, biosensing, imaging techniques, and drug delivery systems. Their nanometer size allows for enhanced performance in these areas.
2. **Biological Synthesis for Diverse Applications:** Biologically synthesized silver nanoparticles play a pivotal role in diverse applications. They serve as coatings for efficient solar energy absorption, intercalation materials for electrical batteries, optical receptors, catalysts in chemical reactions, biolabeling agents, and potent antimicrobials.
3. **High Sensitivity Biomolecular Detection and Diagnostics:** Despite being cytotoxic, silver nanoparticles have proven invaluable in high sensitivity biomolecular detection and diagnostics. They contribute significantly to antimicrobials and therapeutics, catalysis, and microelectronics.
4. **Potential Medical Applications:** Silver nanoparticles show promise in diagnostic biomedical optical imaging, as well as in the development of biological implants such as heart valves. In the medical field, they are applied in wound dressings, contraceptive devices, surgical instruments, and bone prostheses.
5. **Antibacterial Properties for Everyday Products:** The antibacterial properties of silver nanoparticles have given rise to innovative products. Nanoparticles are embedded in fabrics, including clothes, sheets, and socks, to mitigate odors. Additionally, antibacterial soap and toothpaste incorporating silver nanoparticles contribute to enhanced hygiene.

The importance of silver nanoparticles lies in their versatility across various sectors, from cutting-edge medical applications to everyday products that enhance our quality of life. As research continues, their unique properties are likely to lead to even more innovations and advancements in different fields.

Advantages of Silver Nanoparticles[7-8]:

1. Ease of Production: Silver nanoparticles are relatively easy to produce, making their manufacturing process more accessible.
2. Low Production Cost: The cost of producing silver nanoparticles is minimal, contributing to cost-effective applications.
3. Longer Shelf-Stability: Silver nanoparticles exhibit longer shelf stability, enhancing their usability over extended periods.
4. High Carrier Capacity: They possess a high carrier capacity, allowing efficient transportation of various substances.
5. Versatility in Drug Incorporation: The ability to incorporate both hydrophilic and hydrophobic drug molecules makes them versatile for pharmaceutical applications.
6. Various Administration Routes: Silver nanoparticles can be administered through different routes, providing flexibility in drug delivery methods.
7. Extended Clearance Time: Longer clearance times contribute to sustained therapeutic effects.
8. Controlled Drug Release: They have the ability to sustain the release of drugs, making them suitable for imaging studies and controlled drug delivery.
9. Increased Bioavailability: Silver nanoparticles enhance the bioavailability of drugs, optimizing their therapeutic effectiveness.
10. Targeted Drug Delivery: They facilitate targeted drug delivery at the cellular and nuclear levels, improving precision in treatment.
11. Safer Medicines: The development of new medicines with silver nanoparticles aims at creating safer alternatives.
12. Prevention of Drug Resistance: They help prevent multi-drug resistance mediated efflux of chemotherapeutic agents.
13. Low Manufacturing Costs: The production of silver nanoparticles does not involve high manufacturing costs.
14. Non-toxic Solvents: The preparation process does not involve the use of harsh toxic solvents.
15. Immune Response and Allergy Avoidance: Silver nanoparticles do not trigger immune responses or allergic reactions, enhancing their biocompatibility.
16. Optimal Tissue Concentrations: Tissues absorb only optimum concentrations of nanoparticles, reducing the risk of drug overdose.

Disadvantages of Silver Nanoparticles:

1. Environmental Hazard: Silver nanoparticles are suggested to be hazardous to the environment due to their small size and variable properties.
2. Use of Harmful Substances: The preparation of silver nanoparticles involves the use of some harmful substances and high energy consumption.
3. Toxicity to Living Forms: Silver nanoparticles, especially in their nanoforms, can be toxic to living organisms and readily enter aquatic ecosystems.
4. Solvent Contamination: The potential for solvent contamination poses a risk during the preparation process.
5. Lack of Uniform Distribution: Achieving a uniform distribution of silver nanoparticles may be challenging in certain applications.

Synthesis Methods:

Various synthesis methods are employed for the production of silver nanoparticles (AgNPs), encompassing physical, chemical, and environmentally friendly green synthesis approaches. These methods play a crucial role in tailoring the properties and applications of the synthesized nanoparticles. Notably, green synthesis methods are gaining prominence for their sustainability and reduced environmental impact. Here are some common synthesis approaches[9-12]:

1. **Chemical Synthesis:**

- *Reduction Methods:* Chemical reduction methods involve the reduction of silver ions using chemical agents. Common reducing agents include sodium borohydride, hydrazine, and citrate. These methods allow precise control over particle size and shape.

2. **Physical Synthesis:**

- *Laser Ablation:* In this method, silver nanoparticles are generated by ablating a silver target using a laser beam. This technique provides control over particle size and minimal contamination.

- *Mechanical Milling:* Mechanical milling involves the grinding of bulk silver into fine particles. This method is suitable for producing nanoparticles in larger quantities.

3. **Green Synthesis:** Green synthesis methods aim to minimize the use of hazardous chemicals and promote sustainability. They often involve biological processes and the reducing ability of natural compounds, such as mono and polysaccharides.

- *Biological Process:* Biological synthesis involves the use of living organisms, such as bacteria, fungi, or plants, to reduce silver ions and produce AgNPs. The biological entities act as reducing and stabilizing agents.

- *Reducing Ability of Mono and Polysaccharides:* Mono and polysaccharides, found in various natural sources like plants and microbes, serve as effective reducing agents in green synthesis. These compounds reduce silver ions to AgNPs, offering a sustainable and eco-friendly approach.

Green synthesis methods are particularly attractive due to their ability to produce AgNPs under mild reaction conditions, reducing the need for energy-intensive processes and minimizing the use of toxic chemicals. The choice of synthesis method depends on the desired characteristics of the nanoparticles and the specific application requirements. As research in nanotechnology progresses, innovative synthesis approaches continue to emerge, contributing to the advancement of nanomaterial science and technology. Figure 1-2 represent methods of Nanoparticle formulation and sliver nanoparticle.

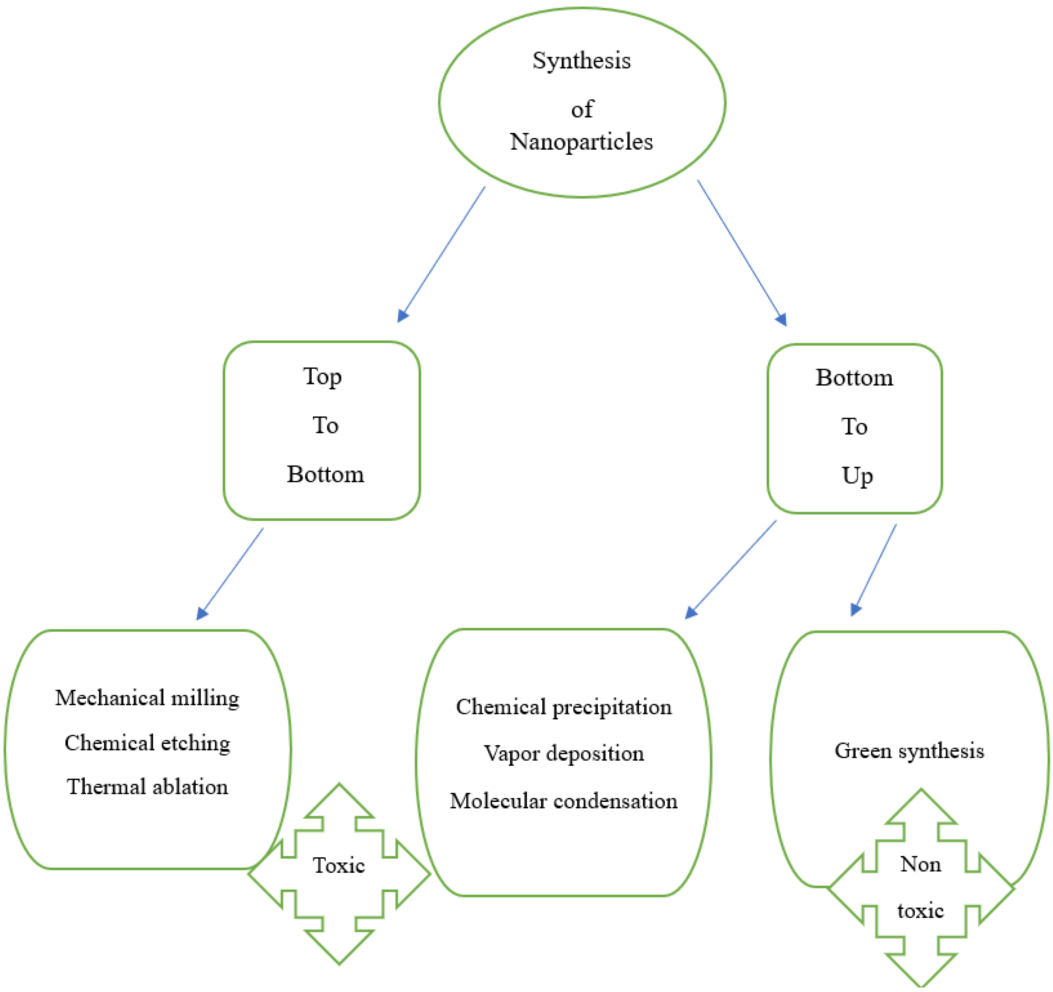

Figure 1: Approach for synthesis of Nanoparticles

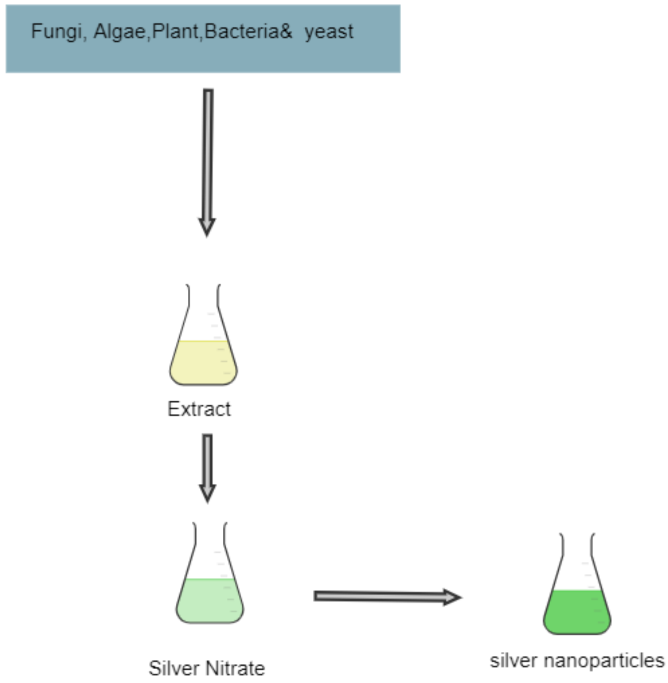

Figure 2: synthesis of Silver Nanoparticles

The adoption of green methods in various processes offers several advantages over traditional physical and chemical methods. Here are key advantages that highlight the superiority of green methods[13-17]:

1. **Increased Efficiency:** Green methods typically demonstrate higher efficiency by requiring fewer reaction steps. This streamlined approach not only accelerates processes but also reduces the overall consumption of resources. The efficiency gains contribute to more sustainable and economical practices.

2. **Simplicity and Stability:** Green methods are simpler to use, often remaining stable in ambient air at normal temperatures and pressures. This characteristic simplifies handling and eliminates the need for complex and energy-intensive conditions, making the overall processes more accessible and user-friendly.

3. **Reduced Resource Consumption:** Green methods demand fewer resources, leading to a more sustainable utilization of raw materials. The decreased resource requirements not only contribute to cost-effectiveness but also align with the principles of responsible resource management.

4. **Minimized Wastage:** Green methods aim to minimize wastage throughout the entire process. By optimizing reaction pathways and improving selectivity, these methods significantly reduce the generation of by-products and waste. This not only enhances the economic viability of the processes but also aligns with waste reduction goals, promoting a cleaner and more sustainable approach.

5. **Environmentally Friendlier Practices:** Green methods prioritize the use of environmentally friendly components, such as non-injurious solvents. This not only ensures the safety of workers involved but also mitigates the environmental impact associated with the release of harmful substances. The focus on eco-friendly practices extends to the generation of less hazardous waste products, further minimizing the ecological footprint of the processes.

6. **Enhanced Safety and Compliance:** Green methods often lead to safer working conditions due to the reduced reliance on hazardous materials. This not only safeguards the health of workers but also ensures compliance with increasingly stringent environmental and safety regulations.

Mechanism of Action

The mechanism of action of silver on microbes is a subject of ongoing investigation, but potential pathways have been proposed based on observed morphological and structural changes in bacterial cells. The effects seem to vary depending on the form of silver, whether metallic silver, silver ions, or silver nanoparticles[18-22].

1. **Interaction with Thiol Groups:**

- Silver interacts with thiol group compounds present in the respiratory enzymes of bacterial cells.
- It attaches to the bacterial cell wall and membrane, hindering the respiratory process.

2. **Inhibition of Respiration:**

- Silver ions, in particular, inhibit the respiration process within bacterial cells.

3. **Effect on DNA Replication:**

- Silver ions impact DNA replication by inducing a condensed state in DNA molecules.

- DNA replication occurs when the DNA is in a relaxed state; however, when silver ions penetrate the bacterial cell, the DNA becomes condensed, impeding its ability to replicate and leading to bacterial cell death.

4. **Efficiency of Silver Nanoparticles:**

- The efficiency of silver nanoparticles is attributed to their extremely large surface area, allowing for enhanced contact with microorganisms.
- Nanoparticles attach to the cell membrane and penetrate bacterial cells.

5. **Interaction with Sulphur-Containing Proteins:**

- Silver nanoparticles interact with sulphur-containing proteins within the bacterial cell membrane.

6. **Formation of Low Molecular Weight Region:**

- Upon entering the bacterial cell, silver nanoparticles form a low molecular weight region at the center of the bacteria.
- This region causes bacteria to agglomerate, protecting DNA from the direct impact of silver ions.

7. **Targeting Respiratory Chain and Cell Division:**

- Silver nanoparticles preferentially attack the respiratory chain and interfere with cell division.
- These actions ultimately lead to bacterial cell death.

8. **Release of Silver Ions:**

- Silver nanoparticles release silver ions within the bacterial cell.
- The presence of silver ions enhances the bactericidal activities, contributing to the overall antimicrobial effect.

Characterization of Silver Nanoparticles

Characterizing silver nanoparticles (AgNPs) is crucial for understanding their physicochemical properties, which, in turn, influences their behaviour, distribution, safety, and efficiency. Various analytical techniques are employed to comprehensively characterize AgNPs, providing valuable insights into their structure and functionality. Here are some commonly utilized characterization techniques[23-27]:

1. **UV-Vis Spectroscopy:** UV-Vis spectroscopy is employed to analyse the absorption and scattering of light by AgNPs. The resulting spectra offer information about the size, shape, and concentration of the nanoparticles.
2. **X-ray Diffractometry (XRD):** XRD is used to determine the crystal structure of AgNPs. It provides data on the arrangement of atoms within the nanoparticles, aiding in the identification of the crystal phases present.
3. **Fourier Transform Infrared Spectroscopy (FTIR):** FTIR is utilized to study the chemical composition and surface functional groups of AgNPs. It helps in identifying the biomolecules or stabilizing agents on the surface of the nanoparticles.
4. **X-ray Photoelectron Spectroscopy (XPS):** XPS is employed to analyze the elemental composition and chemical state of the surface of AgNPs. It provides detailed information about the oxidation states of the elements present.
5. **Dynamic Light Scattering (DLS):** DLS measures the hydrodynamic size distribution of AgNPs in suspension. It provides information about the size distribution and agglomeration state of the nanoparticles in solution.
6. **Scanning Electron Microscopy (SEM):** SEM offers high-resolution images of the surface morphology of AgNPs. It is valuable for visualizing the shape, size, and surface characteristics of the nanoparticles.
7. **Transmission Electron Microscopy (TEM):** TEM provides detailed images of the internal structure of AgNPs, offering insights into their size, shape, and distribution. It is particularly useful for studying individual nanoparticles.
8. **Atomic Force Microscopy (AFM):** AFM is used to study the surface topography and mechanical properties of AgNPs at the nanoscale. It provides three-dimensional images with high resolution.

Regulatory oversight of nanoproducts

Regulatory oversight of nanoproducts, particularly nanosilver, involves various agencies with specific responsibilities. In the United States, three key federal agencies play a role in regulating the environmental and public health impacts of nanosilver[28-32]:

1. **Environmental Protection Agency (EPA):**

- Silver has been listed as a priority pollutant in surface water by the EPA since 1977.
- Separate threshold limits have been established, with the US Conference of Government Industrial Hygienists setting a limit of 0.1 mg/m^3.
- The NIOSH recommends a permissible exposure limit of 0.01 mg/m^3 for all forms of silver.

2. **U.S. Food and Drug Administration (USFDA):**

- The USFDA is involved in the regulatory oversight of nanosilver, particularly in products related to food, pharmaceuticals, and medical devices.

3. **U.S. National Institute for Occupational Safety and Health (NIOSH):**

- NIOSH contributes to the regulatory framework by recommending permissible exposure limits, ensuring occupational safety concerning silver nanoparticles.

In the European Union (EU), nanosilver and its products are regulated under the REACH program, covering safety and environmental regulations. This includes directives for general product safety, medical devices, pharmaceuticals, pollution prevention, and control, as well as major accident hazards involving dangerous substances.

In Australia, regulatory oversight involves multiple agencies:

1. **Food Standards Australia New Zealand:**

- Regulates the food industry, ensuring that all food products, including those potentially containing nanosilver, comply with the Australia New Zealand Food Standard Code (FS Code).

2. **National Industrial Chemicals Notification and Assessment Scheme (NICNAS):**

- Regulates industrial chemicals, including nanomaterials.

3. **Therapeutic Goods Administration (TGA):**

- Concerned with the regulation of pharmaceuticals, including those with nanosilver components.

4. **Australian Pesticides and Veterinary Medicines Authority (APVMA):**

- Regulates veterinary and agricultural chemicals.

Compliance with safety standards in Australia requires thorough safety data, including information on the shape, bioavailability of nano formations, and aggregation characteristics. The safety data must be provided in a plasma model at different concentrations and particle size ranges, ensuring comprehensive understanding and evaluation of nanosilver products. Overall, regulatory efforts are aimed at ensuring the safe use of nanosilver in various products, protecting both public health and the environment.

Applications of Silver Nanoparticles

The applications of silver nanoparticles (AgNPs) are diverse and span various fields due to their unique properties arising from their extremely minute size and large surface-to-volume ratio. Some notable applications include[33-38]:

1. **Antimicrobial Agents:** AgNPs exhibit broad-spectrum bactericidal effects against both Gram-negative and Gram-positive bacteria. Their interaction with bacterial membranes and penetration into cells destabilizes them, leading to cell death. This makes AgNPs a prominent choice in antimicrobial applications, addressing concerns related to drug-resistant pathogens.

2. **Anti-Inflammatory Agents:** Inflammatory responses, involving various blood cells and cytokines, often require effective anti-inflammatory agents to mitigate exaggerated reactions. AgNPs play a role in the anti-inflammatory field, contributing to the management of inflammation.

3. **Anti-Angiogenic Agents:** AgNPs have demonstrated anti-angiogenic properties, making them relevant in the context of pathological angiogenesis associated with cancer, ischemic complications, and inflammatory diseases. Studies using both in vitro and in vivo models have provided evidence of the potential of AgNPs in inhibiting angiogenesis.

4. **Anticancer Therapeutic Potential:** AgNPs serve as nanocarriers for targeted drug delivery and chemotherapeutic agents. Additionally, they enhance the effects of radiation and photodynamic therapy, showcasing their potential in anticancer therapeutic applications.

5. **Dental Applications:** Dental caries, a widespread oral-cavity-related infection, pose a global health and economic burden. Nanotechnology-based dental strategies, involving AgNPs, focus on enhancing the remineralization process and controlling biofilm development. This aims to limit and eliminate the clinical impact of caries, making AgNPs valuable in dental applications.

The versatility of AgNPs in various applications underscores their potential contributions to healthcare, disease management, and materials science. Ongoing research continues to explore new avenues for the application of silver nanoparticles, offering promising solutions in fields ranging from medicine to dentistry.

Summary and conclusion

The evolution of nanotechnology has shifted towards green synthesis, emphasizing sustainable practices. Silver nanoparticles (AgNPs), especially biologically synthesized ones, showcase significant efficacy against microorganisms, contributing to their diverse applications in various industries.

AgNPs, with their unique physicochemical properties, are pivotal in addressing challenges ranging from air purification to medical applications. Their advantages, such as ease of production, low cost, and high carrier capacity, make them preferred in drug delivery systems.

Understanding the mechanism of AgNPs' action on microbes is crucial, and various analytical techniques aid in characterizing their behaviour. Regulatory oversight, varying by country, ensures the safe use of nanoproducts, balancing their benefits with environmental considerations.

Despite concerns, the applications of AgNPs in antimicrobial, anti-inflammatory, anti-angiogenic, anticancer, and dental fields showcase their versatility. Ongoing research promises further advancements, positioning AgNPs as key contributors to progress in nanotechnology, medicine, and materials science.

Conflicts of interest: The authors report no financial or any other conflicts of interest in this work.

Authors contribution: All authors contributed equally to the preparation of this manuscript

Funding source: All authors declare that no specific financial support was received for this study.

Source of Support: Nil

Data Availability Statement: The data supporting in this paper are available in the cited references.

Informed Consent to participate: Not applicable.

Ethics approval: Not applicable.

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