Green-Synthesized Silver Nanoparticles for Photocatalytic Degradation of Organic Dyes: a Comprehensive Review

[1]Harsh Chhangani and [2]Herendra Kumar
[1]Student and [2]Assistant Professor
Department of Physics
Bhaskaracharya College of Applied Sciences, University of Delhi, Delhi, 110075, India

Abstract- Silver nanoparticles (AgNPs) have received a lot of interest for their several applications, including their remarkable potential as photocatalysts for organic dye degradation. This review explores the photocatalytic capabilities of silver nanoparticles (AgNPs)—specifically those synthesized via green, eco-friendly methods—in treating synthetic dye-contaminated wastewater. The paper emphasizes the synthesis of AgNPs from various biological substrates, highlighting their economic feasibility, high conductivity, and biocompatibility. The growing concern over the improper disposal of persistent, non-biodegradable synthetic dyes is addressed by showcasing the role of AgNPs as effective agents for breaking down harmful industrial dyes.

Key target dyes investigated include methyl orange, congo red, nitrophenol, methylene blue, and malachite green, with performance data reflecting the success of AgNPs from different biological sources. The review outlines the mechanisms of photocatalytic degradation facilitated by these nanoparticles, illustrating how they convert toxic dyes into less hazardous compounds. It also examines the toxicity of AgNPs themselves and strategies for their environmental remediation. Lastly, a comparative analysis of multiple biological substrates is presented to guide the selection of optimal sources for enhanced photocatalytic efficiency and sustainable wastewater treatment solutions.

Index Terms: Silver nanoparticles (AgNPs), Green synthesis, Photocatalytic degradation, Biogenic nanoparticles, Nanoparticle toxicity

I. INTRODUCTION

Nanoparticles (NPs) are defined as particulate materials with at least one dimension under 100 nm and can be classified based on morphology, size, and chemical composition into categories like carbon-based, metal, ceramic, semiconductor, polymeric, and lipid nanoparticles. Among them, metallic nanoparticles, especially silver nanoparticles (AgNPs), are extensively studied due to their unique optical, chemical, and antimicrobial properties (Gola et al., 2021).

AgNPs can be synthesized through top-down and bottom-up approaches, utilizing various techniques such as physical (e.g., spark discharge, pyrolysis), chemical (e.g., reduction using solvents), biological (green synthesis), photophysical/photochemical, and electrochemical methods like sonoelectrochemistry (Gola et al., 2021). While physical methods require high energy and chemical methods allow shape and size control, both pose environmental hazards due to toxic reagents. In contrast, green synthesis using biological materials (plants, fungi, bacteria, algae) is cost-effective, eco-friendly, and biocompatible, though it may suffer from lower yields and less structural control (Vadakkan et al., 2024).

Recent studies have demonstrated advanced synthesis techniques, including hydrothermal reduction of $AgNO_3$ to form nanowires and pulsed-laser ablation in liquid (PLAL) for colloidal nanoparticle formation (Khairani et al., 2024). Synthetic organic dyes, used extensively in industries such as textiles, paper, food, leather, and cosmetics, include harmful compounds like methylene blue (MB), malachite green (MG), congo red (CR), methyl orange (MO), rhodamine B (RhB), and 4-nitrophenol (4-NP). These dyes are non-biodegradable, toxic, and often carcinogenic, making them significant environmental pollutants (Kishor et al., 2021).

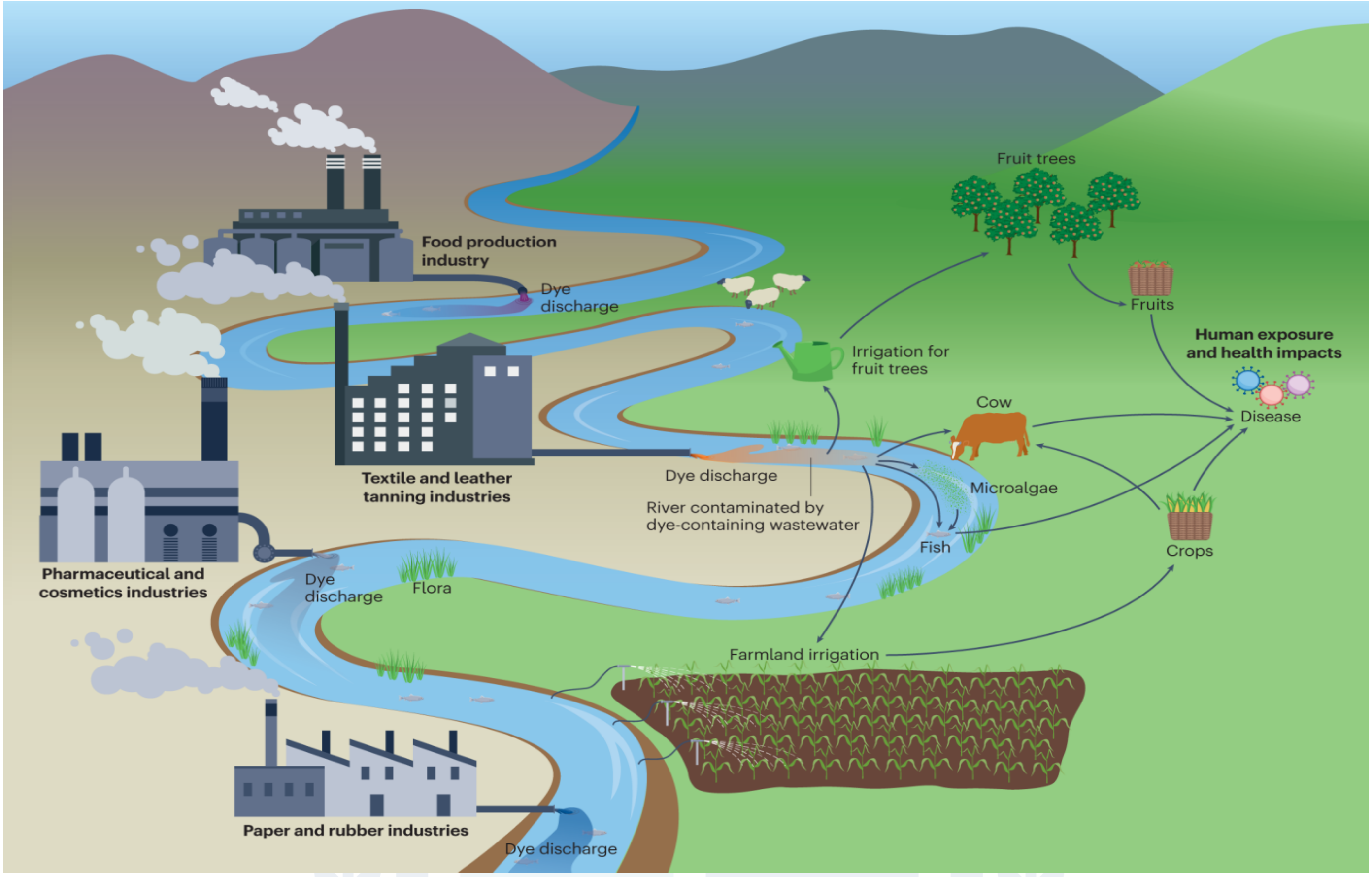


Figure 1 Major sources of dye and pathways of dye pollution (Lin et al., 2023)

Although traditional dye removal techniques like adsorption, filtration, ion exchange, and coagulation exist, many are either expensive or inefficient (Chandhru et al., 2020). Chemical methods such as ozonation and electrodialysis are more effective but resource-intensive. In contrast, catalytic degradation using AgNPs has gained attention for its efficiency, low cost, and scalability (Chandhru et al., 2020). AgNPs synthesized via chemical methods like trisodium citrate reduction exhibit strong dye degradation capacity (Gola et al., 2021), but the green synthesis approach is favored for its cost-effectiveness and environmental safety.

This review comprehensively discusses the biosynthesis of AgNPs and their effectiveness in degrading a broad spectrum of hazardous dyes including methylene blue, congo red, safranine, 4-nitrophenol, methyl red, methyl orange, rhodamine B, eosin, acid red, direct yellow, bromophenyl blue, and malachite green. The efficiency of AgNPs depends on synthesis parameters such as precursor type, solvent, reducing agent, and reaction time, all of which influence the catalytic degradation rate and potential environmental applications.

II. GREEN SYNTHESIS OF SILVER NANOPARTICLES

The green synthesis of silver nanoparticles (AgNPs) is a sustainable and eco-friendly technique that replaces toxic chemicals with natural biological materials. It leverages the reducing and stabilizing potential of various biological entities such as plants, fungi, algae, bacteria, and yeast. Typically, biological extracts are mixed with metal salt solutions, wherein the metallic ions are reduced from a positive oxidation state to a zero oxidation state by naturally occurring compounds like alkaloids, phenolics, terpenoids, proteins, enzymes, co-enzymes, and sugars (Mittal et al., 2013). These phytochemicals—especially flavonoids, terpenoids, polyphenols, and aldehydes—play a pivotal role in both the reduction and stabilization of AgNPs (Eswaran et al., 2021).

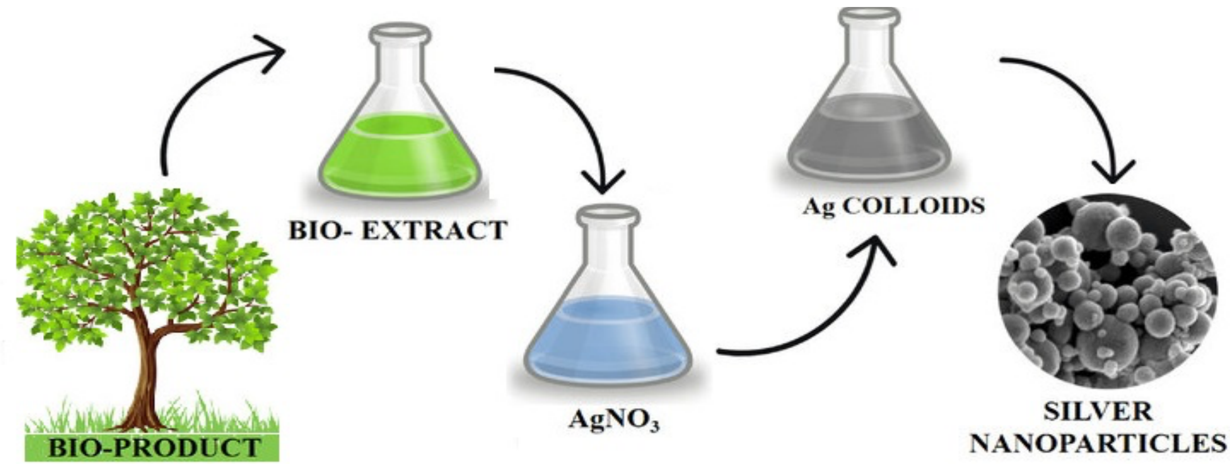


Figure 2 Schematic representation of synthesis of silver nanoparticles from bio- product (Sharma et al., 2024).

The strength of reductants in the extract influences reaction kinetics and nanoparticle size, favoring smaller particles and narrower size distribution with rapid nucleation. The resulting AgNPs display diverse morphologies, such as spherical or rod-like structures. Green synthesis stands out for its biocompatibility, affordability, simplicity, and minimal environmental impact. Increasing awareness of the toxicity of chemical synthesis and the demand for renewable sources has elevated the importance of green protocols for AgNP synthesis in recent research (Eswaran et al., 2021).

III. PATHWAYS FOR ORGANIC DYE DEGRADATION

The degradation of organic dyes primarily occurs via two mechanisms: photocatalysis in the presence of sunlight and reduction with the aid of reducing agents.

3.1 Photocatalytic Degradation under Sunlight

Photocatalysis is the dominant degradation route where biosynthesized AgNPs utilize sunlight to initiate electron excitation from the valence band to the conduction band, creating electron–hole pairs.

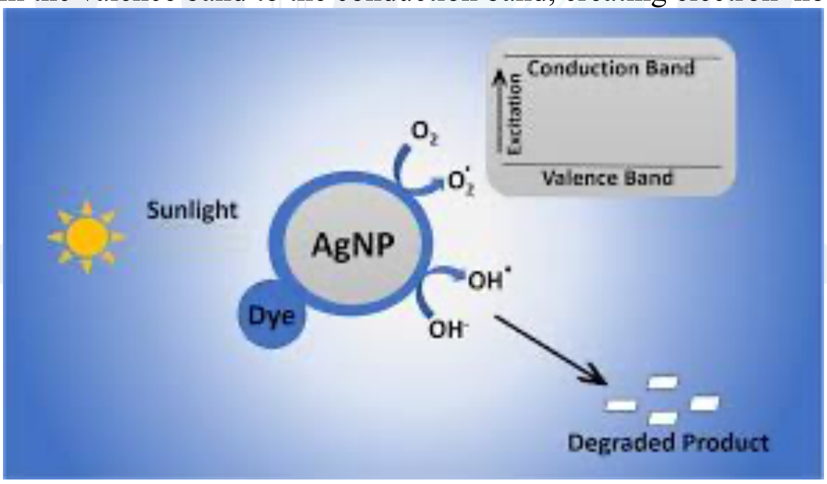


Figure 3 Schematic representation of Photocatalytic mechanism of degradation of dyes using AgNPs (Sharma et al., 2024).

These pairs trigger redox reactions that generate hydroxyl radicals (OH^-), powerful oxidants that decompose dyes into harmless compounds like CO_2 and H_2O (Eswaran et al., 2021). The surface plasmon resonance (SPR) and interband transitions in AgNPs under UV-visible irradiation further enhance their photocatalytic properties. When photons strike the nanoparticle surface, band electrons absorb energy, elevating to higher energy states. The resulting plasmonic excitation produces hot electrons, which interact with atmospheric O_2 to generate superoxide radicals (O_2^-). These reactive species degrade dye molecules through oxidative pathways. Additionally, electron-hole recombination in the sp and d orbitals contributes to enhanced degradation by forming more free radicals, including both O_2^- and OH^- (Eswaran et al., 2021).

3.2 Reductive Degradation

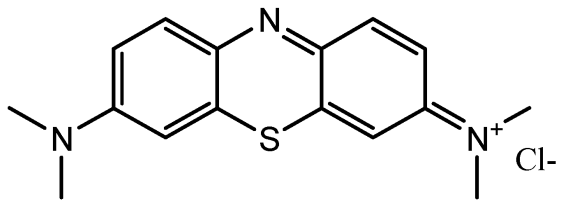
In this mechanism, $NaBH_4$ acts as both a hydrogen donor and electron source. When both dye and $NaBH_4$ are adsorbed on AgNPs' surfaces, $NaBH_4$ functions as a nucleophile while the dye serves as an electrophile. AgNPs mediate electron transfer between donor and acceptor, facilitating dye breakdown. The efficiency depends on AgNP size, as smaller particles offer larger surface areas for interactions (Edison et al., 2020).

IV. AgNP-MEDIATED DEGRADATION OF ORGANIC DYES

A comparative analysis of a few major organic dye pollutants and their degradation activity is discussed below.

4.1 Methylene blue

Methylene blue (MB, $C_{16}H_{18}N_3SCl$) is a widely used organic dye and one of the most prevalent aquaticpollutants, originating from various industrial activities. While it has applications in clinical medicine and industry, including recent roles during the COVID-19 pandemic (Ghahestani et al., 2020), MB poses significant health concerns such as central nervous system (CNS) toxicity and carcinogenicity.Due to its complexchemical structure, degradation of MB is challenging and necessary for environmental safety. MB degrades into leuco-methylene blue, a colorless form, when reduced. This reduction can be facilitated either by sunlight-driven photocatalysis or by chemical catalysts such as $NaBH_4$, with silver nanoparticles (AgNPs) acting as effective mediators. AgNPs provide catalytic surfaces and enhance the efficiency and speed of degradation reactions.



Numerous biological substrates have been employed in the green synthesis of AgNPs for MB degradation. The performance of these catalysts varies based on substrate type, AgNP morphology, size, and catalytic conditions. For instance, AgNPs synthesized using *Ageratum conyzoides* achieved MB degradation in 105 minutes under sunlight (Chandraker et al., 2019). More rapid degradation was reported using κ-carrageenan gum-derived AgNPs, achieving 100% degradation in just 70 seconds in the presence of $NaBH_4$ (Pandey et al., 2020). These spherical, nanosized particles exhibited unusual and highly efficient degradation kinetics.

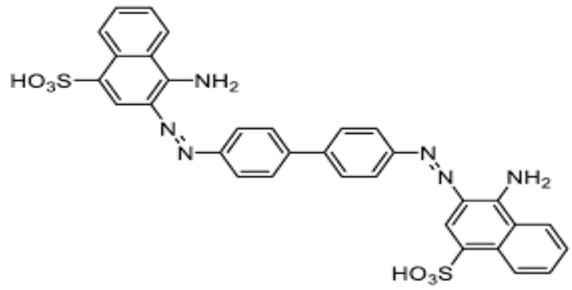
Further, AgNPs synthesized using *Vaccinium macrocarpon* extract, immobilized on clinoptilolite (a natural zeolite), showed even faster results. While clinoptilolite alone degraded MB in 30 minutes, the AgNPs/clinoptilolite system achieved degradation in just 40 seconds (Khodadadi et al., 2017). Similarly, *Kyllinga brevifolia*-derived AgNPs, quasi-spherical in shape (5–30 nm), degraded MB in 1.5 minutes with $NaBH_4$. Phytochemical analysis showed abundant proteins, carbohydrates, and plant sterols (e.g., campesterol, stigmasterol). These act as both reducing and capping agents, enhancing nanoparticle stability and performance (Isa and Lockman, 2019). When AgNPs were combined with K. brevifolia extract (KBE) and $NaBH_4$, degradation efficiency was 93% in 12 minutes, but 100% efficiency in 1.5 minutes with just $NaBH_4$ and AgNPs. However, sunlight-only degradation is comparatively slower.

Overall, the efficiency of MB degradation by AgNPs depends on nanoparticle synthesis route, substrate, particle size and shape, and the presence of co-reactants like $NaBH_4$. Biosynthesized AgNPs, particularly when combined with suitable supports or matrices, offer highly efficient and environmentally friendly routes to degrade MB and other toxic dyes.

4.2 Congo red

Congo red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$) is a water-soluble, azo-anionic dye widely used in textile industries due to its vibrant color, stability, and low cost (Obayomi et al., 2023).

Its structure, comprising six benzene rings, contributes to its non-biodegradable and toxic nature. When metabolized, it can yield benzidine, a known human carcinogen and mutagen, leading to its ban in several countries (Asses et al., 2018). Exposure to CR has been associated with severe health issues including respiratory problems, skin and eye irritation, and reproductive disorders (Obayomi et al., 2023).

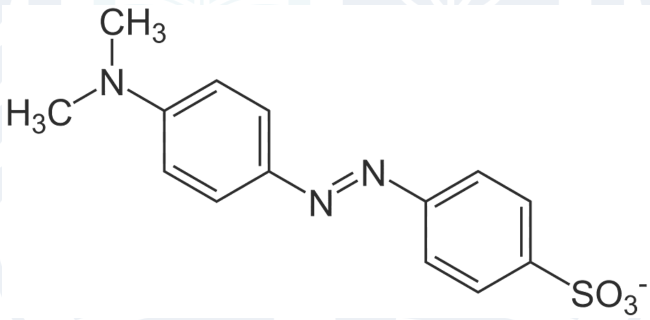


Reduction of CR results in less toxic, colorless aromatic amines, which have been verified through phytotoxicity and microtoxicity assays (Asses et al., 2018). Several studies illustrate effective degradation using green-synthesized AgNPs. AgNPs (11–15 nm) derived from *Amaranthus gangeticus* achieved 100% CR degradation in 15 minutes under sunlight (Kolya et al., 2015). In contrast, *Vaccinium macrocarpon*-derived AgNPs (15–30 nm) supported on clinoptilolite degraded CR in just 27 seconds (Khodadadi et al., 2017). CR reduction without AgNPs proceeds extremely slowly, underscoring the nanoparticles' catalytic importance. Notably, *Cuphea procumbens*-based AgNPs enabled sunlight-mediated CR degradation without any reducing agent, achieving 86.6% efficiency in 5 minutes (González-Pedroza et al., 2023).

Overall, substrate type, nanoparticle morphology, and presence of $NaBH_4$ significantly influence CR degradation efficiency, establishing biosynthesized AgNPs as potent, eco-friendly catalysts for environmental dye remediation.

4.3 Methyl orange

Methyl Orange (MO, $C_{14}H_{14}N_3NaO_3S$) is an anionic azo dye, widely used in textile industry,



Methyl Orange

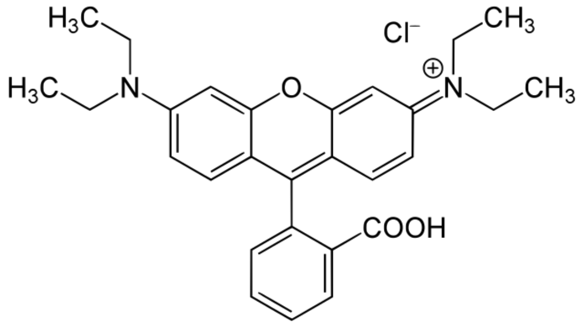
laboratory pH indicators, and across pharmaceutical, paper, printing, and culinary sectors. It is environmentally hazardous and toxic to aquatic life, and acute human exposure may lead to symptoms like jaundice, vomiting, and tissue necrosis. Therefore, MO must be reduced to colorless products like aromatic amines and sulfanilic acid for safe disposal.

AgNPs synthesized using *Plukenetia volubilis L* achieved only 60% MO degradation in 180 minutes under sunlight (Kumar et al., 2017). AgNPs from *Sterculia acuminata* achieved 100% degradation in 3 minutes (Bogireddy et al., 2016), while *Anacardium occidentale* (cashew nut shell) derived AgNPs completed degradation in 20 minutes (Edison et al., 2016), possibly due to non-spherical nanoparticle morphology.

Vaccinium macrocarpon AgNPs facilitated MO removal in 138 seconds using $NaBH_4$ (Khodadadi et al., 2017), whereas substrates like *Simarouba glauca* and *Punica granatum* achieved 100% and 99% degradation in 40 and 12 minutes, respectively, despite different particle sizes (5 nm and 36 nm) (Thomas and Thalla, 2023). Thus, no direct correlation between nanoparticle size and degradation time is conclusive, though smaller particles generally yield higher efficiency. Using *A. occidentale* extract, AgNPs catalyzed complete MO degradation in 20 minutes, while control reactions without AgNPs showed no effect even after 30 minutes (Edison et al., 2016).

4.4 Rhodamine B

Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$) is a widely used organic fluorescent dye employed in textile, printing, leather, paper, plastic, and food industries due to its bright crimson hue, water solubility, and cost-effectiveness. It is also used as a fluorescent water tracer in hydrological studies. However, RhB is chemically complex and resistant to biodegradation, making it a persistent pollutant in aquatic ecosystems (Saigl, 2021). Toxicologically, RhB has been associated with carcinogenic, mutagenic, and chronic health effects, including skin and respiratory inflammation, hemolysis, neurotoxicity, and organ degeneration (liver, lungs, brain, and kidneys) in both humans and animals (Saigl, 2021).



Rhodamine B

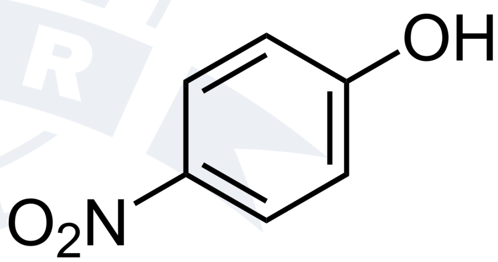
AgNPs synthesized from κ-carrageenan and *Vaccinium macrocarpon* achieved complete RhB degradation in just 15 and 90 seconds, respectively, when used with $NaBH_4$. These rapid results are linked to the small size of AgNPs—ranging from 9–15 nm for κ-carrageenan and 15–30 nm for *Vaccinium macrocarpon* (Khodadadi et al., 2017).

Additionally, AgNPs derived from *Myristica fragrans* (nutmeg) seed shells, rich in phenolic compounds and proteins, demonstrated over 90% photocatalytic degradation of multiple dyes (including RhB) under UV light. The degradation followed pseudo-first-order kinetics and the Langmuir isotherm model, indicating strong adsorption of dye molecules onto AgNPs and radical-mediated breakdown (Thomas and Thalla, 2023). These results validate green-synthesized AgNPs as efficient, eco-friendly catalysts for the rapid and safe degradation of Rhodamine B and other industrial dyes.

4.5 4-Nitrophenol

Nitrophenols, including 4-nitrophenol (4-NP), are toxic pollutants commonly generated through the manufacture and degradation of pesticides like DNoc and Dinoseb. They also find usage in pharmaceuticals, photography, polymer synthesis, and as preservatives.

Its detoxification is often achieved through catalytic conversion to 4-aminophenol (4-AP). AgNPs synthesized from *Dimocarpus longan* seed extract completed the conversion in 12 minutes, compared to 26 minutes with commercial AgNPs (Bogireddy et al., 2016).

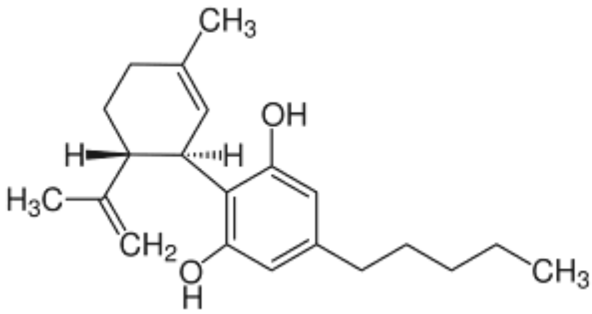


AgNPs synthesized from *Cestrum nocturnum* leaf extract via sunlight exposure showed high catalytic activity, confirmed by a color change from pale yellow to dark brown (Kumar et al., 2022). When used with $NaBH_4$, these AgNPs achieved over 90% degradation of 4-NP within 8 minutes. Their high efficiency is attributed to the primary and secondary metabolites in the plant extract, acting as both reducing agents and catalysts. Moreover, *Durio zibethinus*-based AgNPs, due to their spherical shape, small size, and natural capping agents, showed a notably fast reduction rate of 4-NP.

These findings reinforce that the efficacy of 4-NP degradation depends not only on the presence of $NaBH_4$ but significantly on the nature of the biosynthesized AgNPs—including their size, shape, source of synthesis, and capping agents. Smaller, stable nanoparticles synthesized from polyphenol-rich extracts consistently show faster and more efficient degradation of nitrophenols, with excellent environmental applicability.

4.6 Malachite green

Malachite Green (MG, $C_{23}H_{25}ClN_2$) is a synthetic, cationic, water-soluble dye used across multiple industries. It serves as an antibacterial and antifungal agent in pharmaceuticals, a colorant in food and cosmetics, and a printing agent in the paper and textile sectors, owing to its vibrant pigmentation and antimicrobial properties.However, MG is environmentally persistent and toxic to both aquatic and terrestrial organisms, particularly freshwater fish. Research highlights its multi-organ toxicity,



including teratogenic effects, and its ability to damage the liver, kidneys, spleen, heart, and reproductive systems, while also causing lesions in skin, eyes, lungs, and bones. Therefore, its conversion to less harmful leuco MG, is essential. Various green-synthesized AgNPs show promising MG degradation. AgNPs synthesized from *A. officinarium* demonstrated 91% MG degradation (10 ppm) under UV light in 2 hours, while only 38% degradation was observed under visible light (Li et al. 2020).

Another study using *Cuphea procumbens*-derived AgNPs under sunlight showed 82.1% degradation in 7 minutes using minimal catalyst and dye volume, with UV absorption shift confirming breakdown (González-Pedroza et al., 2023). These studies underscore the rapid, eco-friendly, and efficient catalytic degradation potential of biosynthesized AgNPs for removing MG from aqueous systems.

4.7 Few other dyes

Several additional organic dyes have been successfully degraded using biosynthesized silver nanoparticles (AgNPs). Brilliant Green (BG), a heat- and light-sensitive aromatic dye, was removed by 80% in 20 minutes under a mercury lamp using AgNPs synthesized from *Petroselinum crispum* extract, rich in flavonoids and phenolic esters (Khan et al., 2020). The enhancement in photodegradation is attributed to AgNPs' high light absorption, small spherical size, and minimal aggregation, as morphology and crystallinity significantly influence catalytic performance. Direct Yellow-12, a water-soluble anionic azo dye used in textile and printing industries, was degraded to less harmful products like 4-ethoxyaniline using AgNPs derived from *Terminalia cuneata* bark extract with $NaBH_4$ in 40 minutes (Edison et al., 2016). For Direct Blue-24, AgNPs synthesized from *Sterculia acuminata* fruit extract enabled complete degradation in just 3 minutes, whereas $NaBH_4$ alone showed no activity even after 25 minutes (Bogireddy et al., 2016).

V. TOXICOLOGICAL PROFILE AND ECOLOGICAL IMPACTS OF AgNPs

Although silver nanoparticles (AgNPs) offer substantial potential for dye degradation in wastewater treatment, their toxicological and ecological risks must be critically evaluated. Due to their small size and high reactivity, AgNPs can easily interact with biological systems, potentially inducing oxidative stress, DNA damage, and cellular disruption in aquatic organisms, plants, and microorganisms—even at low concentrations (Sharma et al., 2019).

AgNPs can transform into more hazardous species, such as silver nitrate, which dissociates into toxic Ag^+ ions (Ihtisham et al., 2021). The oxidation and interaction of AgNPs with oxygen, sulfur, chlorine, and thiol-containing compounds influence their short persistence in natural environments, though their smaller particle size accelerates corrosion compared to bulk silver.

A major concern is their bioaccumulation in aquatic ecosystems, raising the possibility of nanoparticle transfer through food chains, including potential human exposure via seafood consumption. The fate and transport of AgNPs depend on water chemistry, sediments, and biological activity, while transformations into silver ions can enhance their environmental mobility and toxicity.

AgNPs introduced during wastewater treatment may accumulate in sediments, impacting benthic organisms. Strategies like sulfidation—which converts AgNPs to less toxic silver sulfide—have shown promise in reducing toxicity (Fan et al., 2019). Aggregation into larger particles also lessens their environmental impact. While AgNPs are effective photocatalysts, their long-term ecological effects demand further study.

Regulatory frameworks must ensure safe deployment by balancing performance with ecosystem and human health safeguards.

VI. CONCLUSION

The green synthesis of silver nanoparticles (AgNPs) emerges as a sustainable and effective method for photocatalytic degradation of organic dyes, reducing the ecological impact associated with conventional nanoparticle production. AgNPs possess excellent photocatalytic properties due to their high surface area and reactivity, enabling efficient degradation of various toxic dyes under UV and visible light, often through the formation of reactive oxygen species (ROS). Immobilization on solid supports enhances their stability and reusability.

The efficacy of biosynthesized AgNPs has been demonstrated in degrading dyes such as Methylene Blue (MB), Congo Red (CR), Methyl Orange (MO), Rhodamine B (RhB), 4-Nitrophenol (4-NP), and Malachite Green (MG). AgNPs from substrates like *Vaccinium macrocarpon*, *κ-carrageenan*, *Dimocarpus longan*, and *Cuphea procumbens* have shown rapid dye degradation with enhanced performance compared to commercial AgNPs.

MB degradation was achieved in 138 seconds using *Vaccinium macrocarpon*-derived AgNPs. *Ageratum conyzoides* and *Kyllinga brevifolia* also showed notable catalytic potential. CR, a carcinogenic dye, was degraded 100% in 15 minutes using *Amaranthus gangeticus* under sunlight. MO degradation reached 90–100% within minutes using AgNPs from substrates like *Eucalyptus globulus* and *Dodonaea viscosa*. RhB, a resistant fluorescent dye, was effectively degraded within seconds using *κ-carrageenan* and *Vaccinium macrocarpon*-based AgNPs. Likewise, 4-NP, a pollutant from pesticide industries, was converted into 4-AP, outperforming commercial catalysts. MG, despite its use in industries, poses environmental threats; biosynthesized AgNPs efficiently catalyzed its breakdown to less toxic leucoMG.

AgNPs have also shown catalytic potential in degrading dyes like eosin Y, Victoria blue B, crystal violet, and others. Though $NaBH_4$ accelerates degradation, it introduces toxicity (boranes) and raises cost and environmental concerns, making it less viable for large-scale applications.

VII. PROSPECTS FOR FUTURE RESEARCH

Recent progress in dye wastewater treatment highlights the potential of functionalized magnetic nanomaterials, which offer high surface area, chemical stability, biocompatibility, and ease of regeneration. Among various techniques, adsorption remains highly effective due to its simplicity, cost-efficiency, and reusability. The selection of biological substrates for AgNPs synthesis is critical, influencing morphology, size, and thus photocatalytic efficiency. However, the toxicity of AgNPs remains a major concern, especially in open systems, prompting the need for robust environmental regulations and risk assessments.

Future research should explore green co-catalysts, closed system operations, and less toxic reducing agents to replace $NaBH_4$, which presents environmental hazards. The sulfidation process, converting AgNPs to less toxic silver sulfide, offers a promising natural mitigation strategy. Future efforts must also address the potential toxicity of degraded dye products, ensuring holistic environmental protection.

Finally, for real-world application, industrial-level scalability and compliance with safety protocols are essential. While green-synthesized AgNPs hold promise as sustainable agents for dye degradation, their responsible deployment depends on comprehensive regulation, cost-effective alternatives, and a clear understanding of their environmental impact.

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