Spectrum of Engineering Sciences
ISSN (e) 3007-3138 (p) 3007-312X
Volume 4, Issue 6, 2026

BIOGENIC SILVER NANOPARTICLES AS SUSTAINABLE CATALYSTS FOR THE DEGRADATION OF ORGANIC POLLUTANTS IN WASTEWATER

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DOI: https://doi.org/10.5281/zenodo.21204990

Keywords
biogenic silver nanoparticles; green synthesis; catalytic degradation; organic pollutants; wastewater treatment; photo catalysis; environmental remediation.

Article History
Received on: 26 May, 2026
Accepted on: 21 June, 2026
Published on 27 June, 2026

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Abstract

The release of organic contaminants such as synthetic dyes, nitro aromatics, pesticides, and traces of pharmaceuticals into aquatic environments is one of the biggest environmental challenges of industrialized countries. Most of the conventional treatment technologies have a high energy demand, create secondary sludge, or cannot break down recalcitrant molecules. In this context, nanocatalysis is deemed a viable approach to the efficient degradation of such pollutants and, in particular, silver nanoparticles (AgNPs) possess a high surface-to-volume ratio, tunable surface Plasmon resonance, and high redox activity. In this research paper, both plant extracts (organic compounds) and the bacterial, fungal, and algal metabolites mediate the reduction, capping, and stabilization of AgNPs, acting as both reductants and surfactants, without the need for the toxic reductants and surfactants of traditional colloidal chemistry. The mechanisms of the biogenic synthesis, the physicochemical parameters that affect the particle size and shape of the product, and the analytical methods developed to characterize the product are discussed. Next, the catalytic activity of the biogenic AgNPs was evaluated on two representative reaction classes, namely borohydride-assisted reduction of nitro aromatics, according to the electron-relay theory of Langmuir–Hinshelwood, and photocatalytic mineralization of dyes in the presence of light and reactive oxygen species. A collection of representative literature values for degradation efficiency and apparent rate constants is presented, and the factors that affect activity, such as size, shape, dose, pH, and nature of the bimolecular capping layer, are assessed. Finally, the reusability, real-effluent applicability, green-chemistry aspects, and the major challenge to large-scale deployment are considered. Biogenic AgNPs constitute a technically viable and environmentally protective catalytic platform with respect to wastewater treatment, the focus of which needs to be statistically ensured and standardized, as well as methodologically addressed through a growing body of nanotoxicological research.

Introduction

Clean water represents one of the most critical limiting factors of public health and the economic progress of nations. Nevertheless, the enormous growth and increased demand caused by rapid industrialization, urbanization, and population explosion have put significant strain on this essential resource. Various industries, namely the textile, leather, paper, and chemical industries, including pharmaceuticals, agrochemicals, and petrochemicals industries, contribute a wide variety of organic pollutants to water sources. For example, synthetic dyes, hundreds of thousands of tons of which are produced per year worldwide, are extensively employed in many industries, and hundreds of thousands of tons are lost during the dyeing and finishing steps to effluents.

Many synthetic organic dyes are poorly biodegradable, extremely stable chemically, and mutagenicity or carcinogenicity are common at extremely low concentrations; release into rivers, lakes, or ground waters results in a long-lived ecological and potential human threat. Therefore, the development of new, efficient, and environmentally friendly methods for the degradation of organic pollutants from wastewater is necessary. Limitations of conventional treatments: Adsorption and coagulation simply transfer the pollutants from one phase (aqueous) to another (solid waste), and the waste needs subsequent disposal. The effectiveness of biological treatment procedures against highly persistent xenobiotic organic molecules like dyes is very limited and generally slow. Membrane technologies are efficient but also susceptible to fouling and are relatively expensive to operate.

Chemical oxidation methods (Fenton reaction, zonation, etc.) can be efficient but are associated with energy-intensive requirements and generation of undesirable by-products. Catalytic and photocatalytic degradation offer promise in degrading various hazardous organics to benign products or achieving complete mineralization of organics to inorganic compounds under milder conditions.

Nanomaterials offer a suitable approach due to their large surface area to volume ratio, leading to high surface area and hence a large number of catalytically active sites per unit surface or mass.

Silver nanoparticles (Ag NPs) are very promising as catalysts due to a large surface Plasmon resonance (SPR) in the visible spectrum with good chemical stability, favorable redox activity, and documented antimicrobial activity. Ag NPs have successfully catalyzed a wide range of organic reactions, including the reduction of nitro aromatic compounds and decolourisation of azo and polyaromatic heterocyclic (PAH) compounds, both with and without visible light. Methods of preparation of NPs – Nanoparticle synthesis – Environmental aspects of Ag NPs Synthesis of metal NPs – Physical methods like laser ablation, vacuum evaporation-condensation methods are typically energy intensive and require costly and specialized equipment.

Chemical reduction processes such as using sodium borohydride or hydrazine have proved to be effective, but these approaches utilize highly reactive and potentially toxic chemical reductants and also use synthetic stabilizers to maintain dispersion, resulting in the production of toxic chemical wastes, which directly contravenes environmental principles. This aspect of hazardous chemical use, waste production, or excessive energy input necessitates alternative, more benign routes. "Green" or biogenic synthesis is where living organisms (or extracts from organisms) play both the role of reducing agent and capping agent. For plant extract-based synthesis, natural substances like phenols, flavonoids, proteins, and sugars are often available, and are abundant, inexpensive, and non-toxic. These reduce the silver ions (Ag+) and, at the same time, form complexes around the nascent Ag NP, stabilizing them against agglomeration.

Environmental application and need for green approach- In developing nations and water-stressed areas with textile, leather, and dyeing industries, river systems are often used for irrigation and household water supply, and heavily colored wastewater is discharged, often with minimal or no treatment, into these rivers. Low-cost, simple, and energy-efficient, without hazardous consumables like those in advanced oxidation processes or membrane technologies, the process will therefore have considerable benefit for use in these countries. Biogenic Ag NPs, prepared from readily available and inexpensive local natural resources like various plant materials, can destroy organic pollutants, dyes, and nitro aromatics under mild conditions using light or a small amount of reducer. This is one of the important reasons behind the great research interest in biogenic Ag NPs.

Moreover, local plant sources are ubiquitous in such areas, and many of them are potential agricultural or food wastes, which can add more environmental value to the approach. Purpose of this review: The purpose of this review is to present a consistent mechanistic framework for understanding the role of biogenic Ag NPs as catalysts for the degradation of organic pollutants in industrial effluents. This review will provide insights into various synthesis pathways and key reaction parameters, a range of spectroscopic characterization methods used for this material, the underlying catalytic photo catalytic degradation mechanisms with relevant kinetic modelling, and a comparative review of reported catalytic performances towards various classes of organic pollutants. The focus will be on the practical challenges in applying biogenic Ag NPs for water remediation, including reusability, performance in real wastewater samples, and the associated green chemistry considerations. Finally, the critical issues to be addressed before the potential large-scale application of this nanotechnology will be discussed.

2. Organic Pollutants in Wastewater

Synthetic Dyes, the major concerns associated with synthetic dyes, which range from brightly colored, harmless substances to environmentally harmful substances, have led to numerous studies. Due to their brightly colored structure, they are visually easy to identify in wastewater streams, and they inhibit the photosynthesis of aquatic plants by blocking sunlight penetration in receiving water. More than half of all commercial colorants, mainly from the textile, printing, and packaging industries, belong to the group of azo dyes, which contains one or more –N=N- chromophores, including 4-methyl orange, Congo red, methyl red, orange G, and various other related analogues, which can be employed as target pollutants.

Furthermore, thiazine, heteropolyaromatic (e.g., Methylene blue), xanthene (e.g., Rhodamine B), and triarylmethane (e.g., Brilliant blue FCF) dyes are used as model pollutants. Azo dyes and their degradation products can form toxic, mutagenic, and potentially carcinogenic substances. 4-Nitrophenol. Another very important class of target compounds, including pesticides, dye and drug precursors, and their intermediates, is nitro aromatics (e.g., 4-nitrophenol). Due to their strong withdrawing characteristics, these are very often highly resistant to oxidation or simple hydrolysis processes. The catalytic conversion of 4-nitrophenol to 4-aminophenol, which is also a valuable intermediate used in the pharmaceutical and photography industry, can be used as a clean and well-characterized spectroscopic model for catalytic activity evaluation of new materials. In the same way as pesticides, organic micro pollutants from pharmaceutical and personal-care products, PPCPs, represent an emerging class of environmental contaminants, and they are often combined in literature studies with other priority organic pollutants, like phenols and certain synthetic organic dyes. All mentioned contaminants share a common characteristic in that they are often very difficult to degrade via common biological treatment methods, and thus the need for alternative catalytic degradation processes becomes more significant.

2.1 Environmental and health impacts

These pollutants are hazardous on several fronts. Vivid color hinders the transmission of light into the water column and thus interferes with photosynthesis in plants and algae and can disrupt the food web; even when they don't confer a strong hue in low concentrations, many dyes and their transformation products are harmful to aquatic life. A variety of azo dyes cleave at the -N=N- bond to form aromatic amines when subjected to reductive conditions in the absence of air or in the gut of mammals, and many of these are carcinogens; these properties are responsible for the controls that are in place on some azo colorants. Nitro aromatics like 4-nitrophenol are toxic to the liver, the kidney, and the nervous system, and have been nominated as priority pollutants.

Since many dyes have been engineered to be light-, heat-, and oxidation-fast in service, i.e., they have low degradability in the light and also against other degradation factors, they are very persistent and can accumulate through food webs. It is this interplay of persistence, toxicity, and potential carcinogenicity that is the basis of elevating the problem of dye pollution to a health concern that justifies research on treatment technologies that aim for complete degradation rather than simple partitioning of pollutants between phases.

Biogenic Synthesis of Silver Nanoparticles

Biogenic synthesis, based on the reducing and stabilizing ability of living organisms, involves transforming silver ions into metallic nanoparticles in a mild aqueous medium at room temperature or a slightly increased temperature. This technique meets the goals of green chemistry by:

- avoiding the use of hazardous chemical agents
- utilizing water as the solvent
- operating at low temperatures
- producing less waste.

Synthesis routes

Plant-mediated synthesis is the most prevalent route as it is easy to perform, fast, and large amounts can be synthesized. An extract of any part of a plant - such as the leaves, fruit, bark, root, or flowers - is introduced to an aqueous solution containing silver nitrate. The color changes from pale yellow to reddish brown - the visual manifestation of surface Plasmon resonance - indicate the production of nanoparticles, which often occurs within minutes. For example, extracts from leaves of neem (Azadirachta indica), tulsi (Ocimum sanctum), turmeric (Curcuma longa), and guava (Psidium guajava) have been shown to effectively synthesize silver nanoparticles.

In microbial synthesis, silver is reduced by microorganisms such as bacteria, fungi, yeast, and actinomycetes. These organisms employ a variety of pathways - the reduction occurring outside the cell, mediated by released enzymes and metabolites, or within the cell itself. Microorganisms that prefer secreted reduced enzymes and proteins are favored because they are more resistant to silver toxicity. Algae are another source of biomass, due to their abundant polysaccharide and pigment content. Microorganisms can provide fine-tuning of nanoparticles; however, these processes require sterility, may take more time to complete, and necessitate product isolation, thereby restricting scalability with plants.

Mechanism of formation

The biogenic process may readily be illustrated as three interconnected stages. During the activation stage, biomolecules contribute electrons to silver ions for reducing silver ions into Ag to zero-valent Ag atoms; in the case of green plant extract systems, most of the electron-donating sources are the hydroxyl group- rich compounds, phenolic acids, and flavonoids, which are oxidized to their respective quinines, accompanying reduction. The second stage, the growth/nucleation phase, is characterized as a thermodynamic process when the atoms aggregate to form smaller nuclei, which further coalesce to form larger nanoparticles, and can even merge into larger particles if they are in contact. In the last stage, the termination step, biomass molecules bind to the surface of the particles as capping agents that cease particle growth, determine the particle shape, and provide stability via steric and electrostatic repulsive forces.

Studies demonstrated that various types of phytochemicals can serve different functions in specific roles during biogenesis. In one systematic research, phenolic acids and flavonoids acted as reducers, whereas xanthones and phloroglucinols primarily functioned as capping agents. This is evident from the fact that reduction, capping, and stabilization are differentiated processes but collaborate together rather than an indifferent function.

Parameters governing size and morphology

Since catalysis is an 'event on the surface ', the control of size and shape is the focal point of the synthetic strategy. Essential parameters are those of the concentrations of the silver salt precursor (silver nitrate, AgN), the amount and quality of the bio extract, e.g., the content of phytochemicals, the source, the pH, temperature, and reaction time. High pH is favorable because it increases the concentration of phenolate species, which are more deprotonated and thus stronger reducers, thus favoring a faster reaction rate, leading to the formation of smaller, more homogeneous particles. The temperature increases the reaction rate; thus, it can reduce dispersion in size, but high precursor concentrations can lead to agglomeration and an increase in particle size. Varying the ratio between extract and precursor silver varies both the rate and the thickness of the cap layer. This systematic tuning of parameters is a standard procedure during the biosynthesis, aiming at catalysis.

Biogenic Synthesis in Relation to Physical and Chemical Routes

The justification for using a biogenic route becomes evident when comparing the three primary nanoparticle generation pathways. Physical synthesis-which deconstructs bulk silver through processes such as laser ablation, mechanical milling, and evaporation-condensation-can create high-purity particles without chemical contaminants but requires sophisticated and expensive machinery and significant energy input. Chemical reduction-whereby silver ions are reduced and assembled using reductants including sodium borohydride, hydrazine, and citrate, and synthetic capping agents-is swift and well controlled but utilizes hazardous reagents and toxic waste products. Biological or biogenic nanoparticle synthesis uses a bottom-up pathway but instead relies on biomolecules to act as the reducing and capping agents, combining the controlled process of chemical methods with a substantially improved environmental impact **(Table 1).**

Criterion	Physical	Chemical	Biogenic (green)
Reducing agent	None (energy)	$NaBH_4$, hydrazine, citrate	Phytochemicals / microbial metabolites
Capping/stabilizer	Often none	Synthetic surfactants	Native biomolecules

Criterion	Physical	Chemical	Biogenic (green)
Energy demand	High	Moderate	Low (ambient–mild)
Toxic waste	Low	High	Very low
Cost	High	Moderate	Low
Scalability	Limited	Good	Good (plant routes)
Size control	Good	Excellent	Moderate–good
Green-chemistry fit	Partial	Poor	Strong

Table 1. Comparison of physical, chemical, and biogenic routes to silver nanoparticles against the criteria most relevant to sustainable catalytic application.

The comparison draws out the trade-offs sharply: while chemical synthesis still achieves the best size and shape control and remains the standard in terms of uniformity, its use of dangerous reactants and stabilizers is incompatible in principle with a technology aiming to address environmental problems. By closing much of the gap in control-with attention to pH, temperature, and the extract-to-silver ratio, monodisperse particles within the relevant range can be readily made-while dramatically outperforming on the waste, energy, and cost front, the favorable overall picture for biogenic AgNPs drives the continuing research effort in this area, with a particular focus on water purification.

5. Characterization of Biogenic Silver Nanoparticles

The formation of nanoparticles is validated, and the properties such as size, shape, crystallinity, surface chemistry, and colloidal stability, which dictate their behavior, are quantified by a suite of spectroscopic, diffraction, and microscopic methods. The key methods and their relevant properties are outlined in **Table 2.**

Technique	Information obtained	Typical signature for biogenic AgNPs
UV–Visible spectroscopy	Formation, Plasmon behavior, relative size	SPR absorption band at ≈ 400–450 nm
X-ray diffraction (XRD)	Crystalline phase, crystallite size	FCC Ag peaks: (111),(200),(220),(311)
FTIR spectroscopy	Surface functional groups / capping biomolecules	O–H, C=O, N–H, C–O bands of phenolic/proteins
TEM / HR-TEM	Size, shape, lattice fringes	Spherical particles, commonly 5–50 nm
SEM / FE-SEM	Surface morphology, aggregation	Dispersed near-spherical particles
EDX	Elemental composition	Strong Ag signal (≈ 3 keV)
DLS / zeta potential	Hydrodynamic size, colloidal stability	Narrow PDI; |zeta| high enough for stability

Technique	Information obtained	Typical signature for biogenic AgNPs
TGA	Organic capping content, thermal stability	Mass loss from bound biomolecules

Table 2. Principal techniques used to characterize biogenic silver nanoparticles and the information each provides.

Ultraviolet-visible spectroscopy offers a primary, simpler test; the collective mode of the conduction electrons results in a surface Plasmon resonance band, which, in the case of biogenic AgNPs, falls roughly in the 400 to 450 nm range; the precise location and bandwidth are determined by particle size, shape, and disparity. The X-ray diffraction spectrum reveals a face-centered cubic (FCC) metallic silver structure by (111), (200), (220), and (311) peaks, and the crystallite size can be determined by peak broadening using the Scherrer equation. Fourier-transform infrared spectroscopy determines functional group contribution, hydroxyl, carbonyl, amide, and amine from capping, by position shifts from the free extract, confirming binding.SEM, TEM, and HR-TEM provide images of particle shape and size, with biogenic AgNPs reported as being mainly spherical and ranging in size from 5-50 nm in most systems; energy-dispersive X-ray spectroscopy checks elemental composition, and dynamic light scattering and zeta-potential studies offer insight into hydrodynamic size and colloidal stability; thermogravimetric analysis determines organic capping.

Mechanisms of Catalytic Degradation

The two different mechanisms by which biogenic AgNPs break down the organic contaminants are: a reductive pathway (via electron transfer) occurring in the presence of a chemical reducing agent like sodium borohydride (SBH), and a photocatalytic pathway in the presence of UV-vis light, producing reactive oxygen species (ROS). In both cases, the processes are surface-based and are further facilitated by the high surface-area to volume ratio and efficient electronic properties of the Nano silver.

Borohydride-assisted reductive degradation

The reaction of reduction of 4-nitrophenol to 4-aminophenol using NaBH4 is a classical, standard test for metal nanocatalysts due to being clean, easily followed by uv-vis spectroscopy and also clean. Upon adding borohydride, the color intensifies to become deeply yellow, caused by the nitrophenolate 4-nitrophenolate, the characteristic absorption of which is around 400 nm. Without a catalyst, this process cannot happen, as it is not catalyzed (no kinetic energy), and this reaction can remain unchanged even for several days, because the mutual repellence of borohydride anions and the nitrophenolate causes them to repel and not transfer electrons to each other, not causing anything to happen. Upon placing the metal nanoparticles on it, the 400nm line then falls, as it becomes replaced with a new line around the 300 nm marker, representing the new compound, 4-aminophenol; thus, the solution returns to its original, transparent state, usually after minutes. This procedure can usually be monitored with a standard UV-Vis spectroscopy procedure.

Mechanistically, the metal nanoparticles behave as an electron transfer relay, operating on the Langmuir-Hinshelwood model. The borohydride then attaches itself to the surface of the particle and donates an electron to the metal, raising its'Fermi level. 4-Nitrophenolate anions also bind to the surface, where the transfer of an electron to the surface substrate occurs via nitroso and hydroxylamine derivatives, resulting in an amine. Because there must be both reactants bound to the surface of the particle, the standard kinetics must be those from a Langmuir-Hinshelwood equation. Because excess borohydride must be used, otherwise the reaction cannot be a standard one, the reaction kinetics must therefore become one in which the relative amount of reactant that has not yet reacted falls logarithmically to 0, meaning that in practice it can be followed with pseudo-first-order analysis. Often, it is observed that the reaction occurs very rapidly with an initial acceleration phase. This is caused by any rearrangement occurring on the particle and also due to the removal of dissolved oxygen from the solution and from the metal surface as oxygen, and also any oxidation present on the surface of the metal nanoparticle, will get in the way of any reaction occurring. Any rate constant calculated from the initial linear region of this part of the reaction (specifically any rate constant that has been corrected for the available surface area) will give an objective and thorough comparison with other candidates for the same process. The rate at which dyes such as azodyes and others lose their color upon being reacted with borohydride in the presence of such a nanoparticle is also due to a similar process of the breakage of the conjugation and the chromophoric bonds.

Photo-catalytic oxidative degradation

The photoactivity of biogenic AgNPs is due to their ability to carry out the oxidative degradation and mineralization of dyes in solution without external reactants. Thus, light excites surface Plasmon resonance, generating energetic ("hot") charge carriers; photogenerated electrons reduce dissolved molecular oxygen to the superoxide radical anion, O2−•, while photogenerated holes oxidize surface hydroxyl groups or water to hydroxyl radical, •OH. O2−• and •OH are potent, non-specific oxidants which attack the chromosphere and aromatic frame of the dye, sequentially breaking down and eventually mineralizing it into carbon dioxide, water and inorganic species.

In composite and supported materials, silver often performs a second function of "electron trap," accepting photo-generated electrons from another semiconductor component, thus hindering recombination of electron-hole pairs and enhancing photocatalytic performance.

A schematic outline of the principal steps of the oxidative process can be described as:

$$AgNP + h\nu \rightarrow AgNP\,(e^- + h^+)$$

$$e^- + O_2 \rightarrow \bullet O_2^- \;;\; h^+ + H_2O\,/\,OH^- \rightarrow \bullet OH + H^+$$

$$\bullet OH\,/\,\bullet O_2^- + dye \rightarrow \rightarrow CO_2 + H_2O + \text{inorganic ions}$$

Photo-catalytic decolourisation efficiencies close to total removal were found for some model dye systems (e.g., Methylene blue) in visible or simulated solar light using bio-produced materials; evidence for the roles of OH and O2-radicals can be found in the decrease in decolourisation caused by some radical scavengers.

Kinetic and thermodynamic treatment

The quantitative comparisons between Nano reactions of nonreactors are dependent upon a steady-state kinetic analysis. For the reductive use of borohydride to reduce 4-nitrophenol, the concentration of borohydride was kept in extreme excess so that the concentration of borohydride did not change significantly over the course of the reaction, so the rate is dependent only on the concentration of the pollutants, which can be approximately a first-order reaction.

$$-\,d[C]/dt = k_{app}\,[C]$$

Upon integration, the result is the working equation for the rate constant from the ultraviolet-visible time-course in which the ratio of concentrations is substituted for the ratio of absorbance values at the monitored wavelength (for 4-nitrophenolate, this is near 400 nm):

$$\ln([C]_t\,/\,[C]_0) = \ln(A_t\,/\,A_0) = -\,k_{app}\,t$$

A graph of ln (A/A 0) vs time shows a linear plot in the main part of the reaction, whose gradient gives the apparent rate constant k. Rate constant with respect to the total surface area of catalyst per unit volume, S, is that which is meaningful to the mechanism since catalysis is a surface process:

$$k_{ee} = k_{ap\ \ p} / S$$

The fact that k, rather than k alone, is plotted allows comparison of catalysts with different loadings and particle sizes on equal ground, and failure to do this is often an overlooked feature of the literature. Two other features of the kinetics are more specific. Firstly, there is often a pre-induction time t before the linear region; this corresponds to the time for which surface reconstruction and desolation of surface oxides or of dissolved oxygen occur before steady catalysis commences, and this induction time decreases with increasing catalyst loading. Secondly, k obeys the Arrhenius relation,

$$ln\ k_{ap\ \ p} = ln\ A - E_a / (R\ T)$$

Hence, measuring the rate constant at several temperatures leads to the apparent activation energy, E, by the slope of ln k versus the reciprocal of the temperature. Activation energies cited for nanoparticle-catalyzed 4-nitrophenol reduction are well below those of the unanalyzed pathway, representing the decreased activation energy of the catalyzed reaction. The same pseudo-first-order formalism at the maximum absorbance of the dye is used for photocatalytic and reductive decolourization of heterocyclic-aromatic and azo dyes.

7. Catalytic Performance across Pollutant Classes

A significant and increasing number of studies indicate that biogenic AgNPs have proven to be effective in removing structurally varying types of pollutants. To emphasize the variability of the origin of organisms, the size of particles, and the results and outcomes, we gathered representative examples in Table 3. These results come from individual articles published in the literature and indicate general effects not comparable with one another because we did not consider similar experiments.

Biological source	Pollutant(s)	Size (nm)	Efficiency/rate	Ref.
Viburnum opulus fruit	Tartrazine, carmoisine, brilliant blue FCF ($NaBH_4$)	≈ 16	Efficient decolourisation	[1]
Trigonella foenum-graecum	Methylene blue	≈ 21	96.6%; k ≈ 0.167 min^{-1}	[12]
Trigonella foenum-graecum	Rhodamine B	≈ 21	92.7%; k ≈ 0.200 min^{-1}	[12]
Trigonella foenum-graecum	Methyl orange	≈ 21	71.5%; k ≈ 0.105 min^{-1}	[12]

Biological source	Pollutant(s)	Size (nm)	Efficiency/rate	Ref.
Sodium guava leaf	4-Nitrophenol ($NaBH_4$)	Nano	Colorless in ≈ 8 min	[11]
Convolvulus ardencies	Environmental dyes	Nano	Efficient degradation	[3]
Sanitaria procumbent	Orange G, Direct Blue-15	Nano	Photo-catalytic degradation	[13]
Multiple plant extracts (six dyes)	MB, methyl orange, Congo red, phenol red, orange G, safari O	spherical	Broad-spectrum activity	[14]

Table 3. Representative reports of catalytic and photocatalytic degradation of organic pollutants by biogenic silver nanoparticles. Values are illustrative and taken from the cited primary studies under their respective conditions.

Various observations are made in the broader literature. Cationic dyes are found to be degraded more extensively than anionic ones, such as methyl orange or methylene blue, under the same operating conditions, and the rationale for this is attributed to the attraction between the dye and the biomolecule–coated particle surface. In most cases, reductive color bleaching by borohydride occurs faster than the only photoreduction reaction, but the merit is the generation of oxidative mineralization under light alone, with a concomitant consumption of chemical oxidant. Typical rate constant values are observed in a wide range due to intrinsic differences in reactivity and a great impact of the amount of catalyst, substrate concentration, and temperature on the measured value, and thus comparison of rate constants must be conducted under the full details of the conditions, and ideally, they should be calculated per surface area of catalyst.

8. Factors Affecting Catalytic Efficiency

The catalytic activity of biogenic AgNPs is dictated by a complex interplay of material and operating conditions:

- Particle size and surface area. Since the catalytic process takes place on the particle surfaces, smaller particles with a high surface-to-volume ratio are associated with increased numbers of active sites and higher reaction rates; the nanoparticle surface area has a clear relationship with the observed rate constant of catalyzed reactions.
- Shape and exposed facets. Different crystalline faces of particles expose unique surfaces with differing energies, so a particle's non-spherical nature (anisotropic nature) may influence its behavior when compared to a spherical nanoparticle of the same volume.
- Catalyst dose: Increasing amounts of catalyst add additional active sites, which result in faster rates up to a certain limit imposed by

either limitations in reactant transport or light absorption within the reaction vessel.

- The capping layer, in addition to stabilizing biogenic particles against aggregation, the bimolecular shell can mediate adsorption of reactants; however, a too-thick or strongly adhering shell may block the active sites and hinder reactivity. Factors that affect the thickness and composition of this layer can play a major role and often represent the most poorly defined aspect of a biogenic catalyzed process.
- PH and temperature. pH alters the electrostatic charge of the catalyst and reactant, thus controlling their electrostatic attraction, while the reaction rate increases with temperature according to the Arrhenius relationship, which can be used to calculate activation energy
- Substrate and reluctant concentration. The relative concentration of the pollutant being degraded has a critical influence on the kinetics observed and the applicability of any simplifications

9. Reusability, Stability, and Real-Effluent Applicability

However, for application as a catalyst, the nanoparticles must maintain activity during re-use and be effective in the chemically complex environment of wastewater, rather than in simplified, single-component model solutions. In many reports of the use of biogenic AgNPs, the activity is maintained at high levels for many cycles, with loss in activity attributed to some nanoparticle aggregation, losses during nanoparticle recovery, and blockage or poisoning of the catalytic surface by the accumulated reaction products. To enhance the recovery and durability of the nanoparticles, many reports utilize supports, for example, reduced graphene oxide, cellulose, chitosan, polymer beads, or metal oxides, in order to fix the AgNPs in position. Furthermore, the use of supports has often been found to contribute to the catalytic performance through the facilitation of charge transfer.

Biogenic AgNPs are inherently colloidally stable, largely due to the bimolecular coating on the particles, and this may also result in improved shelf life of stored dispersions of the particles. The performance of these biogenic catalysts in real industrial wastewater or solutions with a closer approximation to industrial wastewater, i.e., competitive systems, has been much less studied compared to single-pollutant model systems, and it is this aspect that requires significant strengthening for future development and industrial translation of biogenic AgNPs technology. Real wastewater includes other ions, natural organic matter, and mixtures of products and dyes at varying concentrations and pH, all of which will affect catalytic activity. Some preliminary studies on biogenic AgNPs in real or simulated industrial effluents have shown useful activities, but significant progress requires detailed investigations of these systems under realistic competitive conditions, coupled with consideration of the eventual fate of the silver.

10. Green-Chemistry and Sustainability Assessment

The main attraction of biogenic AgNPs is that they match their catalytic action with the spirit of green chemistry. Typical chemical synthesis of AgNPs often uses hazardous reagents, organic solvents, and synthetic stabilizers that produce toxic by-products; instead, biogenic synthesis uses renewable biological reductants, works in aqueous media, and operates at near room temperature, requiring low energy input. When measured against the 12 principles of green chemistry, this approach performs favorably on the principles of waste prevention, design for safer solvents and auxiliaries, energy efficiency, use of renewable raw materials, and use of inherently safer chemistry. As is often the case, these raw materials come from agricultural and food waste, and the process can add valorization of this biomass as well.

A level assessment, however, needs to factor in the costs, which can be quite high, as silver is a relatively costly precursor, while any released nanoparticles have established ecotoxic effects on aquatic life, so a life-cycle perspective balancing the destruction of pollutants with silver usage and release burden is needed. The most environmentally sound systems are therefore the ones using low silver loading, immobilizing the particles so that they will not leach and recover/re-use the catalyst at optimum efficiency. In these conditions, the production of AgNPs by the biological route will make a less damaging process in terms of the production process when contrasted to conventionally synthesized nanoparticles.

11. Comparison with Other Catalytic Nanomaterials

But silver is far from the only metal or material being used for the catalytic destruction of organic pollutants, and contextualizing the use of biogenic AgNPs is illuminating both in terms of where they excel and when you might want to use something else instead. Gold and palladium nanoparticles are other well-established noble metal catalysts that perform well in borohydride-assisted reductions, and, in common with AgNPs, are often prepared in a biogenic manner via the same plant-extract protocols; indeed, palladium is especially active for hydrogenation-style reactions, though both metals cost considerably more than silver and silver provides the additional advantage of inherent antimicrobial properties beneficial in water purification. Semiconductor oxides such as titanium dioxide and zinc oxide represent the standard photocatalysts and do a good job of mineralizing dyes, but typically suffer from wide band gaps, and their photocatalysis only extends into the visible part of the spectrum with additional doping or coupling with a plasmonic metal.

It is precisely at this point where silver is integrated into these oxide frameworks to enhance performance: the plasmatic properties of AgNPs allow light absorption across the whole spectrum from UV to visible while also functioning as a charge sink to improve the overall photo-efficiency.

Green synthesized iron nanoparticles provide an alternative and complementary pathway for dye degradation through the generation of Fenton/Fenton-like oxidation of the pollutants via hydroxyl radicals and also offer excellent opportunities in terms of cost and resource availability. Ultimately, what you get is not a single "best" material, but a collection of options, with biogenic AgNPs standing out due to the excellent synergistic combination of highly active catalytic sites for both oxidation and reduction, a versatile plasmatic functionality enabling light absorption over the full solar spectrum, antimicrobial capability, and the environmental benefit of the green production method, all of which together render them a broadly appealing solution for wastewater treatment.

12. Challenges and Future Perspectives

There are a few challenges to overcome, however, before the current state-of-the-art can be used outside the lab, despite promising laboratory outcomes. First is reproducibility. Variations between batches can be experienced in terms of particle size, morphology, and capping chemistry, and subsequently in catalytic activity, because the chemical composition of botanical extracts differs according to species, source, season, part of the plant, and preparation process. A standard process for extract production and quantified reporting of process parameters is needed for comparing and transferable results.

The incomplete knowledge of how biogenic synthesis operates- the exact identities of the capped/reduced molecules are typically assumed rather than demonstrated, and for this reason, rational design has become impeded. Scale-up of these from volumes of milliliters to liter capacities required for treating water on an industrial scale poses unanswered questions in respect of cost, continuous operation, and product quality. The nanotoxicological profile and effects of any particles released into water environments should be determined and managed. Lastly, the majority of currently existing studies have concentrated solely on either a single polluting chemical or a model solution, whereas industrial wastewater streams contain multiple pollutants.

Future research will need to focus on improving production reproducibility and standardized reporting; establishing identities of catalytically active molecules using advanced analytical techniques; design of immobilized or supported catalysts that simultaneously are highly efficient but easy to remove and with very low release of silver ions; real-time monitoring and validation under realistic industrial wastewater conditions in the presence of competing species, along with rigorous analyses of techno-economic benefits and total lifecycle. In the long term, hybrid processes combining various treatment technologies would be beneficial.

13. Conclusion

An Attractive Nano-catalytic Platform for Environmental Remediation Based on Biogenic Silver Nanoparticles and Environmental Applications. Biogenic silver nanoparticles are favorably poised at the interface between nano-catalysis and green chemistry. Derived from microorganisms or plant extracts under environmentally benign aqueous conditions and avoiding many hazardous reagents of colloidal chemistry, these particles exhibit potent catalytic activity against those pollutant groups that typically resist classical treatment. Specifically, these particles are highly efficient toward both nitro aromatic reduction and dye photo catalytic degradation with the underlying mechanisms readily explained by an electron-relay, Langmuir-Hinshelwood mechanism in borohydride-driven reductions and a reactive-oxygen-species (ROS) based photo catalytic pathway in oxidative transformations of pollutants. Extensive reports document the rapid degradation of a broad range of pollutants by diverse biomaterial-derived AgNPs, with performance being tuned via particle size and morphology, dose, temperature, pH, and composition of the biomolecular surface corona. These features, together with significant efforts toward their scale-up and use as immobilized heterogeneous catalysts, suggest that biogenic AgNPs are technically feasible and ecologically sound photocatalysts. This narrative review explores a wide body of work that demonstrates the potential to effectively mitigate pollutants through this approach while it addresses remaining scientific challenges such as catalytic reproducibility, mechanical understanding, material stability/reuse, nanotoxicological aspects, and the need to validate activity with realistic effluent.

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