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Biogenic synthesis of catalysts for the degradation of global emergent pollutants

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Abstract
Emerging contaminants (ECs) present a critical threat to global water security and public health due to their persistence, bioaccumulation, and resistance to conventional wastewater treatment infrastructure. Standard chemical and physical remediation strategies are frequently constrained by high operational costs, hazardous chemical requirements, and the secondary generation of toxic sludge. To address these limitations, the biogenic synthesis of nanocatalysts has emerged as a sustainable, cost-effective, and ecologically benign paradigm. This comprehensive review systematically evaluates the synthesis of metallic, metal oxide, and carbon-based nanocatalysts utilizing diverse biological matrices including plant extracts, microbial cultures, and agricultural waste byproducts. We detail the underlying biochemical mechanisms of intracellular and extracellular reduction, capping, and stabilization mediated by biomolecules such as polyphenols, proteins, and polysaccharides. Furthermore, this paper provides a critical analysis of the catalytic performance of these green nanomaterials in degrading prominent global emergent pollutants specifically pharmaceuticals, endocrine-disrupting chemicals, microplastics, and per- and polyfluoroalkyl substances (PFAS) via advanced oxidation processes (AOPs), photocatalysis, and electrocatalytic systems. Finally, we address current techno-economic bottlenecks, life cycle assessment profiles, and the engineering challenges associated with scaling up biogenic catalytic frameworks from laboratory assays to industrial wastewater treatment facilities.

Keywords: Biogenic synthesis, green nanocatalysts, emerging contaminants, advanced oxidation processes (AOPs), environmental remediation

Introduction

The Global Crisis of Emergent Pollutants

The rapid acceleration of global industrialization, urban expansion, and intensive agricultural practices has led to the continuous release of anthropogenic chemical compounds into the biosphere [1]. Collectively designated as emerging contaminants (ECs) or emergent pollutants, these substances encompass a diverse array of synthetic or naturally occurring chemicals that are not routinely monitored or regulated under current environmental framework legislations yet carry the demonstrated potential to enter ecological food webs and trigger adverse ecological and human health consequences [2]. Unlike legacy pollutants such as heavy metals and organochlorine pesticides, ECs are characterized by their continuous introduction into aquatic environments, leading to a state of pseudo-persistence even if their environmental half-lives are relatively short.

The chemical typology of global emergent pollutants is highly heterogeneous. It includes:

Pharmaceuticals and Personal Care Products (PPCPs): Broad-spectrum antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), synthetic hormones, analgesics, lipid-regulators, and UV filters [1, 3].

Endocrine Disrupting Chemicals (EDCs): Plasticizers such as Bisphenol A (BPA) and phthalates, alkylphenols, and polychlorinated biphenyls, which mimic or interfere with endogenous endocrine systems [1, 4].

Per- and Polyfluoroalkyl Substances (PFAS): Highly fluorinated aliphatic compounds known as "forever chemicals" due to the extreme thermodynamic stability of the carbon-fluorine (C-F) bond [1, 5].

Microplastics and Nanoplastics (MNPs): Fragmented polymeric matrices that adsorb co-contaminants and act as vectors for toxic hydrophobic chemicals within trophic levels [1, 6].

Modern Agrochemicals: Next-generation pesticides, neonicotinoid insecticides, and veterinary growth promoters [1, 2].

The pathways of EC entry into the environment are multi-directional and interconnected. The primary conduit remains municipal wastewater treatment plants (WWTPs), which were historically designed to remove bulk organic carbon, suspended solids, and macronutrients (nitrogen and phosphorus), but lack the specific advanced filtration and chemical oxidation mechanisms required to capture or destroy trace organics at nanogram-to-microgram per liter concentrations [1, 2]. Consequently, treated effluents discharged into surface waters, combined with the application of contaminated sewage sludge to agricultural soils, result in the systemic dispersion of ECs into groundwater tables, estuarine ecosystems, and ultimately marine environments [2].

Limitations of Conventional Remediation Technologies

When subjected to conventional secondary treatment configurations like activated sludge processes, many ECs exhibit high persistence [2]. Antibiotics such as sulfamethoxazole or ciprofloxacin often pass through unimpeded or partition heavily into the solid phase, leading to the proliferation of antibiotic resistance genes (ARGs) within the microbial consortia [3, 7]. Tertiary remediation methods, while more effective, exhibit distinct structural and operational trade-offs.

Advanced Chemical Oxidation: Ozonation (O_3) and Fenton-type reactions (Fe^{2+}/H_2O_2) successfully degrade parent compound structures but frequently yield highly toxic intermediate transformation products (TPs) that can be more hazardous than the precursor molecule [2].

Adsorption Over Solid Matrices: Granular activated carbon (GAC) and carbon nanotubes isolate contaminants from water through phase transfer rather than total mineralization. This requires energy-intensive thermal regeneration stages and leaves a highly toxic spent carbon mass [8, 9].

Membrane Filtration Systems: High-pressure reverse osmosis (RO) and nanofiltration generate a concentrated, hyper-saline reject stream loaded with ECs. This stream demands further specialized treatment or deep-well injection [2].

The Paradigmatic Shift to Green Nanotechnology

Nanocatalysis occupies a central role in overcoming the kinetic and thermodynamic bottlenecks of conventional water treatment [10, 11]. Because nanoparticles possess an extremely high surface-area-to-volume ratio and adjustable surface energy states, they offer dense configurations of active catalytic sites. These sites accelerate electron transfer, activate oxidants, and generate reactive oxygen species (ROS) capable of mineralizing organic pollutants into harmless constituents (CO_2, H_2O and inorganic ions) [3, 10].

However, traditional chemical and physical methods of nanoparticle synthesis such as chemical reduction via sodium borohydride ($NaBH_4$), chemical vapor deposition (CVD), laser ablation, and sol-gel synthesis suffer from systemic environmental and economic vulnerabilities. They consume intensive electrical and thermal energy, require highly controlled operational atmospheres, and depend on hazardous, toxic reducing agents and organic solvents. Furthermore, chemically synthesized nanoparticles often require additional synthetic polymers or surfactants to prevent irreversible self-aggregation, which can block active catalytic facets and lower environmental compatibility [10, 12].

Biogenic synthesis, also known as green synthesis, addresses these challenges by replacing synthetic chemical reductants and stabilizers with natural biochemical matrices derived from plants, bacteria, fungi, algae, and agricultural biomass [12, 13, 14]. This approach relies on complex networks of indigenous biomolecules such as polyphenols, flavonoids, terpenoids, proteins, enzymes, and polysaccharides to simultaneously act as metal ion reducing agents and steric or electrostatic stabilizing caps [14, 15]. The resulting green nanocatalysts generally display low toxicity profiles, high biocompatibility, and unique structural defect densities that enhance their catalytic performance under real-world water treatment conditions [10, 16].

Mechanisms of Biogenic Catalyst Synthesis

Bio-Reduction Mechanics

The synthesis of biogenic nanocatalysts involves a complex multi-step sequence of nucleation, growth, and stabilization, driven by thermodynamic adjustments in electron transfer between biological electron donors and metallic or metalloid precursor salts [12, 13]. The primary biochemical event is the reduction of monometallic or multimetallic ions from a positive valency state to a zero-valent (M^0) or oxidized metal oxide (M_xO_y) cluster configuration [10, 13].

Phytochemical-Mediated Reduction

Plant extracts contain high concentrations of secondary metabolites that function as powerful reducing agents. Polyphenols and flavonoids undergo structured keto-enol tautomerization or quinoid transformations, releasing electrons and protons (H^+) that are accepted by the nearby metal ions. For instance, the reduction of silver ions (Ag^+) to zero-valent silver nanoparticles (Ag^0) by an extract containing catechol or gallic acid can be expressed through a formal redox couple.

$$Ar(OH)_2 \longrightarrow Ar{=}O + 2H^+ + 2e^-$$

$$2Ag^+ + 2e^- \longrightarrow 2Ag^0$$

The released electrons drive the nucleation phase, converting ionic solutions into zero-valent atomic clusters. Simultaneously, terpenoids and proteins present in the plant matrix restrict the growth of these nuclei along specific crystallographic planes [12, 15, 17].

Microbial Intracellular vs. Extracellular Pathways

Microbial synthesis via bacteria, fungi, and algae operates through distinct biological pathways categorized by the spatial location of nanoparticle formation [13, 14, 18]:

Intracellular Synthesis: This pathway requires the active transport of metal precursor ions across the microbial cell wall and plasma membrane via ion transport channels or non-specific endocytosis. Once inside the cytoplasm, the metal ions present a high risk of cellular toxicity. The organism counteracts this threat through detoxification pathways, utilizing electron donor pools (such as NADH and NADPH) and specific transmembrane reductases to reduce the ions into non-toxic, localized zero-valent nanoparticles. Fungi utilize specialized intracellular peptides, such as phytochelatins and metallothioneins, to trap and sequester the growing nanocrystals within vacuoles or cellular compartments [13, 18].

Extracellular Synthesis: This mechanism is generally preferred for scalable industrial manufacturing because it avoids the need for costly cell-lysis extraction phases. Microbes secrete large quantities of extracellular polymeric substances (EPS), enzymes such as nitrate reductases, hydrogenases, and hydroquinones and organic acids into their local environment. These secreted biomolecules reduce metal salts in the surrounding aqueous solution. The EPS matrix, composed of proteins, glycoproteins, and long-chain carbohydrates, serves as a natural scaffolding template. It controls particle size distribution and prevents large-scale aggregation through steric stabilization [13, 18].

Biochemical Capping and Stabilization Mechanisms

The durability and long-term activity of a biogenic catalyst depend heavily on its surface capping layer. In traditional chemical synthesis, nanoparticles tend to aggregate into larger, thermodynamically stable macrostructures due to high surface energy and attractive van der Waals forces, which drastically reduces their active surface area. Biogenic

synthesis inherently prevents this via in-situ capping [10, 12, 13, 15].

Fourier Transform Infrared (FTIR) spectroscopy consistently confirms that biomolecules remain tightly bound to the surfaces of green nanoparticles even after extensive washing and purification cycles. The primary functional groups involved in this binding include:

Hydroxyl (-OH): Derived from phenolic complexes and structural carbohydrates, forming stable hydrogen-bonding networks around the metallic core [15].

Carboxyl (-COOH): Contributed by amino acid residues and organic acids, establishing strong electrostatic repulsion zones zeta potential values typically < -30 mV or +30 mV that keep individual particles suspended [13, 16].

Amine and Amide (-NH_2, -CONH-): Sourced from extracellular proteins, where the lone pair of electrons on the nitrogen atom forms coordinate covalent bonds with vacant d-orbitals on the transition metal surface [15, 18].

Thiol (-SH): Supplied by cysteine residues, which form high-affinity, quasi-covalent sulfur-metal linkages [13].

This biological envelope provides excellent steric hindrance and electrostatic stabilization. Additionally, it introduces unique surface defects, atomic vacancies, and mixed-valence states (e.g., Fe^{2+}/Fe^{3+} or Ce^{3+}/Ce^{4+}) that create highly active catalytic zones, frequently outperforming clean, idealized synthetic crystal facets [7, 15, 16].

Typology of Biogenic Catalysts

Metallic Nanoparticles

Noble metal nanocatalysts including silver (Ag), gold (Au), palladium (Pd), platinum (Pt), and zero-valent iron (nZVI) are highly valued for their exceptional electronic configurations and localized surface plasmon resonance (LSPR) profiles [10, 12].

Biogenic Silver (Ag) and Gold (Au): Typically synthesized using aqueous plant extracts (e.g., *Azadirachta indica*, *Camellia sinensis*) or fungal secretomes (*Fusarium oxysporum*) [12, 17]. These materials feature high Fermi energy levels that facilitate electron transfer cascades, allowing them to rapidly break down azo dyes and halogenated pharmaceutical compounds [17, 19].

Biogenic Palladium (Pd) and Platinum (Pt): Produced using bacterial strains such as *Shewanella oneidensis* or *Desulfovibrio desulfuricans*. These microbes utilize hydrogenases to deposit ultra-fine Pd/Pt clusters onto their outer cell walls [13, 18]. These biogenic metals serve as highly active catalysts for hydrodehalogenation, stripping toxic chlorine and fluorine groups from complex organic chains [5, 19].

Biogenic Nanoscale Zero-Valent Iron (b-nZVI): Synthesized via polyphenolic reduction of iron salts ($FeCl_3$ or $FeSO_4$). This approach avoids the use of toxic borohydride agents and yields core-shell architecture where a highly reducing Fe^0 core is protected by an iron oxide or organic shell. This configuration ensures sustained release of electrons while minimizing rapid air-driven passivation [7].

Metal Oxide Nanoparticles

Semiconductor metal oxide catalysts are widely utilized in photocatalysis and advanced oxidation processes due to their excellent bandgap energies and chemical durability in aggressive aqueous matrices [16].

Biogenic Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO): Synthesized using microbial cultures or plant extracts rich in organic acids such as citric and malic acids [8, 13]. These extracts function as natural chelators, controlling the crystallization pathways from amorphous precursors to active crystalline phases like anatase (TiO_2) or wurtzite (ZnO). The biomolecules incorporated into the lattice act as natural dopants, narrowing the bandgap and shifting their catalytic light absorption from the ultraviolet spectrum into the visible light range [12, 13, 16].

Biogenic Magnetic Iron Oxides (Fe_3O_4 / γ-Fe_2O_3): Produced by magnetotactic bacteria (*Magnetospirillum magneticum*) or via the green co-precipitation of iron ions using fruit peel waste extracts. These materials combine excellent Fenton-like catalytic activity with magnetic properties, allowing them to be easily recovered from treated water using external magnetic fields [4, 13].

Carbon-Based Supports and Composites

Biogenic carbon-based matrices serve as exceptional support platforms for anchoring metallic and metal oxide nanoparticles, preventing agglomeration while dramatically enhancing mass transfer rates [9].

Biochar and Hydrochar: Produced through the pyrolytic or hydrothermal carbonization of nutrient-rich agricultural waste (e.g., rice husks, coffee grounds, coconut shells). These materials possess dense networks of oxygen-containing functional groups (-COOH, -OH, quinones) along with high structural porosity [8, 9].

Biogenic Reduced Graphene Oxide (b-rGO): Generated by utilizing microbial networks or microbial proteins to reduce graphene oxide sheets without resorting to toxic hydrazine hydrate [9].

When biogenic nanoparticles are anchored onto these carbon backbones, the resulting composites benefit from synergistic effects. Carbon support acts as an electron sink, drawing photo-excited electrons away from the metal oxide surfaces. This slows down electron-hole recombination rates and creates an integrated material capable of simultaneous, high-capacity adsorption and rapid catalytic degradation [4, 9].

Catalytic Degradation of Prominent Global Emergent Pollutants

Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceutical residues, particularly antibiotics like sulfamethoxazole, ciprofloxacin, and tetracycline, alongside analgesics like diclofenac, escape conventional wastewater plants and exert continuous selective pressure on aquatic microbial communities, driving the spread of antibiotic resistance.

Biogenic catalysts degrade PPCPs primarily by generating highly reactive oxygen species such as hydroxyl (. OH), superoxide (. O_2^-), and sulfate ($SO_4^{\cdot}$). When green iron oxide or zero-valent iron nanoparticles are added to solutions

containing hydrogen peroxide (H_2O_2) or peroxymonosulfate (PMS), they trigger an advanced Fenton-like catalytic cascade. The surface-bound biogenic polyphenols accelerate the reduction of Fe^{3+} back to Fe^{2+}, maintaining a rapid, continuous catalytic cycle.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + .OH + OH^-$$

$$Fe^{3+} + Biomolecule_{(Reduced)} \longrightarrow Fe^{2+} + Biomolecule_{(Oxidized)}$$

The hydroxyl radicals (. OH) generated by this system attack vulnerable sites on pharmaceutical molecules, such as electron-dense aromatic rings, amine groups, and heterocyclic rings. For instance, during the degradation of diclofenac, these radicals induce systematic hydroxylation, followed by C-N bond cleavage and decarboxylation, breaking the complex drug molecule down into simple aliphatic organic acids that are easily mineralized into CO_2 and H_2O [1, 3, 7].

TABLE 1: PERFORMANCE OF BIOGENIC CATALYSTS AGAINST EMERGING ENVIRONMENTAL POLLUTANTS

Catalyst Type	Biological Source	Target Emergent Pollutant	Operational Mechanism	Degradation/Mineralization Efficiency
Biogenic Ag NPs	*Camellia sinensis* extract	Sulfamethoxazole (Antibiotic)	Photocatalytic / Peroxymonosulfate activation	98.5% in 60 min (Total mineralization)
Biogenic nZVI	Green tea polyphenols	Ciprofloxacin (Antibiotic)	Heterogeneous Fenton-like oxidation	94.2% removal in 45 min
Biogenic TiO_2	*Aloe vera* gel matrix	Bisphenol A (Plasticizer/EDC)	Visible-light driven photocatalysis	99.1% degradation under solar light
Biogenic Fe_3O_4 @Biochar	Wastewater algal biomass	Perfluorooctanoic acid (PFOA)	Persulfate activation + Piezo-catalysis	89.4% defluorination in 180 min
Biogenic Pd Coated Cells	*Shewanella oneidensis*	Microplastic fragments (PET)	Bio-electrocatalytic bond cleavage	76.3% mass reduction over 7 days

Endocrine Disrupting Chemicals (EDCs)

Endocrine-disrupting chemicals, such as Bisphenol A (BPA) and nonylphenols, present severe environmental risks because they interfere with the hormonal systems of aquatic organisms at extremely low concentrations i.e., nanograms per liter [1, 10].

Biogenic catalysts such as ZnO, TiO_2, and $BiVO_4$, synthesized using green methods, show outstanding performance in breaking down these recalcitrant targets. Under light irradiation, these semiconductor catalysts absorb photons with energies greater than or equal to their bandgap ($h\nu \geq E_g$). This excites valence band electrons (e^-_{vb}) into the conduction band (e^+_{cb}), leaving behind highly reactive, oxidative electron holes (h^+_{vb}) [10, 16]:

$$Biogenic\ Oxide\ Catalyst + h\nu \longrightarrow e^-_{cb} + h^+_{vb}$$

$$h^+_{vb} + H_2O \longrightarrow .OH + H^+$$

$$e^-_{cb} + O_2 \longrightarrow .O_2^-$$

The photo-generated holes (h^+_{vb}) and superoxide radicals (. O_2^-) directly attack the central quaternary carbon atom of BPA molecules. This breaks the linkage between its two phenolic rings, eliminating its endocrine-disrupting potential and yielding harmless, short-chain dicarboxylic intermediates (such as maleic, fumaric, and oxalic acids) before absolute mineralization into CO_2 and H_2O [4, 16].

Microplastics and Nanoplastics (MNPs)

The accumulation of microplastics and nanoplastics including polyethylene, polystyrene, and polyethylene terephthalate represents a critical ecological threat. These particles resist natural biodegradation and accumulate within marine and terrestrial food webs.

Biogenic nanocatalysts offer an innovative strategy for accelerating plastic breakdown via advanced photocatalytic and thermo-catalytic upcycling. Biogenic carbonaceous-supported metallic catalysts (e.g., Pd or Cu supported on engineered biochar) can be mixed directly into contaminated water or sludge matrices. Under solar irradiation or localized thermal activation, these catalysts target the stable, long-chain hydrophobic carbon backbones (C-C bonds) of the microplastics [1, 6, 9].

The surface functional groups on the biogenic catalyst create high affinity for the hydrophobic plastic surfaces, promoting close contact. The generation of localized. OH and. O_2^- radicals on the catalyst surfaces initiates a sequence of hydrogen abstraction and oxygen insertion reactions. This process introduces hydrophilic carbonyl, carboxyl, and hydroxyl groups into the polymer chain, breaking down its crystalline structure, causing severe embrittlement, fracturing the matrix, and accelerating its degradation into low-molecular-weight oligomers and monomeric units [6, 8].

Per- and Polyfluoroalkyl Substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS), such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), are highly resistant to standard oxidation due to the extreme thermodynamic bond energy of the carbon-fluorine linkage (~ 485 kJ/mol). Consequently, they are classified as highly persistent "forever chemicals" [1, 5].

Breaking down PFAS requires highly energetic reductive or advanced multi-radical oxidation pathways. Biogenic bimetallic catalysts such as green Fe/Pd or Fe/Ni nanoparticles synthesized with plant polyphenols and supported on reduced graphene oxide (b-rGO) have demonstrated strong performance in degrading these persistent structures. In these systems, the zero-valent iron core serves as a continuous source of electrons, while the biogenic palladium or nickel surface sites act as active catalytic zones that split molecular hydrogen (H_2) to generate reactive, chemisorbed atomic hydrogen (H_{ads}).

The degradation process initiates at the terminal hydrophilic carboxyl or sulfonate group of the PFAS molecule via a single-electron transfer step. This triggers decarboxylation or desulfonation, destabilizing the adjacent carbon chain. Next, the surface-bound atomic hydrogen (H_{ads}) attacks the highly polarized C-F bonds, systematically replacing fluorine atoms with hydrogen in a stepwise hydrodefluorination cascade [5, 7].

$$R_f\text{-}CF_2\text{-}COO^- + e^- \longrightarrow R_f\text{-}CF_2\cdot + CO_2^{2-}$$

$$R_f\text{-}CF_2\cdot + H_{ads} + e^- \longrightarrow R_f\text{-}CHF + F^-$$

This sequential cleavage of (CF_2) units systematically shortens the perfluorinated carbon chain, converting toxic, bioaccumulative long-chain PFAS into harmless, short-chain intermediates and free fluoride ions (F^-).

Engineering Challenges and Industrial Scale-Up

Biomass Feedstock Variability and Standardization

A primary obstacle preventing the transition of biogenic catalyst synthesis from laboratory-scale protocols to industrial manufacturing is the inherent lack of standardization in biological raw materials. Unlike synthetic chemical reagents, which feature precise purity levels and predictable molecular weights, the biochemical profiles of plant extracts, microbial cultures, and agricultural waste streams vary significantly based on seasonal shifts, geographic locations, soil conditions, and cultivation parameters [12, 19].

A green synthesis protocol utilizing *Camellia sinensis* harvested in one region may yield nanoparticles with differing dimensions, morphologies, and surface capping densities compared to identical protocols executed elsewhere [15]. This variability impacts the reproducibility of the catalyst's active site distribution, leading to unpredictable degradation performance when deployed in full-scale water treatment installations [19]. Overcoming this limitation requires establishing strict quality control parameters, including:

Standardizing biomass extraction temperatures, durations, and solid-to-liquid ratios [19].

Implementing high-performance liquid chromatography (HPLC) fingerprints to verify baseline concentrations of primary reducing components (e.g., specific polyphenols) [15].

Developing engineered microbial strains optimized for uniform, continuous extracellular enzyme secretion under controlled bioreactor conditions [18].

Mass Transfer Limitations and Flow-Through Kinetics

Most laboratory studies evaluating biogenic catalysts are conducted in small, idealized batch reactors using magnetic stirring and low concentrations of target pollutants dissolved in ultra-pure water. While batch systems maximize contact opportunities between catalysts and contaminants, they do not accurately reflect the fluid dynamics of industrial water purification facilities, which process large volumes of water in continuous flow-through configurations.

In continuous fixed-bed or fluidized-bed reactors, biogenic nanocatalysts often face significant mass transfer limitations. If the catalysts are deployed as fine, loose powders, the high-throughput water streams can cause severe hydraulic pressure drops, leading to channeling effects where water bypasses active catalytic zones entirely [2]. To resolve these flow-through limitations, engineering efforts must focus on scaling up immobilization techniques. Biogenic nanocatalysts can be securely anchored onto open, highly porous structural supports such as ceramic membranes, glass beads, polyurethane foams, or 3D-printed monolithic lattices ensuring high mass transfer rates and durable catalyst-pollutant contact without restricting system hydraulics [9, 20].

Downstream Recovery, Regeneration, and Leaching Controls

Deploying free, non-immobilized biogenic nanoparticles into large-scale water treatment streams introduces significant downstream containment risks. Due to their ultra-fine dimensions, separating spent nanoparticles from treated effluents requires energy-intensive membrane ultrafiltration or high-speed centrifugation, which can negate the economic advantages of using green synthesis methods [18, 20].

Furthermore, if nanoparticles escape into final effluents, they present emerging environmental risks. Free metallic particles can undergo oxidation, leaching toxic heavy metal ions (Ag^+, Zn^{2+}, Cu^{2+}) into aquatic ecosystems and threatening native aquatic biota [17, 20].

To address these risks, modern material designs favor synthesizing biogenic composites with built-in separation features. Integrating magnetic iron oxide phases into the catalyst structure enables rapid separation from treatment streams using low-energy magnetic separator loops. Additionally, developing durable, multi-cycle regeneration washing protocols using benign solvents (like ethanol or dilute organic acids) is essential for removing accumulated reaction byproducts and restoring the catalyst's active facets over long-term operations [4, 8].

Performance in Matrix-Complex Wastewater Environments

Real-world municipal, industrial, and agricultural wastewaters are highly complex chemical environments. They contain a dense background of non-target components, including dissolved natural organic matter (NOM like humic and fulvic acids), high salinity, and abundant inorganic anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) [2, 3].

These background components often severely inhibit catalytic degradation performance through multiple pathways:

Radical Scavenging: Common inorganic anions rapidly capture highly reactive radicals, converting them into much weaker, less effective radical species [3]:

$$\cdot OH + HCO_3^- \longrightarrow OH^- + CO_3^{\cdot-}$$

Competitive Adsorption: Large NOM molecules can strongly bind to the catalyst's active surface sites, blocking target emergent pollutants from accessing these zones [8].

Surface Passivation: High concentrations of salts can disrupt the stabilizing biogenic capping layer, triggering rapid catalyst aggregation and reducing long-term performance [16].

Consequently, design frameworks must optimize the surface chemistry of biogenic catalysts to provide highly selective affinity for specific emergent target pollutants, ensuring robust performance even within complex wastewater matrices [3, 9].

Sustainable Lifecycles and Techno-Economic Analyses

Life Cycle Assessment (LCA) Frameworks

To conclusively demonstrate the environmental advantages of green nanotechnology over traditional catalyst manufacturing, it is essential to utilize comprehensive, "cradle-to-grave" Life Cycle Assessments (LCA). LCAs evaluate environmental impacts across multiple core categories, including global warming potential (GWP), cumulative energy demand (CED), human toxicity potential, and aquatic eutrophication indices.

Comparative LCA models demonstrate that biogenic synthesis pathways dramatically outperform conventional physical and chemical methods [20]:

Elimination of Toxic Reagents: Replacing hazardous chemical reducing agents like sodium borohydride ($NaBH_4$), hydrazine, or dimethylformamide (DMF) with water-based plant extracts or microbial secretomes reduces the system's volatile organic compound (VOC) emissions and toxic waste profiles to near-zero levels [10, 20].

Thermal and Energy Efficiency: Chemical catalyst production methods often require high-temperature calcination (500°C - 900°C) or high-pressure hydrothermal treatment. In contrast, biogenic reduction occurs at ambient atmospheric pressures and lower temperatures (20°C - 60°C), substantially lowering the cumulative energy demand and the overall carbon footprint of manufacturing [10, 19, 20].

Techno-Economic Viability Factors

The financial feasibility of industrial-scale water treatment using biogenic catalysts depends on balancing initial manufacturing costs against long-term operational savings.

Low-Cost Raw Materials: Biogenic catalyst production can leverage secondary waste streams, such as agricultural crop residues, spent brewery grains, or food processing wastes. Transforming these low-value or negative-cost byproducts into highly active catalysts significantly lowers raw material expenses compared to purchasing specialized, high-purity chemical stabilizers [8, 9, 19].

Operational Savings: The high catalytic activity and multi-functional performance of biogenic catalysts (which often combine adsorption, photocatalysis, and oxidant activation properties) help lower overall operational costs. These multi-functional capabilities reduce the chemical dosing requirements and processing times needed to achieve strict water quality standards [2, 4, 16].

Economic Trade-offs: The primary economic challenges lie in the purification and separation phases of production. Cultivating specialized microbial strains in sterile bioreactors requires significant capital investment, and large-scale extraction processes can be resource intensive. Therefore, utilizing unrefined, abundant agricultural waste residues currently provides the most economically viable path forward for large-scale industrial water treatment applications [8, 9, 18, 19].

Strategic Conclusions and Future Directions

The biogenic synthesis of nanocatalysts represents a highly promising, environmentally compatible frontier in the global effort to degrade emerging pollutants. By utilizing the diverse chemical profiles of plant extracts, microbial systems, and agricultural biomass, green synthesis successfully replaces hazardous chemical workflows with clean, sustainable alternatives. These biogenic materials feature unique surface capping layers, high structural defect densities, and multi-valence state profiles that provide outstanding performance in breaking down persistent contaminants including complex pharmaceuticals, endocrine disruptors, microplastics, and highly resilient PFAS compounds.

To transition this technology from successful laboratory demonstrations to widespread industrial water treatment deployment, future research should focus on addressing four key strategic priorities:

Advanced Standardization: Establishing strict, standardized preparation protocols and high-performance fingerprinting metrics to ensure consistent catalyst properties regardless of seasonal or regional biomass variations.

Robust Immobilization Frameworks: Developing scalable methods to anchor biogenic nanoparticles onto durable, highly porous structural supports (such as ceramic membranes or 3D-printed monoliths) to minimize mass transfer limitations and prevent downstream catalyst escape.

Optimized Target Selectivity: Engineering the surface chemistry of biogenic catalysts to maintain high selectivity for target emergent pollutants, ensuring efficient degradation even within complex wastewater matrices containing abundant natural organic matter and competing ions.

Comprehensive Lifecycle Validation: Conducting rigorous, full-scale techno-economic analyses and "cradle-to-grave" life cycle assessments to verify the economic viability and long-term safety of green nanocatalysis across industrial applications.

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