

Green Synthesis of Nanoparticles from Plant Extracts for the Removal of Microplastics and Emerging Contaminants from Water: A Critical Review

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Abstract

The unchecked release of microplastics (MPs) and emerging contaminants (ECs) pharmaceuticals, personal-care products, pesticides, endocrine disruptors, and industrial dyes into aquatic systems has outpaced the capability of conventional treatment plants, which typically remove only a fraction of these pollutants and generate secondary chemical waste in the process. Green (biogenic) synthesis of metal and metal-oxide nanoparticles (NPs) using plant extracts has emerged as a low-cost, low-toxicity alternative to chemical and physical nanofabrication routes, exploiting phytochemicals such as polyphenols, flavonoids, terpenoids, and proteins as natural reducing and capping agents. This review consolidates evidence on phyto-synthesized silver, zinc oxide, titanium dioxide, copper oxide, and iron/iron-oxide nanoparticles and nanocomposites, and examines their performance in degrading or adsorbing dyes, antibiotics, pesticides, and heavy metals pollutant classes that are mechanistically and analytically representative of the emerging-contaminant burden that also includes microplastics. Reported removal efficiencies for these green nanomaterials frequently exceed 80–99% under optimized photocatalytic or adsorptive conditions, governed by hydroxyl-radical generation, surface complexation, electrostatic attraction, and, for magnetic iron-based NPs, facile field-assisted recovery. The review further surveys the nascent but rapidly growing literature applying nanomaterials specifically to microplastic capture and degradation, highlighting magnetic and adsorptive nanoplatforms while noting that dedicated green-synthesis studies on MPs remain comparatively scarce relative to the wider emerging-contaminant literature. Key challenges synthesis reproducibility, particle agglomeration, nanoparticle recovery and secondary contamination, and the absence of standardized life-cycle and ecotoxicological assessment are discussed alongside future research priorities, including scale-up, agro-waste valorization, and hybrid photocatalytic-adsorptive nanocomposites tailored to co-existing microplastic and emerging-contaminant mixtures.

Keywords: *Green synthesis; phytonanotechnology; emerging contaminants; microplastics; photocatalysis; adsorption; wastewater treatment; nanoparticles.*

1. Introduction

Freshwater and marine ecosystems are under mounting pressure from two overlapping classes of pollutants. The first, microplastics (MPs), are plastic fragments smaller than 5 mm that originate from the breakdown of larger plastic debris, synthetic textiles, tyre wear, and personal-care products; their persistence, ubiquity, and capacity to adsorb and transport other toxicants have made them a defining environmental concern of the last decade. The second, emerging contaminants (ECs), comprise pharmaceuticals, endocrine-disrupting compounds, pesticides, per- and polyfluoroalkyl substances, and industrial dyes that are not yet or only recently regulated, but which are increasingly detected in surface water, groundwater, and treated effluent at biologically active concentrations.

Conventional wastewater treatment, built around coagulation-flocculation, sand filtration, activated sludge, and chlorination, was not designed to intercept nanoscale or trace-level pollutants and consequently allows a substantial fraction of MPs and ECs to pass into receiving waters. Advanced oxidation, membrane filtration, and activated-carbon adsorption improve removal but are energy-intensive, costly to operate at scale, and in some cases generate their own secondary waste streams.

Nanotechnology offers an alternative route to pollutant capture and degradation because nanoscale materials possess a high surface-area-to-volume ratio, tunable surface chemistry, and, in the case of semiconductor metal oxides, band gaps suited to solar-driven photocatalysis. However, the conventional chemical and physical synthesis of nanoparticles relies on hazardous reducing agents (sodium borohydride, hydrazine), organic solvents, and high energy inputs, which undermines the environmental rationale for using nanomaterials in pollution control in the first place. Green or biogenic synthesis addresses this contradiction by substituting plant-derived phytochemicals polyphenols, flavonoids, alkaloids, terpenoids, and proteins for hazardous chemical reductants, yielding nanoparticles through a comparatively benign, low-energy, single-pot aqueous reaction. This review synthesizes the literature on plant-extract-mediated (phytogenic) synthesis of metal and metal-oxide nanoparticles and their demonstrated performance against dyes, pharmaceuticals, pesticides, and heavy metals the same mechanistic and application space into which microplastic-targeting nanomaterials are now being extended. Because dedicated studies applying green-synthesized nanoparticles specifically to microplastics remain few relative to the broader emerging-contaminant literature, this review deliberately draws on the closely related and better-established photocatalytic and adsorptive evidence base, while devoting a focused section to the nanomaterial strategies so far reported for MP capture and degradation, so that the reader can assess both the current state of the art and the translational gap that remains.

2. Microplastics and Emerging Contaminants: Scope of the Problem

2.1 Sources and Occurrence

Microplastics enter aquatic systems from both primary sources (microbeads in cosmetics, pre-production pellets) and secondary sources (fragmentation of larger plastic debris through UV weathering, mechanical abrasion, and biodegradation). Wastewater treatment plants act as both a sink and a conduit: while plants can remove a large proportion of influent MPs into sludge, the sheer volume of water processed means that even low percentage breakthrough translates into substantial daily loads discharged to rivers, estuaries, and coastal waters. Emerging contaminants, by contrast, enter primarily through human excretion of pharmaceuticals and their metabolites, agricultural runoff of pesticides and veterinary drugs, and industrial or municipal effluent bearing dyes and personal-care chemicals.

2.2 Environmental and Health Significance

Microplastics act as vectors for co-contaminants, adsorbing hydrophobic organic pollutants and heavy metals onto their surfaces and thereby facilitating trophic transfer through aquatic food webs. Emerging contaminants such as antibiotics contribute to the proliferation of antibiotic-resistance genes in aquatic microbial communities, while endocrine-disrupting compounds have

been linked to reproductive and developmental effects in aquatic organisms even at nanogram-per-litre concentrations. The chemical diversity and low concentration of these pollutants make them difficult to remove using a single unit process, motivating the search for multifunctional nanomaterial-based treatments capable of simultaneous adsorption and catalytic degradation.

3. Green Synthesis of Nanoparticles: Principles and Mechanisms

Plant-mediated nanoparticle synthesis broadly follows three stages: (i) bioreduction, in which phytochemicals donate electrons to reduce metal ions (M^{n+}) to their zero-valent or oxide form; (ii) nucleation and growth, in which reduced metal atoms aggregate into nanoscale clusters; and (iii) capping/stabilization, in which residual biomolecules adsorb onto the nanoparticle surface, arresting further growth and preventing agglomeration [1,2]. Flavonoids reduce metal ions through tautomeric conversion from the enol to the keto form, releasing a reactive hydrogen atom; polyphenols and tannins act through hydroxyl-group oxidation; and proteins contribute reducing amine and carboxyl functional groups while also providing steric stabilization [1].

The choice of plant species, plant part (leaf, peel, root, seed, or latex), extraction solvent, precursor salt concentration, pH, temperature, and reaction time collectively determine nanoparticle size, morphology, crystallinity, and consequently, functional performance [1,2]. Alkaline reaction media generally favour smaller, more stable nanoparticles because higher pH deprotonates and activates phenolic reducing groups, whereas excess unconsumed phytochemicals in the reaction mixture can drive secondary reduction on existing nuclei, enlarging particle size.

Compared with chemical reduction (which requires hazardous reagents such as sodium borohydride or hydrazine) and physical methods (ball milling, laser ablation, which are energy-intensive), green synthesis operates at ambient or mild temperature, uses water as the primary solvent, and produces a biomolecule-capped nanoparticle surface that is often directly functionalized for pollutant binding without additional surface-modification steps. This combination of low cost, low toxicity, and functional surface chemistry is the central rationale for applying phyto-nanoparticles to water treatment.

4. Performance of Green-Synthesized Nanoparticles Against Emerging Contaminants

4.1 Dyes and Industrial Colourants

Industrial dyes are among the most extensively studied targets for green-synthesized nanoparticles, both because they are optically easy to quantify and because they serve as convenient surrogate pollutants for other recalcitrant organics. Silver nanoparticles synthesized from *Albizia procera* and *Parkia speciosa* leaf extracts have shown strong photocatalytic activity against organic dyes alongside antibacterial effects [3,4]. *Acacia ehrenbergiana* cortex-derived silver nanoparticles reduced rhodamine B by roughly 96% within about half an hour in the presence of a hydride donor, following zero-order kinetics [5]. *Adhatoda vasica* leaf-extract silver nanoparticles achieved over 92% degradation of several azo dyes within fifteen minutes [6], while bark-derived silver nanoparticles from *Thespesia populnea* degraded methylene blue by roughly 92% after two hours of sunlight exposure, with hydroxyl and superoxide radicals identified as the principal reactive species. Citrus peel-derived (Kinnow mandarin) silver nanoparticles and *Eupatorium adenophorum* leaf-extract silver nanoparticles have likewise demonstrated efficient sunlight-

driven degradation of malachite green and rhodamine dyes, underscoring the versatility of agro-waste and ornamental plant biomass as reducing agents.

Zinc-oxide- and copper-oxide-based nanomaterials extend this activity to a broader visible-light response. Citrus limetta rind-derived, copper-doped zinc oxide nanoparticles achieved 85–90% methylene blue degradation under ultraviolet and visible irradiation [7], and *Melia azedarach*-mediated copper–zinc oxide heteronanostructures degraded the organophosphate pesticide chlorpyrifos under solar illumination, indicating that the same nanoplateforms effective against dyes also address pesticide contamination [8]. *Annona glabra* leaf-extract-mediated CuO/ZnO nanocomposites and Neem-leaf-mediated ZnO/CuO/NiO nanoparticles have similarly reported strong, tunable photocatalytic dye-degradation activity depending on the metal-oxide ratio [9,10].

4.2 Pharmaceuticals and Antibiotics

Titanium dioxide is the most widely investigated green-synthesized photocatalyst for pharmaceutical degradation because of its strong oxidative capacity and chemical stability. Aloe-extract-assisted three-dimensional tripyramid TiO₂ architectures degraded the antibiotic ciprofloxacin with high efficiency under visible light through synergistic generation of hydroxyl radicals and photogenerated holes [11]. Neem-leaf-derived anatase-phase TiO₂ degraded the aquaculture antibiotic oxytetracycline by roughly 87% in real wastewater matrices [12], while *Ocimum basilicum* leaf-extract TiO₂ removed amoxicillin residues from aqueous solution [13], and *Azolla pinnata*-mediated TiO₂ degraded the beta-blocker propranolol under artificial light [14]. Collectively, these studies indicate that green-synthesized TiO₂ and related metal-oxide photocatalysts can achieve pharmaceutical degradation efficiencies comparable to, and in several cases exceeding, those reported for chemically synthesized analogues, while avoiding the toxic by-products associated with conventional reduction routes.

4.3 Pesticides and Agrochemicals

Beyond the chlorpyrifos degradation noted above, palladium nanoparticles synthesized using *Lallemantia royleana* seed extract have been applied as adsorbents for the fungicide tebuconazole and the insecticide chlorpyrifos as well as the dye Congo red, illustrating multi-pollutant adsorption capacity within a single biogenic nanomaterial [15]. Engineered green titanium dioxide nanoparticles have also achieved near-complete removal of the herbicide florasulam and the fungicide zoxamide under ultraviolet irradiation, with pseudo-first-order kinetics typically providing the best fit to the degradation data [15].

4.4 Heavy Metals

Iron and iron-oxide nanoparticles synthesized from plant extracts are the most consistently reported nanomaterial class for heavy-metal remediation, owing to their high affinity for redox-active and cationic metal species and, in the case of magnetite/maghemite phases, the practical advantage of magnetic recovery. Oak, mulberry, and cherry leaf-extract-derived zero-valent iron nanoparticles removed both As (III) and Cr (VI) from aqueous solution [16], while a three-plant-extract zero-valent iron formulation achieved efficient Cr (VI) removal governed by Langmuir-type adsorption and pseudo-second-order kinetics [17]. Green tea-derived nanoscale zero-valent iron has been used to treat Cr (VI)-contaminated groundwater, and *Verbascum thapsus* leaf-

derived zero-valent iron nanoparticles removed roughly 85% of Cr (VI) over twelve hours while remaining stable against oxidative deactivation [18]. Eucalyptus globulus-extract-derived superparamagnetic iron-oxide nanoparticles were applied directly to heavy-metal-contaminated agricultural soil, demonstrating that green iron oxides are effective in solid soil matrices as well as in aqueous solution [19,20]. Clove- and green-coffee-extract iron-oxide nanoparticles sorbed cadmium and nickel ions from aqueous solution with structure (magnetite versus mixed magnetite–hematite) dependent on the extract used [21], and myco-synthesized iron-oxide nanoparticles derived from *Aspergillus niger* achieved removal efficiencies exceeding 90% for several heavy metals in both synthetic and real industrial wastewater [22].

5. Green Nanoparticles and the Microplastic Removal Challenge

Direct evidence for green-synthesized nanoparticles applied specifically to microplastic capture or degradation is still limited relative to the dye, pharmaceutical, pesticide, and heavy-metal literature reviewed above, reflecting the comparatively recent recognition of microplastics as a priority pollutant. The nanomaterial strategies that have been reported for MP removal, largely using conventionally synthesized nanomaterials, fall into three broad mechanistic categories that are directly transferable to green nanoplatforms: magnetic separation, in which iron-oxide nanoparticles are functionalized to bind microplastic surfaces (frequently via silane or biopolymer coupling agents) and are then recovered under an external magnetic field, achieving reported recovery rates exceeding 90% for micrometre-scale particles [23,24]; adsorptive capture, in which high-surface-area nanomaterials, including carbon-based nanostructures, metal–organic frameworks, and functionalized nanocomposites, remove MPs through electrostatic interaction, hydrophobic association, hydrogen bonding, and π – π stacking, with reported efficiencies above 90% under optimized conditions [25]; and photocatalytic degradation, in which semiconductor metal-oxide nanoparticles the same ZnO and TiO₂ families synthesized via green routes for dye and pharmaceutical degradation above generate reactive oxygen species under UV or visible irradiation that oxidize polymer chains at the microplastic surface, as demonstrated for plasmon-enhanced ZnO photocatalysts against low-density polyethylene films [26].

Because phyto-synthesized iron oxides, ZnO, and TiO₂ already possess the magnetic, adsorptive, and photocatalytic properties exploited in these conventional MP-removal strategies, the translational step of substituting green-synthesized nanoparticles for chemically synthesized ones in microplastic treatment trains is mechanistically straightforward and represents one of the more promising near-term extensions of the phytonanotechnology literature. Biopolymer- and plant-derived natural coagulants (for example, *Moringa oleifera* seed extract and cactus mucilage) have themselves been evaluated as microplastic coagulant aids, achieving up to 99% removal in hybrid systems, further reinforcing the compatibility of plant-derived materials with MP-focused water treatment [27]. Nonetheless, the field currently lacks studies that report green-synthesized nanoparticle performance against microplastics using the standardized dosage, kinetic, and recovery metrics that are already well established for dyes and pharmaceuticals, and this represents the clearest research gap identified in this review.

6. Removal Mechanisms: A Comparative Perspective

Across the pollutant classes reviewed, three mechanisms recur: (i) photocatalytic oxidation, in which band-gap excitation of a semiconductor metal oxide by UV or visible light generates electron-hole pairs that produce hydroxyl and superoxide radicals capable of mineralizing organic pollutants and oxidizing polymer surfaces; (ii) adsorption, governed by electrostatic attraction, surface complexation, hydrogen bonding, and π - π interactions between the biomolecule-capped nanoparticle surface and the target pollutant, typically described by Langmuir, Freundlich, or Temkin isotherms and pseudo-first- or pseudo-second-order kinetics; and (iii) reductive transformation, most prominent in zero-valent iron systems, where the nanoparticle itself acts as an electron donor to reduce redox-active metal species such as Cr(VI) to the less mobile and less toxic Cr(III) state. The biomolecule capping layer inherited from the green synthesis process is not incidental to these mechanisms: phenolic and carboxyl surface groups directly participate in pollutant binding, meaning that the same phytochemicals responsible for nanoparticle formation also enhance downstream removal performance.

7. Advantages, Challenges, and Research Gaps

7.1 Advantages over Conventional Nanofabrication

Green synthesis eliminates or greatly reduces the use of hazardous reducing agents and organic solvents, operates at near-ambient temperature and pressure, and is compatible with inexpensive, often waste-derived plant biomass. The resulting biomolecule capping layer confers biocompatibility and, as noted above, functional pollutant-binding capacity without additional surface engineering.

7.2 Challenges

Batch-to-batch reproducibility remains a persistent limitation because phytochemical composition varies with plant species, geographic origin, season, and extraction protocol, complicating standardization and regulatory approval. Nanoparticle agglomeration during storage or under variable ionic strength can reduce effective surface area and therefore removal efficiency. Recovery and reuse of non-magnetic nanoparticles after treatment is technically demanding, raising the risk of nanoparticles themselves becoming a secondary contaminant if not adequately immobilized or magnetically separable. Scale-up from laboratory batch synthesis to pilot- or industrial-scale continuous production has been demonstrated in relatively few studies, and rigorous life-cycle and ecotoxicological assessment of green nanoparticles remains comparatively underdeveloped relative to the pace of synthesis-focused publication.

7.3 Future Research Priorities

Priority research directions include: (i) systematic application of green-synthesized nanoparticles directly to microplastic-contaminated water using the standardized performance metrics already used for dyes and pharmaceuticals; (ii) development of magnetically recoverable, multifunctional nanocomposites capable of simultaneous adsorptive and photocatalytic action against co-occurring microplastic and emerging-contaminant mixtures; (iii) valorization of agro-industrial and food-processing waste streams as low-cost, standardized phytochemical feedstocks to improve synthesis

reproducibility; and (iv) comprehensive toxicological and environmental-fate assessment of green nanoparticles prior to field-scale deployment.

8. Conclusion

Plant-extract-mediated green synthesis provides an environmentally coherent route to nanoparticles capable of removing a wide range of emerging contaminants dyes, pharmaceuticals, pesticides, and heavy metals through photocatalytic, adsorptive, and reductive mechanisms, frequently achieving removal efficiencies above 80–90% under optimized laboratory conditions. The evidence base for these pollutant classes is now substantial and methodologically mature. Direct application of green-synthesized nanoparticles to microplastic removal is mechanistically well supported by this broader literature but remains comparatively underexplored, representing both the principal limitation of the current evidence base and the most promising direction for near-term research linking phytonanotechnology to the microplastics crisis.

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