



The role of green chemistry in addressing microplastic and chemical pollution

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Abstract

Environmental contamination from microplastics and synthetic chemical pollutants represents a critical threat to global ecosystems, biodiversity, and human health. Traditional end-of-pipe remediation and linear production models have proven fundamentally insufficient to mitigate this compounding planetary crisis. This review paper systematically evaluates the transformative role of green chemistry in mitigating both microplastic fragmentation and hazardous chemical pollution. By analyzing recent advancements in sustainable molecular design, biodegradable polymer engineering, benign alternative synthesis, and catalytic upcycling technologies, this paper demonstrates how the twelve principles of green chemistry can systematically dismantle toxic industrial loops. We examine current bioremediation strategies, computational toxicological models, catalyst developments, and industrial scaling challenges, providing a comprehensive, life-cycle-based framework for future research and global policy integration.

Keywords: Green chemistry, microplastics mitigation, chemical pollution, biodegradable polymers, sustainable design, circular economy

Introduction

Anthropogenic chemical pollution and the pervasive dispersion of microplastics have crossed safe planetary boundaries, destabilizing global ecological stability and threatening human survival ^[1]. For decades, industrial chemistry relied almost exclusively on a linear "take-make-dispose" paradigm. This legacy model prioritizes immediate material functionality and short-term economic return over long-term environmental consequences and material persistence. Consequently, millions of metric tons of non-biodegradable polyolefin matrix polymers and hazardous synthetic chemicals enter terrestrial, marine, and atmospheric sinks annually ^[2].

Microplastics originate from two primary pathways: the physical fragmentation of macro-plastics via weathering and solar radiation, or the deliberate formulation of primary micro-beads for industrial and consumer applications. These micro particles exhibit unique hydrophobic surface attributes that readily adsorb persistent organic pollutants (POPs) from surrounding waters, serving as mobile vectors of concentrated toxicity up the trophic web ^[3]. Simultaneously, volatile organic compounds (VOCs), endocrine-disrupting chemicals (EDCs), and per- and polyfluoroalkyl substances (PFAS) exert severe chronic ecotoxicological pressures on organisms across all trophic levels. To address these overlapping crises, the framework of Green Chemistry offers a proactive, molecular-level design philosophy. First codified by Anastas and Warner ^[4], green chemistry seeks to reduce or eliminate the use and generation of hazardous substances throughout the entire lifecycle of chemical products. This represents a fundamental paradigm shift from conventional remediation:

Linear Chemical Economy (Old): Extraction → Hazardous Synthesis → Linear Waste

Green Chemistry Framework (New): Bio-based Feedstocks → Catalytic Efficiency → Non-toxic Biodegradable Output

This review synthesizes recent literature to evaluate how green chemistry principles directly address microplastic fragmentation and chemical leaching, focusing on bio-based alternatives, closed-loop catalytic recycling, and benign-by-design materials as essential pathways toward an eco-compatible chemical economy.

The Nexus of Microplastic and Chemical Pollution

1. Environmental Mechanics and Vector Effects

Microplastics are not inert physical nuisances they function as dynamic chemical vectors within aquatic and terrestrial ecosystems. Due to their exceptionally high surface-area-to-volume ratio and hydrophobic surface chemistry, microplastics readily adsorb hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), from surrounding aquatic environments, concentrating them far above background levels ^[5]. When marine or terrestrial organisms ingest these loaded microparticles, the altered chemical equilibrium within the organism's digestive tract facilitates the desorption and systemic bioavailability of these bound toxins ^[6]. This vector mechanism induces severe biological stress, including:

- Cellular oxidative stress and tissue damage
- Chronic inflammatory responses and localized physical lesions
- Systemic bioaccumulation and biomagnification across marine and terrestrial food chains ^[3].

2. Chemical Additives and Endocrine Disruption

The intrinsic toxicity of microplastics is severely exacerbated by the complex cocktail of low-molecular-weight chemical additives incorporated during polymer compounding. Plasticizers (e.g., phthalates), flame retardants (e.g., polybrominated diphenyl ethers or PBDEs), and stabilizers (e.g., Bisphenol A or BPA) are typically blended physically into the polymer matrix rather than being covalently bound ^[7].

As plastics weather via solar ultraviolet irradiation and mechanical abrasion, the polymer chains degrade, and these low-molecular-weight additives leach rapidly into the environment. Many of these additives are confirmed endocrine-disrupting chemicals (EDCs). They mimic or interfere with endogenous hormones, causing reproductive failure, developmental abnormalities, and metabolic disorders in wildlife and humans alike ^[8].

Green Chemistry Frameworks for Pollution Mitigation

The twelve principles of green chemistry offer a systematic methodology to remediate existing pollution and design out future hazards at the molecular level. Key principles applied to this dual crisis include:

1. Waste Prevention and Atom Economy (Principles 1 & 2)

Preventing waste formation at the source is inherently more efficient than treating or cleaning up pollution post-generation. Designing synthetic pathways with high atom economy ensures that the maximum mass of starting materials is incorporated into the final target product, minimizing hazardous by-products and eliminating the streams that form primary microplastics.

2. Designing Safer Chemicals and Degradation (Principles 4 & 10)

Chemical products must be engineered to preserve material efficacy while reducing intrinsic toxicity. Furthermore, synthetic polymers must be deliberately designed so that, upon completing their functional life, they break down into innocuous, non-persistent degradation products via environmental or enzymatic pathways, avoiding the formation of secondary microplastics entirely.

3. Use of Renewable Feedstocks (Principle 7)

Shifting away from petroleum-derived monomers toward agricultural waste, lignocellulosic biomass, and algae mitigates carbon emissions and avoids the production of recalcitrant polyolefin matrices that persist in ecosystems for centuries.

Bio-Based and Biodegradable Polymers: Replacing Recalcitrant Plastics

To halt the generation of secondary microplastics, green chemistry focuses heavily on synthesizing polymers that undergo complete enzymatic mineralization rather than mere physical fragmentation.

Petroleum Plastics: Weathering via Solar Radiation & Mechanical Stress → Recalcitrant Microplastics (Centuries of Persistence)

Bio-Polymers (PLA/PHA): Action by Microbial Enzymes / Compost → CO₂ + H₂O + Biomass (Complete Mineralization)

1. Polylactic Acid (PLA) and Polyhydroxyalkanoates (PHAs)

Polylactic Acid (PLA), derived from fermented plant starch, represents a leading commercial bio-based alternative. While PLA requires industrial composting conditions to degrade rapidly, it significantly reduces fossil fuel reliance and avoids the generation of permanent microplastics ^[9].

Conversely, Polyhydroxyalkanoates (PHAs) polyesters biosynthesized intracellularly by bacteria via carbon fermentation exhibit excellent biodegradability in natural marine and soil environments ^[10]. PHAs degrade into benign organic metabolites, eliminating the risk of long-lived microplastic accumulation.

2. Lignocellulosic and Chitin-Based Material Design

Utilizing abundant natural biopolymers, such as cellulose, lignin, and chitin, provides a direct path to sustainable materials. Recent advancements in green chemistry have enabled the chemical modification of cellulose and chitin nanofibers to produce transparent, high-barrier packaging films ^[11]. These films can directly replace conventional polyethylene and polypropylene wraps. Because these materials utilize existing biopolymers, they degrade naturally via native microbial pathways without generating toxic chemical residues or secondary microparticles.

Macromolecular Engineering of Eco-Compatible Polymers

To eliminate the long-term generation of secondary microplastics, green chemistry shifts material synthesis away from inert polyolefin matrices toward step-growth and ring-opening polymerizations that yield backbones susceptible to environmental and enzymatic cleavage.

1. Ring-Opening Polymerization (ROP) Pathways for PLA

The industrial synthesis of high-molecular-weight PLA relies on the catalytic ring-opening polymerization (ROP) of lactide a cyclic dimer derived from fermented cornstarch or sugarcane glucose ^[9]. Conventional industrial production utilizes tin (II) octoate [Sn (Oct)₂] as a coordination-insertion catalyst due to its high reaction rates and solubility. However, residual tin ions present ecotoxicological risks when materials enter natural sinks or compost infrastructure.

Green chemistry advancements have introduced highly efficient organocatalysts to replace heavy-metal configurations. Organocatalytic systems based on triazabicyclodecene (TBD) and thiourea-amine dual systems operate efficiently under mild ambient temperatures. They achieve precise control over stereoregularity without leaving toxic metallic residues in the polymer matrix. This structural control allows researchers to fine-tune the crystalline-to-amorphous ratio of PLA, allowing them to accelerate or delay environmental hydrolytic degradation based on the material's specific application requirements.

2. Intracellular Fermentation and Extraction Mechanics of PHAs

Polyhydroxyalkanoates (PHAs), specifically poly (3-hydroxybutyrate) (PHB) and its copolymer poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), are synthesized directly as intracellular energy reserves by wild-type or genetically engineered bacterial strains (e.g., *Cupriavidus necator*) under nutrient-limited, carbon-excess regimes ^[10]. The polymer accumulates as discrete granules within the cytoplasm, occasionally exceeding 80% of the dry cellular weight.

The primary green chemistry challenge lies in downstream extraction. Traditional industrial harvesting depends on chlorinated organic solvents such as chloroform or

dichloromethane to lyse the bacterial cell wall and dissolve the hydrophobic granules. Green engineering has replaced these volatile, toxic solvents with benign extraction methods, including:

- High-pressure homogenization
- Enzymatic cocktail digestion utilizing protease and lysozyme
- Supercritical fluid extraction utilizing eco-compatible (scCO₂) with green ethanol co-solvents.

These green extraction techniques prevent hazardous chemical discharges into industrial wastewater systems while preserving the high molecular weight and mechanical properties of the harvested PHAs.

Molecular Toxicological Dynamics of Chemical Leaching

1. Mass Transport Coefficients and Diffusive Flux

Conventional polymer additives such as low-molecular-weight phthalates (e.g., DEHP), brominated flame retardants (PBDEs), and bisphenols are physically blended into polymer matrices rather than being covalently bound [7]. The rate of chemical leaching into surrounding environments is governed by Fick's Second Law of Diffusion, where the spatial concentration gradient over time drives additive transport toward the plastic-water interface:

$$\partial C/\partial t = D\partial^2 C/\partial x^2$$

Here, (D) represents the molecular diffusion coefficient of the additive within the specific glassy or rubbery polymer phase. Because secondary microplastics have an exceptionally high surface-area-to-volume ratio, the diffusion path length (x) approaches sub-micron scales. This drastically accelerates the leaching rate of entrapped toxins into surrounding marine and terrestrial pore waters. When microplastics are ingested by living organisms, the surfactant-rich, warm, and acidic conditions within the digestive tract increase the diffusion coefficient (D). This shifts the thermodynamic equilibrium, causing rapid chemical desorption directly into biological tissues [6].

2. Intracellular Disruption and Endocrine Receptors

Once leached from the microplastic matrix into biological systems, compounds like Bisphenol A (BPA) cross lipophilic cellular membranes via passive transport. BPA behaves as a molecular mimic due to structural similarities to endogenous steroidal hormones. Its phenolic rings bind directly to estrogen receptors alpha (ER_α) and beta (ER_β), disrupting normal endocrine feedback loops [8,12]. This competitive receptor binding triggers aberrant gene transcription, leading to reduced reproductive fertility, altered metabolic rates, and developmental abnormalities across marine organisms. These cellular disruptions can trigger cascading population declines within fragile aquatic trophic networks.

Designing Benign-by-Design Chemicals

1. Structure-Activity Relationship (SAR) Modeling

Green chemistry leverages computational toxicology to design industrial molecules that lack toxicological activity. By utilizing Structure-Activity Relationship (SAR) models, chemists can predict the mutagenicity, carcinogenicity, and endocrine-disrupting potential of a molecular structure before physical synthesis occurs^[13]. Altering functional groups such as replacing aromatic rings or halogen atoms

with linear hydrocarbon chains or ester bonds can dramatically reduce a chemical's affinity for biological receptors.

2. Next-Generation Non-Phthalate Plasticizers

The ban on specific low-molecular-weight phthalates has accelerated the green design of alternative plasticizers. Green chemists have successfully synthesized bio-derived alternatives from vegetable oils, citric acid, and succinic acid, such as acetyl tributyl citrate (ATBC) and epoxidized soybean oil [14]. These green plasticizers offer comparable elastomer flexibility to conventional polymers while exhibiting minimal toxicity and significantly lower leaching rates into aquatic matrices.

Advanced Catalysis and Green Recycling Technologies

Conventional mechanical recycling degrades polymer mechanical properties, leading to downcycling and eventual disposal. Green chemistry addresses this limitation through chemical recycling via advanced catalysis.

1. Organocatalysis and Biocatalysis in Chemical Upcycling

Chemical upcycling employs selective catalysts to depolymerize waste plastics back into pure monomer units or valuable chemical intermediates. Organocatalysts and engineered biocatalysts (such as optimized PETase enzymes) break down complex polyesters under mild, energy-efficient conditions [15]. This circular economy model allows post-consumer waste plastics to be infinitely re-polymerized without quality loss, directly reducing the demand for virgin petrochemical feedstocks.

2. Supercritical Fluid and Benign Solvent Extraction

The extraction of hazardous chemical additives from post-consumer plastics is a major bottleneck in recycling. Green chemistry employs supercritical carbon dioxide (scCO₂) as a non-toxic, tunable solvent to selectively dissolve and remove flame retardants and heavy metals from polymer matrices [16]. This process produces clean, non-toxic polymer streams ready for high-grade mechanical or chemical recycling, bypassing hazardous organic solvents like chloroform or dichloromethane.

Comparative Analysis of Remediation Strategies

To understand the operational shifts required, the table below contrasts conventional engineering remediation approaches with proactive green chemistry methodologies across key sustainability indicators:

Table 1: Comparative Analysis of Remediation Strategies

Evaluation Metric	Conventional Remediation Approaches	Green Chemistry Methodologies
Primary Intervention Point	End-of-pipe capture (filtration, incineration, landfills).	Molecular design and source prevention.
Energy Consumption	High energy required for mechanical collection and processing.	Low energy via ambient catalytic transformations.
By-Product Generation	Secondary microplastics and toxic ash/sludge emissions.	Innocuous metabolites (CO ₂ , H ₂ O) and closed loops.
Economic Longevity	Linear cost center; ongoing operational expenses.	Circular economy asset; value retention of materials.

Economic and Technical Barriers to Global Scale-Up

Transitioning from a petroleum-based material infrastructure to an economy rooted in green chemistry requires overcoming significant economic and engineering challenges, historically referred to as the industrial "Scaling Valley of Death":



1. Capital Expenditure (CAPEX) and the Petrochemical Cost Advantage

The global chemical infrastructure has spent over a century optimizing petroleum refining and polymer synthesis. Consequently, commodities like polyethylene (PE) and polypropylene (PP) achieve unprecedented economies of scale, maintaining low production costs that bio-based alternatives struggle to match on a pure cost-per-kilogram basis. Building commercial-scale fermentation plants for PHAs or catalytic upcycling facilities requires massive initial Capital Expenditure (CAPEX), which often deters risk-averse chemical manufacturers. Furthermore, raw bio-based feedstocks face seasonal price volatility, which complicates long-term corporate budget forecasting.

2. Supply Chain Integration and Compatibility

Most existing mechanical recycling infrastructure is designed to identify and sort high-volume petroleum plastics using near-infrared (NIR) optical sorting technology. Introducing new biopolymers like PLA into current post-consumer waste management lines can present severe operational challenges. If PLA contaminates traditional Polyethylene Terephthalate (PET) recycling batches, it causes thermal degradation during reprocessing, rendering entire batches of recycled PET brittle, degraded, and unmarketable. Therefore, scaling up green chemistry materials requires a simultaneous re-engineering of municipal waste separation infrastructure, industrial composting networks, and optical sorting systems.

Comprehensive Life-Cycle Assessment Metrics

To prevent unintended environmental trade-offs, green chemical engineering relies on comprehensive Life-Cycle Assessments (LCA) to track net environmental impacts from cradle to grave.

Petroleum Pathway: Extraction → Refining → Production → High GHG Emissions → Microplastic Persistence

Bio-Plastic Pathway: Agriculture → Fermentation → Production → Eutrophication Risks → Complete Biodegradation

While bio-based alternatives like PLA reduce carbon footprints and fossil fuel depletion compared to conventional polymers ^[9], they can introduce other environmental burdens during their agricultural phase. Cultivating first-generation corn or sugarcane feedstocks for green plastics requires substantial arable land, intensive water use, and the application of nitrogen-based fertilizers. Runoff from these fertilizers can cause aquatic eutrophication, while pesticide use can reduce regional biodiversity.

Green chemistry addresses these life-cycle trade-offs by shifting research focus toward third-generation feedstocks. These include agricultural residues e.g., corn stover, wheat straw, non-food halophytic plants, and marine macroalgae. Utilizing these non-food sources allows green chemistry to avoid competing with food security while minimizing the environmental impacts of industrial agriculture ^[17].

Future Horizons and Policy Drivers

Strict regulatory policies are vital to drive the transition from traditional chemicals to green alternatives. Frameworks like the European Union's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulations put pressure on industries to phase out persistent bioaccumulative toxins (PBTs) and EDCs ^[18]. Furthermore, global policy instruments, such as the United Nations Plastics Treaty, incentivize green chemical innovation by establishing legally binding caps on virgin plastic production and mandating circularity-by-design principles. Future horizons rely heavily on pairing computational toxicological screenings with automated, enzyme-catalyzed continuous upcycling systems. By creating closed-loop loops where the polymer is benign-by-design, the threat of secondary microplastic accumulation can be comprehensively dismantled.

Conclusion

The dual crises of microplastic accumulation and hazardous chemical pollution cannot be solved solely through post-generation cleanups or mechanical filtration. Green chemistry offers a comprehensive alternative framework that replaces toxic, persistent materials with sustainable, biodegradable, and benign-by-design solutions. By scaling up bio-based polyesters like PHAs, adopting predictive computational toxicology, and implementing catalytic closed-loop upcycling, modern society can transition toward a truly circular chemical economy. Realizing this shift requires sustained collaboration between academic researchers, industrial engineers, and global policymakers to implement green chemistry as the foundational standard for future material manufacturing.

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