

Polymeric Approach in Microplastic Degradation Mechanisms

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Abstract

Microplastics (> 5 mm size), are silently infiltrating ecosystems on a global scale. The persistence of microplastics in terrestrial and aquatic surroundings poses a significant ecological and surroundings challenge. Thus, understanding and development of effective degradation mechanisms to mitigate the persistence of microplastics in the surroundings is required. Natural degradation pathways, such as photodegradation, biological degradation, and abiotic degradation have been explored. Polymeric materials possess unique properties that can be harnessed to enhance degradation processes. This approach involves the novel polymeric materials or modifications to existing polymers to facilitate the breakdown of microplastics into environmentally benign byproducts. Various processes, including weathering, degradation (involving microbial, oxidative, and hydrolytic mechanisms), aggregation, and the formation of biofilms, have been documented as influential factors affecting the transportation of microplastics within aquatic ecosystems. This review article offers a thorough investigation of the origins, dispersion, destiny, and harmful consequences of MP's in the surroundings. Furthermore, it delves into the examination of the contribution of marine microorganisms and polymers to the degradation of microplastics.

Keywords: Hydrolytic Degradation, Nanoparticle Assisted, Synergistic Mechanisms, Biodegradation, Polymer.

INTRODUCTION

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Plastics are long-chain polymeric man-made material. They are used in every aspect of life due to their excellent properties like strong plasticity, lightweight, thermic and conductivity insulation, attrition impedance, and cost-effectiveness. Global plastic production (excluding Fibers) increased drastically from 1950 to 2018, including polypropylene Fibers [1]. Over the past half century, approximately 12,000 metric tons of plastic have entered landfills and management facilities, marine ecosystems, and the surroundings. In the aquatic surroundings, plastic waste begins to break down into macro-degradation through mechanical (erosion, digestion), chemical (photo-oxidation, hydrolysis) and biological (degradation by microorganisms) changes [2]. Further weathering and fragmentation precede to formation of plastic particles <5 mm, generally known as microplastics and fostering nano-plastics ranging between 1nm and 100nm. While, on the other

hand, industries such as cosmetics, clothing and textiles, and fishing lines utilize primary microplastics, which further breakdowns into secondary microplastics.

Microplastics (MP) mainly consist of various polyamides and nylons. Microplastics debris and nano-plastics pollution is an arising global surrounding predicament in the ecosphere.[3] Key causes of this ubiquitous problem regarding microplastic pollution in the biosphere involve low production costs and high recalcitrance. The prevalence of plastic wastes and microplastics poses possible threats to both the surroundings and living organisms. Moreover, plastic debris can also transport and adsorb organic pollutants like polychlorinated biphenyls, phenanthrene, and dichloro-diphenyl-trichloroethane), thus resulting in the bioaccumulation and amplification of these pollutants within the ecosystem. The existence of microplastics and nano-plastics in our surroundings presents substantial challenges to both ecosystem integrity and human health. Their continuity, capability to enter the food chain, and implicit long-term effects underscore the urgency of addressing this issue. Therefore, management methods of micro-plastics are of utmost importance. Currently, certain nations and organizations, like those in Canada, the United States, United Nations, and the United Kingdom, have developed regulations and national laws to decrease the emission of microplastics. Various efforts have been put to work to alter the generation of plastic waste into the surroundings, including reuse, recycling, incineration, and landfill dumping, still plastic pollution is inevitable.

In the last decade, Bioremediation has garnered the interest of researchers globally as an surroundingsally friendly and sustainable approach to mitigate toxic pollutants in the surroundings. Microbes have an inherent capability to adapt to different habitats and possess the capability to biodegrade different toxic pollutants. The employment of microorganisms for the degradation of MPs in a green manner makes it a promising and sustainable strategy for the clean-up of contaminated surroundings without imparting hazardous impact. [4]

Origin and Destiny of Microplastics in Different Surroundingsal Matrices

Synthetic fabrics, weathering rubber tires, city dust, plastic equipment, recycling particles, landfills, road dust, incineration, waste gas, synthetic particles used in horticultural soil, and sewage sludge are the main contributors of microplastics in the atmosphere which is shown in Figure 1 [5].

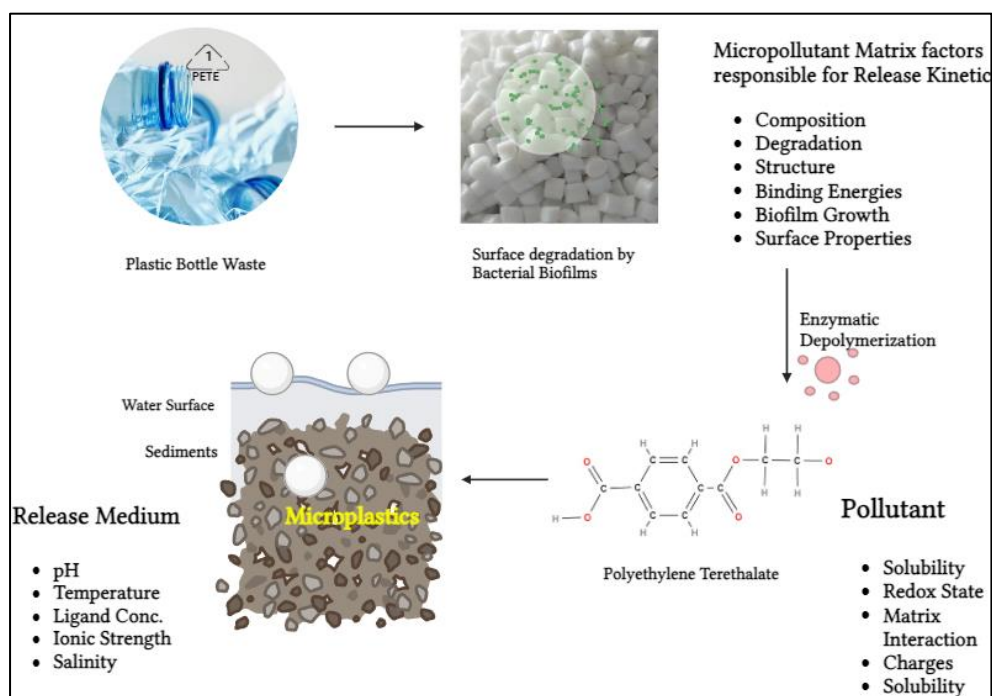


Figure 1. Fate of Microplastics and Affecting Factors [5]

However, the limited detection of airborne microplastics is poorly reported due to constraints in airborne microplastics detection.[6]. Furthermore, air transport has also been found as a key carrier for microplastics to isolated alpine regions or the ocean [7] studied microplastic fallout in several indoor settings in Shanghai, China, and discovered that acrylic (44–60%) and polyester (33–47%) were the most prevalent forms. Factors, including airflow direction along with its speed, upright pollution, variation gradients, local meteorology, urban terrain, thermal cycling, precipitation, and temperature affect the reach of MPs in an surroundings.

Microplastics that survive filtration during wastewater treatment or are not adequately retained in wastewater discharges to inland water. Since inland water bodies act as the main source of consumable water, they are vulnerable to microplastic contamination through human impact [8]. Major industrial sources of MPs in inland water include plastic resin dust, pelletizing via air blasting equipment, personal care products containing microbes, and raw materials for manufacturing plastic products. Factors such as reservoir size, dense urbanization, water retention time, waste management systems, and sewage flows affect the migration or movement of MPs in inland water. Biofilms can profoundly influence the physical and chemical attributes of microplastics (including density and surface charge) and are pivotal in governing the transport and destiny of microplastics in the marine ecosystem. Fish and other higher trophic organisms rely heavily on biofilm as a food source. These plastic particles can be ingested by fish after forming a biofilm due to microbial colonization, which can change their fate in inland water [9].

MPs are also heavily concentrated in the soil. Agricultural practices frequently utilize sewage sludge, which has been proven in several studies to contain significant amounts of microplastic fibers or debris. In addition to PM pollution, other sources of soil pollution include the weathering and spreading of plastic films in agriculture, and plastic waste and dust in landfills. Microplastics can persist and build up in soil after being introduced there, eventually harming soil organisms' ability to grow and reproduce as well as their biodiversity. MPs have been reported as transporters for the release of various pollutants into soil biota and the destruction of soil ecosystems [10].

ECOTOXICITY OF MICROPLASTICS

Microplastic toxicity is evident along with exposure through a variety of channels released into the surroundings, potentially posing health hazards. Following the development of HDPEs and LDPEs in the 1920s and their documented surroundingsal distribution in 1993, The construction of landfills has created an echo loop around the world in coastal areas and oceans. When microplastics sink, they form marine settlements in the basin of the sea and suspended particles additionally with nanoscale fragments, which have an impact on both marine and inland water biota when they are digested and metabolized. The transfer of microfibers among different trophic levels is a persistent problem for marine ecosystems, with a direct biological impact that surpasses that of non-fiber equivalents. This impact is dependent on differential ingestion rates across various marine zones. It is crucial to acknowledge that microfibers and nano-scaled particles have a significant impact on human health through their ability to cause diseases, alter biochemical pathways, and affect gene expression via metabolic processes. [11] Ingestion, inhalation, and skin contact are major exposing ways for humans to MPs. A recent study found that microplastics as small as 0.2 and 2 μm may infiltrate the leaves of plants such as lettuce (*Lactuca sativa*) and wheat (*Triticum aestivum*) and reach their roots. Due to the absorption in plants, a major influence on food security and safety as well as human health can be a future threat. To elucidate the penetration of nanoplastics into seed and fruit skins, a fundamental inference suggests that they could potentially enter the human body through food consumption, as well as through other primary plant sources. In a model related to human health, they report the involvement of ROS (reactive oxygen species) via mediators that increase the activity of glutathione S-transduction, which then leads to the activation of enzymes related to antioxidants and mitogen factors via protein kinase signaling. The neurotoxicity factor is a possible mechanism observed by MPs that facilitate the inhibition of acetylcholinesterase

Jeong and Choi [12] which is mentioned in table 1. In addition, the uptake of MPs by paracellular presorption in the endocytic layer affects their size, surface activity, charge, protein corona formation, and hydrophobicity.

Table 1. Ecotoxicity of Microplastics on Different Organisms.

Species	Size/exposure time	Toxicity	References
Zebrafish	5 μm 0-7 days	Inflammatory actions and lipid accumulation in fish liver.	[13]
<i>Carcinus maenus</i>	<5mm 14 and 21 days	Surface absorption on gills.	[14]
<i>Carassius auratus</i>	<5mm 1.5 hours to 6 days	Gut Accumulation and further co-related toxicities.	[15]
<i>Paracentrotus lividus</i>	<5mm 24 hours	Impact on larval length.	[16]
Collembolan	<5mm 0-24 days	Reproduction inactiveness and growth instability observation.	[5]
Mice	5 and 10 μm 1,2,4,7,14,21,28 days	Site-specific accumulation in key organs such as kidney, liver and gut.	[17]
Wheat	50,500,4800 nm 24,48,72 hours	Disturbed growth	[18]
Lettuce	0.2 and 1.0 μm 0-30 days	Accumulated in tissue.	[19]

BIODEGRADATION OF MICROPLASTICS

Microbes can find a special ecological niche in MPs that support their growth and colonization and serve as a carbon source. The three phases that make up MP biodegradation are biodeterioration, biofragmentation, and assimilation. Numerous microorganisms that can break down MPs were isolated from various surroundingsal sources to research the biodegradation of MPs.

Bacteria

The capability of many bacterial species to degrade surroundingsal pollutants is one of their distinguishing traits. Microbial breakdown is one of the prime mechanisms for MPs based on the activity of the microorganisms (bacteria) in the surroundings. The biological remediation mechanisms involve the production of extracellular enzymes, and surface attachments, followed by degradation of the MPs into smaller structures, and finally mineralization into oxidized metabolites. Since MPs are abundantly present in the surroundings, microorganisms have evolved their survival ability by synthesizing the enzymes needed for the breakdown processes complex in nature. The bacteria first create extracellular enzymes that boost the MPs' hydrophilicity by forming alcohol or carbonyl groups on their surface, enabling more deterioration to take place. The second mechanism involves the surface bonding ability of chemical groups on the surface of MPs, which causes the polymer to break down into smaller parts (oligomers and monomers). The other major process involves the integration of MPs pieces into the bacterial cells in the mineralized monomeric forms through specialized classes of enzymes serving as a carbon source for microbial development. Additionally, it is hypothesized that the tricarboxylic acid cycle (TCA) serves as a catalyst for the full breakdown of plastic into CO₂, H₂O, and other metabolic products. Due to the development of hazardous chemicals when MPs are degraded by a single species of microbes, the microflora evolves and creates combined degradation by reducing the drawbacks brought on by a single mode of degradation. Findings on the bacterial-mediated breakdown of MPs have concentrated on using bacterial biofilms, bacterial consortiums, and pure bacterial cultures in lab settings. By enrichment culture, this culture has been isolated from various sources including sediment, mud, wastewater, soil, and marine surroundings [20].

A recent study by Park and Kim [21] demonstrated the isolation of mesophilic mixed bacterial cultures, particularly *Bacillus* sp. and *Paenibacillus* sp., for micro-sized polyethylene (40 μm to 600 μm)

from biodegradable municipal waste. The findings revealed that, according to field emission scanning electron microscopy, the average particle diameter of microplastics decreased by 22.8%, and dry weight decreased by 14.7% after 60 days. Similarly, Auta et al. [22] showcased the biodegradation of polypropylene using *Bacillus* sp. strain 27 and *Rhodococcus* sp. strain 36 from mangrove sediment. Their research indicated that after 40 days of incubation, these bacterial strains could degrade polypropylene and reduce the polymer mass by 6.4% and 4.0%, respectively which is shown in Table 2.

Table 2. Bacterial strains capable of degradation of microplastics.

Source	Bacterial Strain	Type of MP	Degradation Efficiency	References
Marine	<i>Salinibacterium</i> sp. <i>Lysinibacillus</i> sp.	PE	19% within 6 months	[23]
Gut of <i>Lumbricus terrestris</i>	<i>Bacillus simplex</i> , <i>Bacillus</i> sp.	LDPE	60% degradation of LDPE within 21 days	[10]
Compost	<i>Bacillus thuringiensis</i>	PP and poly-L-lactide	12% degradation within 15 days	[24]
Contaminated site	<i>Streptomyces</i> sp	LDPE	15-19% weight loss within 30 days	[25]
Lake Sediments	<i>Bacillus cereus</i> CH6	PS MPs	10.7% post-incubation of 50 days	[26]
Contaminated Soil	<i>Anoxybacillus flavithermus</i> Gecek4s and <i>Bacillus firmus</i> ST5	PEP	17% in 25 days	[27]

Fungi

109 fungal isolates were gathered from 12 different places along the west coast of India, categorized according to the country's geographical regions. According to research using morphological and molecular methods, the most effective fungi for polyethylene degradation are *Aspergillus terreus* strain MANGF1/WL and PNP15/TS *Aspergillus sydowii* strain. The researchers found that 2 marine fungi (*A. tubingensis* VRKPT1 and *A. flavus* VRKPT2) degraded HDPE films without the need for pretreatment or oxidizing chemicals. “*A. flavus* VRKPT2 outperformed *A. tubingensis* VRKPT1” in HDPE film colonization, biofilm formation, and biodegradation. Furthermore, according to the authors, *in-vitro* HDPE degradation is possible with fungal strains which is shown in Table 3. As a result, they offer a workable remedy for the surroundingsal threat posed by HDPE polymers.

Table 3. Fungal strains capable of degradation of microplastics.

Source	Fungal Strain	Type of MP	Degradation Efficiency	References
Marine sediments	<i>Bjerkandera adusta</i> (smoky bracket fungus)	Gamma-treated polypropylene	Production of Ligninase	[28]
Contaminated site	<i>Aspergillus niger</i> , <i>Fusarium oxysporum</i>	LDPE and PU	Decrease in percent elongation and tensile strength of LDPE and PU after 90 days.	[29]
Contaminated Farmlands	<i>Nectriaceae</i> , <i>Pleosporaceae</i> and <i>Didymellaceae</i>	PE and PBAT/PLA microplastics	PE and PBAT/PLA plastic sphere attachments	[30]

Algae

In a recent investigation, “*Scenedesmus dimorphus*, *Anabaena spiroides*, and *Navicula pupae* were frequently observed in polyethylene bags”. Next, its effect on PE degradation was investigated. *Anabaena spiroides* demonstrated a high potential for PE breakdown in comparison to other algae, and microalgae strains for LDPE relative to HDPE [31]. Still, it is interesting to explore the scope for developing the approaches mediated through micro-algae up to a commercial scale.

Enzymatic basis of microplastic degradation

Depolymerization of petro-plastic waste for recycling or mineralization has become possible using

microbial enzymes to break down plastic [32]. The first step in this plastic biodegradation process involves microorganisms releasing extracellular enzymes, which are then incorporated into the plastic surface. The reaction between the plastic and the enzyme produces a short polymer hydrolysis. Gaps form, and microbial cells are eventually utilized as a carbon source to produce CO₂. Consequently, numerous strategies have been devised and implemented for eliminating microplastics from the surroundings. While every technique has its own set of benefits and drawbacks, there is insufficient information on certain microplastic removal techniques to recommend a single best approach. Further research could explore various microorganisms and methods that have proven effective in removing other contaminants from the surroundings.

BIOTECHNOLOGICAL TOOLS FOR MICROPLASTIC BIODEGRADATION

We have been able to change the genetic makeup of microbes and increase the efficiency of their biodegradation thanks to the development of several genetic engineering methods. Various methods, such as recombinant DNA technology, gene cloning, genetic engineering, and metabolic engineering, can enhance microbial biodegradation in polluted surroundings.[33]. Until now, there have been limited studies on employing genetic engineering to develop strains with enhanced microplastic biodegradation capabilities. Genetic modification has also been done to increase PVX uptake in bacterial biofilms. To promote the production of sticky exopolysaccharides, which enhances the bacteria's capacity to concentrate MPs in its biofilm, the *wspF* gene was deleted from *Pseudomonas aeruginosa*. A promoter that was activated by arabinose was also used to produce and introduce the *yhjH* gene into the bacteria. The function of the *yhjH* gene is to downregulate the expression of cyclic dimeric GMP level and to increase the expression of the gene that inhibits the formation of biofilms to a level that permits the release of MPs that have been trapped in the biofilm. Through the use of the "catch and release" method, effective MP scavengers for aquatic ecosystem bioremediation may be created. To increase the capacity of *Archaeoglobus fulgidus* to degrade polyethylene terephthalate, Lamah et al. carried out in silico site-specific mutagenesis of carboxylesterases to produce BTA hydrolases.[34] The primary enzyme responsible for MP biodegradation, such as Mn peroxidases and laccases, were synthesized by genetically modified strains of *E. coli* BL21 and *S. cerevisiae* BY 4741 and *P. chrysosporium*. These enzymes can more efficiently break down polyethylene terephthalate. By introducing sugars at certain locations that enable the enzyme to remain folded even at high temperatures and by creating physical barriers, genetically modified yeast produces microbial cutinases. This approach produces microbial cutinases that break down polyester linkage and may be used to break down polyethylene terephthalate at an optimal temperature of 75 °C. Using *Saccharomonospora viridis* AHK190. Some other prominent researches have been discussed which talks of plant fibre, polymer composite application, fibre composites, structured polymer composites [35-39].

CONCLUSION

Microplastics have emerged as a serious predicament due to the ability of extensive movement and hazardous impacts on ecosystems and human health. Extensive research conducted on microplastics has provided significant findings into their sources, pathways, and effects, Facilitating a comprehensive grasp of their overall ramifications. Studies have displayed a variable source including deterioration of plastic items, fragmentation of bigger plastic trash, and the shedding from synthetic fabrics. Several studies on the outcomes of microplastics on organisms have revealed potential ecological repercussions. Fish, shellfish, and plankton are examples of aquatic species that can consume microplastics through the food chain. Microplastic buildup in the digestive tract can result in physical harm, inflammation, and changes in eating behavior, all of which affect growth, reproduction, and survival. Polymeric approaches encompass various degradation methods such as enzymatic degradation, photodegradation, and chemical degradation. Each method offers unique advantages and challenges, allowing for a multifaceted approach to microplastic remediation. In conclusion, Microplastics have emerged as a notable surroundingsal concern, impacting both ecosystems and human health. Continued research and monitoring are necessary to further elucidate the extent of their impacts and develop effective strategies for mitigation. Urgent actions are needed at global, regional, and individual levels to remediate the pollution and prevent further proliferation of microplastics in the surroundings.

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