

Microbial Enzymes from Nigerian Dumpsites as Natural Biocatalysts: A Critical Review of LDPE Degradation Mechanisms and Biotechnological Potential

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ABSTRACT

Microbial communities thriving in Nigerian dumpsites represent an underexplored ecological reservoir of potent oxidative and hydrolytic enzymes with remarkable biocatalytic capabilities. These organisms inhabit chemically complex, stress-laden environments that select for metabolic versatility, enabling certain taxa to initiate and sustain the biodegradation of low-density polyethylene (LDPE), one of the most recalcitrant synthetic polymers. This critical review interrogates the strength of current evidence supporting LDPE biodegradation by indigenous bacteria, highlighting both the promise and the limitations of existing studies. Whilst numerous reports attribute polymer breakdown to enzymes such as oxygenases, peroxidases, esterases, and oxidoreductases, most findings rely on indirect assays, lack mechanistic validation, and are constrained by methodological inconsistencies. By reframing these microbial enzymes as natural biocatalysts, the review underscores their broader biotechnological and pharmacognostic potential, including applications in green chemistry, biotransformation, and environmental detoxification. Significant knowledge gaps persist, particularly in enzyme purification, kinetic characterization, structural elucidation, and omics-driven discovery. Addressing these gaps will be essential for advancing both the scientific understanding of LDPE biodegradation and the translational potential of dumpsite-derived microbial enzymes as valuable natural resources.

Keywords: Biotechnological potential, Dumpsite microbiota, Environmental biotransformation, LDPE biodegradation, Microbial enzymes, Natural biocatalysts, Oxidative and hydrolytic pathways, Pharmacognostic relevance, Polymer-degrading bacteria.

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INTRODUCTION

Global context

The global accumulation of synthetic plastics has intensified environmental concerns, with low-density polyethylene (LDPE) emerging as one of the most persistent contributors to terrestrial and aquatic pollution. Its hydrophobicity, high molecular weight, and absence of hydrolysable functional groups confer exceptional resistance to degradation, allowing LDPE to persist for decades in unmanaged waste streams.¹ Conventional waste-management strategies, including recycling, incineration, and landfilling, remain insufficient in many developing regions, including Nigeria, where rapid urbanization and inadequate infrastructure exacerbate plastic accumulation.² In this context, microbial

biodegradation has gained attention as a mechanistically compelling and environmentally sustainable alternative. Microorganisms capable of colonizing and oxidizing polyethylene surfaces employ enzymatic systems that initiate oxidative cleavage, generate bioavailable intermediates, and ultimately mineralize polymer-derived carbon, offering a biologically driven route to polymer transformation.³

Pharmacognostic relevance

Although dumpsites fall outside traditional pharmacognostic landscapes, they represent extreme ecological niches that select for microorganisms with exceptional metabolic versatility. Chronic exposure to hydrocarbons, heavy metals, and mixed organic waste drives the evolution of potent oxidative and hydrolytic enzymes, positioning these microbial communities as reservoirs of naturally occurring biocatalysts.⁴ Enzymes such as oxygenases, peroxidases, esterases, lipases, and oxidoreductases can be conceptualized as natural products, analogous to plant- or marine-derived metabolites traditionally studied in pharmacognosy. Their catalytic diversity and capacity for complex biotransformations highlight their potential relevance



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to green chemistry, environmental detoxification, and industrial bioprocessing.⁵ Reframing dumpsite-derived microbial enzymes as natural biocatalysts expands the pharmacognostic domain and underscores their value as biological resources with translational potential.

Rationale for a critical review

Despite increasing interest in LDPE biodegradation across Nigerian research institutions, the existing literature remains predominantly descriptive. Many studies rely on indirect indicators of polymer degradation, such as weight loss or surface oxidation, without providing mechanistic validation or enzyme-level characterization.⁶ Variability in sampling strategies, incubation conditions, polymer pretreatment, and analytical methods further complicates cross-study comparison and limits the reliability of reported degradation efficiencies.⁷ Claims of enzymatic involvement are often inferred rather than experimentally demonstrated, and few investigations have isolated, purified, or kinetically characterized the enzymes implicated in LDPE breakdown.⁸ These limitations highlight the need for a critical, enzyme-centric evaluation that interrogates the robustness of current evidence, identifies methodological weaknesses, and synthesizes cross-regional patterns in microbial diversity and enzymatic potential. This review addresses these gaps by providing a rigorous assessment of microbial LDPE degradation in Nigeria, emphasizing mechanistic interpretation, biochemical plausibility, and the broader pharmacognostic significance of dumpsite-derived microbial enzymes.

Ecological and Microbial Landscape of Nigerian Dumpsites

Environmental gradients shaping microbial selection

Nigerian dumpsites are characterized by dynamic environmental gradients that exert strong selective pressure on resident microbial communities. Temperature ranges typically fall between 25–40°C, conditions that favour mesophilic bacteria capable of producing oxidative and hydrolytic enzymes relevant to LDPE degradation.⁹ Soil pH commonly spans slightly acidic to neutral values (pH 5.5–7.0), a range that supports the growth of metabolically versatile taxa such as *Pseudomonas* and *Bacillus*.¹⁰ Seasonal fluctuations in moisture, driven by alternating wet and dry periods, further influence microbial colonization, biofilm formation, and oxygen availability, thereby modulating the balance between aerobic and anaerobic degradation pathways.¹¹

High organic load, particularly in urban centres such as Lagos and Ibadan, enhances microbial biomass and stimulates cometabolic activity, enabling microorganisms to degrade LDPE incidentally whilst metabolizing more readily available substrates.¹² Conversely, co-contaminants such as petroleum hydrocarbons and heavy metals can induce oxidative stress responses that upregulate oxygenases and peroxidases, potentially enhancing

polymer-degrading capacity but also introducing toxicity that may suppress sensitive taxa.¹³ These environmental gradients not only shape microbial diversity but also bias isolation outcomes, often favouring fast-growing, stress-tolerant genera while underrepresenting slow-growing or unculturable organisms that may possess equally relevant enzymatic systems.

Dominant microbial taxa

Across multiple Nigerian studies, a recurring set of bacterial genera, including *Pseudomonas*, *Bacillus*, *Klebsiella*, *Rhodococcus*, *Streptomyces*, and *Shigella* has been repeatedly associated with LDPE degradation.¹⁴ These taxa are well known for their metabolic flexibility, robust biofilm formation, and capacity to secrete oxidative and hydrolytic enzymes. *Pseudomonas* species, for example, are frequently reported as primary colonizers capable of initiating surface oxidation, whilst *Bacillus* and *Streptomyces* are often implicated in the breakdown of oxidized intermediates.¹⁵

However, the robustness of these claims warrants critical scrutiny. Many studies rely on indirect indicators such as weight loss, FTIR spectral shifts, or surface roughening, which can be influenced by abiotic factors or experimental artefacts.¹⁶ Few investigations have demonstrated direct enzymatic activity through purified enzymes, knockout studies, or kinetic assays. As a result, the reported LDPE-degrading capabilities of these genera may be overstated, reflecting methodological limitations rather than definitive biochemical evidence. Furthermore, the dominance of these taxa in published reports may reflect culturing biases rather than true ecological prevalence, as standard enrichment techniques tend to favour organisms that grow rapidly under laboratory conditions.

Methodological inconsistencies across studies

A major challenge in interpreting LDPE biodegradation research in Nigeria is the substantial methodological variability across studies. Sampling strategies differ widely, with some investigations collecting surface soils whilst others sample deeper layers or mixed waste matrices, leading to inconsistent microbial profiles.¹⁷ Enrichment protocols also vary in nutrient composition, incubation duration, and selective pressures, influencing which organisms are ultimately isolated.

Polymer pretreatment represents another significant source of inconsistency. Some studies employ UV-irradiated or thermally oxidized LDPE to accelerate microbial colonization, whilst others use untreated films, making degradation efficiencies difficult to compare.¹⁸ Incubation conditions, including temperature, agitation, moisture, and oxygen availability are rarely standardized, further complicating cross-study interpretation. Analytical methods also differ, with some studies relying solely on gravimetric analysis whilst others incorporate spectroscopy, microscopy, or chromatographic techniques.

These inconsistencies collectively undermine the comparability and reliability of reported findings. Without standardized protocols, it remains challenging to distinguish genuine microbial degradation from experimental artefacts or abiotic oxidation. A critical, harmonized methodological framework is therefore essential for advancing the field and enabling meaningful evaluation of microbial and enzymatic contributions to LDPE biodegradation.

Enzymatic Systems Implicated in LDPE Degradation

Oxidative enzymes are widely regarded as the primary catalysts initiating LDPE biodegradation because they introduce oxygen-containing functional groups into an otherwise chemically inert polymer backbone. Monooxygenases and dioxygenases are frequently implicated in this early oxidative phase, where they catalyse the insertion of oxygen atoms to generate carbonyl, hydroxyl, and carboxyl functionalities that increase polymer hydrophilicity and weaken carbon-carbon bonds.¹⁹ Laccases and peroxidases have also been reported to contribute to oxidative cleavage, particularly in dumpsite environments enriched with aromatic hydrocarbons or metal ions that induce oxidative stress responses.²⁰ Despite these assertions, the mechanistic evidence supporting oxidative enzyme involvement remains limited. Most studies rely on indirect indicators, such as FTIR carbonyl index shifts, SEM-observed surface erosion, or gravimetric weight loss without demonstrating enzyme specificity or catalytic turnover.²¹ Very few investigations have purified these enzymes, quantified their activity against LDPE-derived substrates, or established kinetic parameters such as (K_m), (V_{max}), or catalytic efficiency. The absence of enzyme-substrate interaction studies, isotopic tracing, or mutational analyses further restricts mechanistic interpretation, leaving the role of oxidative enzymes largely inferential rather than experimentally validated.

Hydrolytic enzymes, including esterases, lipases, and cutinases, are often proposed to act on oxidized LDPE fragments, cleaving ester-like or carbonyl-containing intermediates generated during oxidative pretreatment.²² Reports from Nigerian dumpsites frequently attribute secondary depolymerization to *Bacillus*- and *Streptomyces*-derived hydrolytic enzymes, suggesting a complementary role to oxidative systems. However, the assumption that LDPE oxidation reliably produces hydrolysable bonds warrants critical examination. Many studies extrapolate hydrolytic activity from assays using model substrates such as p-nitrophenyl esters, which do not accurately reflect the chemical complexity of oxidized polyethylene.²³ Direct evidence of hydrolysis, such as cleavage of authentic oxidized LDPE oligomers, identification of hydrolysis products via GC-MS, or enzyme-substrate docking analyses is largely absent. Without such validation, the involvement of hydrolytic enzymes remains speculative, and their mechanistic contribution to LDPE depolymerization cannot be confidently established.

Once oxidative and hydrolytic processes generate shorter, oxygenated intermediates, intracellular oxidoreductases, including alcohol dehydrogenases, aldehyde dehydrogenases, and ketone reductases are believed to convert these compounds into fatty acids or related metabolites that can enter β -oxidation or the tricarboxylic acid cycle.²⁴ These enzymes form the biochemical bridge between depolymerization and mineralization, enabling microorganisms to utilize polymer-derived carbon as an energy source. Yet, direct evidence for these metabolic steps remains sparse. Most studies infer oxidoreductase involvement based on the detection of carbonyl-containing intermediates or the general metabolic capabilities of the isolated taxa. Few investigations have quantified intracellular metabolites, monitored pathway flux, or demonstrated enzyme induction in the presence of LDPE-derived substrates. As a result, the metabolic assimilation phase remains one of the least experimentally substantiated components of the LDPE degradation pathway.

Despite growing interest in enzymatic LDPE degradation, several critical evidence gaps persist, limiting mechanistic clarity and hindering translational progress. A major limitation is the absence of purified enzymes; most studies attribute LDPE degradation to broad enzyme classes without isolating or characterizing the specific proteins involved.²⁵ Without purified enzymes, substrate specificity, catalytic turnover, and reaction mechanisms cannot be confirmed, making it impossible to distinguish true LDPE-active enzymes from general oxidative or hydrolytic enzymes acting on unrelated substrates. Structural biology is also entirely absent from the field. No crystallographic, cryo-EM, or high-resolution computational models exist for enzymes purported to degrade LDPE,²⁶ preventing identification of active-site motifs, substrate-binding pockets, or catalytic residues. This lack of structural insight severely limits rational enzyme engineering and the discovery of novel catalytic mechanisms.

The field is further constrained by an over-reliance on indirect assays. Weight-loss measurements, FTIR spectral changes, and SEM imaging dominate the literature, yet these methods cannot distinguish between abiotic oxidation, biofilm-mediated surface modification, and true enzymatic cleavage.²⁷ Such indirect approaches often overestimate degradation and may misattribute physical weathering or microbial colonization to enzymatic activity. Compounding this issue is the scarcity of metabolite profiling. Few studies have identified or quantified degradation intermediates or end-products using GC-MS, LC-MS, NMR, or isotopic tracing, leaving uncertainty about whether LDPE is fully mineralized, which metabolic pathways are involved, and whether intermediates accumulate or are assimilated. The absence of omics-driven enzyme discovery further limits mechanistic understanding. Without genomic, transcriptomic, or proteomic data, enzyme-encoding genes cannot be identified, expression patterns under LDPE exposure cannot be assessed, and pathway reconstruction remains speculative. Finally, the lack

of standardized protocols for enzyme assays and biodegradation testing undermines reproducibility and comparability across studies. Variability in polymer pretreatment, incubation conditions, and analytical methods makes it difficult to evaluate the true catalytic potential of microbial enzymes or to benchmark degradation efficiencies across different research groups.

Mechanistic Pathways of LDPE Biodegradation

The biodegradation of LDPE proceeds through a multistage sequence involving biodeterioration, depolymerization, and mineralization, each shaped by complex interactions between abiotic forces and microbial enzymatic systems. Understanding these stages is essential for evaluating the mechanistic plausibility of LDPE degradation claims and for identifying the limitations that currently constrain Nigerian studies.

Biodeterioration represents the initial phase in which the LDPE surface undergoes physical and chemical alterations that increase its susceptibility to microbial attack. Abiotic factors such as ultraviolet radiation, thermal fluctuations, and mechanical abrasion can introduce oxidative functional groups into the polymer matrix, creating carbonyl and hydroxyl moieties that enhance hydrophilicity and facilitate microbial adhesion.²⁸ Microorganisms subsequently colonize these modified surfaces, forming biofilms that concentrate oxidative enzymes and reactive oxygen species. However, many Nigerian studies conflate abiotic oxidation with true microbial biodeterioration, attributing surface changes solely to microbial activity without appropriate abiotic controls. This misinterpretation complicates the assessment of microbial contributions and often leads to overestimation of biodegradation potential.

Depolymerization follows as the critical biochemical stage in which microorganisms secrete oxidative and hydrolytic enzymes capable of cleaving the long-chain polyethylene backbone. Oxidative enzymes such as monooxygenases, dioxygenases, and peroxidases are believed to initiate chain scission by introducing oxygen into the polymer structure, while hydrolytic enzymes may act on oxidized intermediates to further reduce polymer length.²⁹ Despite these mechanistic proposals, direct evidence for enzyme-mediated depolymerization remains limited. Most studies rely on FTIR spectral shifts, weight-loss measurements, or SEM imaging to infer chain cleavage, yet these methods cannot distinguish between enzymatic activity and abiotic degradation. The absence of purified enzymes, kinetic assays, or product-profiling data leaves the biochemical basis of depolymerization largely unresolved.

Mineralization constitutes the terminal stage of LDPE biodegradation, during which low-molecular-weight intermediates are fully metabolized into CO₂, H₂O, CH₄, and microbial biomass. Aerobic pathways typically involve β -oxidation and the tricarboxylic acid cycle, whereas anaerobic microzones common in Nigerian dumpsites may support

methanogenic processes.³⁰ However, the quantification of mineralization products remains a major weakness in existing studies. CO₂ evolution is rarely measured, CH₄ detection is virtually absent, and few investigations employ isotopic tracing to confirm the assimilation of polymer-derived carbon. Without robust mineralization data, it is difficult to determine whether LDPE is truly degraded or merely fragmented into smaller, potentially persistent intermediates.

Synergistic microbial interactions play a crucial role in enhancing LDPE degradation efficiency. Primary colonizers such as *Pseudomonas* often initiate surface oxidation, creating functional groups that facilitate subsequent enzymatic attack. Secondary degraders, including *Bacillus* and *Streptomyces*, may metabolize oxidized oligomers, while biofilm-forming species such as *Klebsiella* and *Shigella* help stabilize the microbial community and maintain localized enzyme concentrations.³¹ These cooperative interactions suggest that microbial consortia may outperform individual isolates. However, consortium studies in Nigeria frequently lack mechanistic depth, often reporting enhanced degradation without elucidating the specific roles of each member or the biochemical basis of their synergy. The absence of controlled co-culture experiments, meta-transcriptomic analyses, or enzyme-activity partitioning limits the ability to draw definitive conclusions about the functional dynamics of microbial consortia.

The mechanistic sequence described above from initial abiotic deterioration through oxidative activation, enzyme-mediated depolymerization, and eventual metabolic mineralization can be conceptualized as an integrated biodegradation pathway shaped by both environmental gradients and microbial functional capacities. To contextualize these interactions, Figure 1 provides a consolidated schematic that maps the progressive transformation of LDPE within dumpsite ecosystems, highlighting the interplay between biofilm formation, oxidative and hydrolytic enzyme systems, and the metabolic assimilation of oxygenated intermediates. This visual framework reinforces the multi-stage nature of LDPE biodegradation and highlights the central role of synergistic microbial processes in driving polymer transformation under heterogeneous field conditions.

Environmental and Biochemical Factors Influencing LDPE Biodegradation

The efficiency of LDPE biodegradation in Nigerian dumpsites is governed by a complex interplay of environmental gradients and microbial biochemical responses. Temperature is one of the most influential factors, as most LDPE-associated bacteria isolated from Nigerian soils are mesophiles that exhibit optimal growth and enzyme production between 25°C and 40°C.³² Elevated temperatures increase polymer chain mobility and enhance susceptibility to oxidative attack, thereby accelerating biodeterioration and depolymerization. Seasonal fluctuations,

particularly the transition between wet and dry periods, further modulate microbial activity by altering moisture availability, oxygen diffusion, and the stability of biofilms that anchor enzymatic systems to polymer surfaces.

Soil pH exerts an equally significant influence on microbial colonization and enzyme stability. LDPE-degrading bacteria commonly thrive in slightly acidic to neutral soils (pH 5.5-7.0), conditions frequently observed in Nigerian dumpsites.³³ Acidic microzones generated by organic waste decomposition may enhance oxidative reactions on polymer surfaces, yet extreme pH fluctuations can inhibit enzyme activity or destabilize biofilms. The heterogeneity of pH across dumpsite microenvironments therefore creates spatial variability in biodegradation potential, complicating the interpretation of laboratory-based degradation assays that often rely on uniform pH conditions.

Moisture content and oxygen availability regulate both microbial metabolism and the physicochemical properties of LDPE. High moisture levels during the rainy season promote microbial proliferation, facilitate nutrient diffusion, and support the formation of hydrated biofilms that concentrate oxidative and hydrolytic enzymes.³⁴ Conversely, dry-season desiccation can suppress microbial activity and limit enzymatic diffusion, although some thermotolerant and desiccation-resistant taxa may remain active under these conditions. Oxygen availability determines whether aerobic or anaerobic pathways dominate; aerobic conditions favour oxidative enzyme production, whereas anaerobic microzones common in compacted waste layers may support methanogenic mineralization. The coexistence of these microenvironments complicates mechanistic interpretation and underscores the need for spatially resolved analyses of biodegradation processes.

Organic matter plays a dual role as both a nutrient source and a cometabolic driver. High organic load enhances microbial biomass and stimulates the production of oxidative enzymes involved in polymer breakdown, enabling microorganisms to degrade LDPE incidentally while metabolizing more readily available substrates.³⁵ However, excessive organic enrichment may also divert metabolic activity away from LDPE, reducing selective pressure for polymer degradation. The balance between nutrient availability and selective stress therefore shapes the composition and enzymatic potential of dumpsite microbial communities.

Co-contaminants such as petroleum hydrocarbons, heavy metals, and industrial chemicals further modulate microbial physiology in ways that can either enhance or inhibit LDPE degradation. Hydrocarbon-rich environments, particularly in the Niger Delta, may induce oxidative stress responses that upregulate oxygenases and peroxidases relevant to LDPE depolymerization.³⁶ In contrast, heavy metals can suppress microbial growth or inhibit enzyme activity depending on concentration and speciation. These opposing effects highlight the need for detailed chemical

characterization of dumpsite soils to contextualize microbial degradation outcomes.

Biofilm formation emerges as a critical determinant of LDPE biodegradation efficiency. Biofilms provide structural stability, protect cells from environmental stress, and maintain high local concentrations of extracellular enzymes at the polymer interface.³⁷ Within these biofilms, synergistic interactions among microbial taxa enhance depolymerization and mineralization processes. However, many Nigerian studies overlook the biochemical complexity of biofilms, often attributing degradation solely to planktonic cells or failing to distinguish between biofilm-mediated surface modification and true enzymatic cleavage. This oversight limits mechanistic understanding and may lead to inflated estimates of biodegradation potential.

Intrinsic polymer properties also influence biodegradation outcomes. Molecular weight, degree of branching, crystallinity, surface roughness, and the presence of additives determine how accessible LDPE is to microbial colonization and enzymatic attack. Lower molecular weight and reduced crystallinity enhance microbial accessibility and facilitate oxidative cleavage, whereas highly crystalline or additive-rich LDPE resists enzymatic modification.³⁸ These polymer-specific factors underscore the importance of characterizing LDPE substrates prior to biodegradation assays, yet many studies fail to report polymer properties, hindering cross-study comparison.

The environmental gradients described above, spanning temperature fluctuations, pH variability, moisture availability, oxygen diffusion, organic load, and co-contaminant stress collectively shape the microbial ecology and enzymatic potential of Nigerian dumpsites. These physicochemical drivers modulate oxidative stress responses, influence biofilm stability, and determine the balance between aerobic and anaerobic mineralization pathways. To contextualize these interactions, Figure 2 provides an integrated visual summary of the environmental and biochemical factors governing LDPE biodegradation, illustrating how site-specific conditions regulate microbial selection, enzyme induction, and overall degradation efficiency.

Enzymatic Pathways and Biochemical Mechanisms in LDPE Degradation

The enzymatic degradation of LDPE is driven by a coordinated sequence of oxidative, hydrolytic, and metabolic reactions that collectively transform an inert polymer into bioavailable intermediates. These pathways reflect the metabolic versatility of dumpsite microorganisms and highlight the biochemical sophistication of their enzyme systems. However, the mechanistic basis of these pathways remains incompletely understood, particularly within the context of Nigerian studies, where experimental limitations often obscure the true catalytic contributions of microbial enzymes.

The initial oxidative phase is central to LDPE biodegradation because polyethylene lacks functional groups susceptible to direct enzymatic hydrolysis. Oxidative enzymes—including monooxygenases, dioxygenases, laccases, and peroxidases—are believed to introduce carbonyl, hydroxyl, and carboxyl functionalities into the polymer backbone, thereby increasing hydrophilicity and reducing crystallinity.³⁹ These modifications weaken carbon-carbon bonds and create reactive sites that facilitate subsequent enzymatic attack. Despite the biochemical plausibility of this mechanism, direct evidence remains scarce. Most studies infer oxidative activity from FTIR spectral shifts or surface morphological changes, yet few have demonstrated enzyme-substrate interactions, catalytic turnover, or the formation of specific oxidized intermediates. The absence of purified oxidative enzymes or kinetic data limits mechanistic interpretation and leaves open the possibility that abiotic oxidation may account for a substantial portion of observed polymer modification.

Following oxidative activation, hydrolytic enzymes are thought to act on partially oxidized LDPE fragments. Esterases, lipases, and cutinases may cleave ester-like or carbonyl-containing linkages generated during oxidation, producing shorter oligomers and monomers that can be transported into microbial cells.⁴⁰ However, the assumption that LDPE oxidation consistently

produces hydrolysable bonds remains unverified. Many studies rely on model substrates that do not accurately mimic oxidized polyethylene, and few have characterized the chemical structure of LDPE-derived intermediates. Without direct evidence of hydrolysis, such as cleavage of authentic oxidized oligomers or identification of hydrolysis products—the mechanistic contribution of hydrolytic enzymes remains speculative. This uncertainty underscores the need for detailed chemical analyses and enzyme-substrate validation to confirm the role of hydrolytic pathways in LDPE depolymerization.

Once oxidized and hydrolyzed intermediates are generated, intracellular metabolic enzymes facilitate their assimilation. Oxidoreductases, including alcohol dehydrogenases, aldehyde dehydrogenases, and ketone reductases are believed to convert oxygenated oligomers into fatty acids or related metabolites that can enter β -oxidation or the tricarboxylic acid cycle.⁴¹ These enzymes form the biochemical bridge between depolymerization and mineralization, enabling microorganisms to utilize polymer-derived carbon as an energy source. Yet, direct evidence for these metabolic transformations is limited. Few studies have quantified intracellular metabolites, monitored pathway flux, or demonstrated enzyme induction in response to LDPE-derived substrates. The metabolic fate of polymer-derived carbon

Conceptual Overview of LDPE Biodegradation Pathways in Dumpsite Microbiota

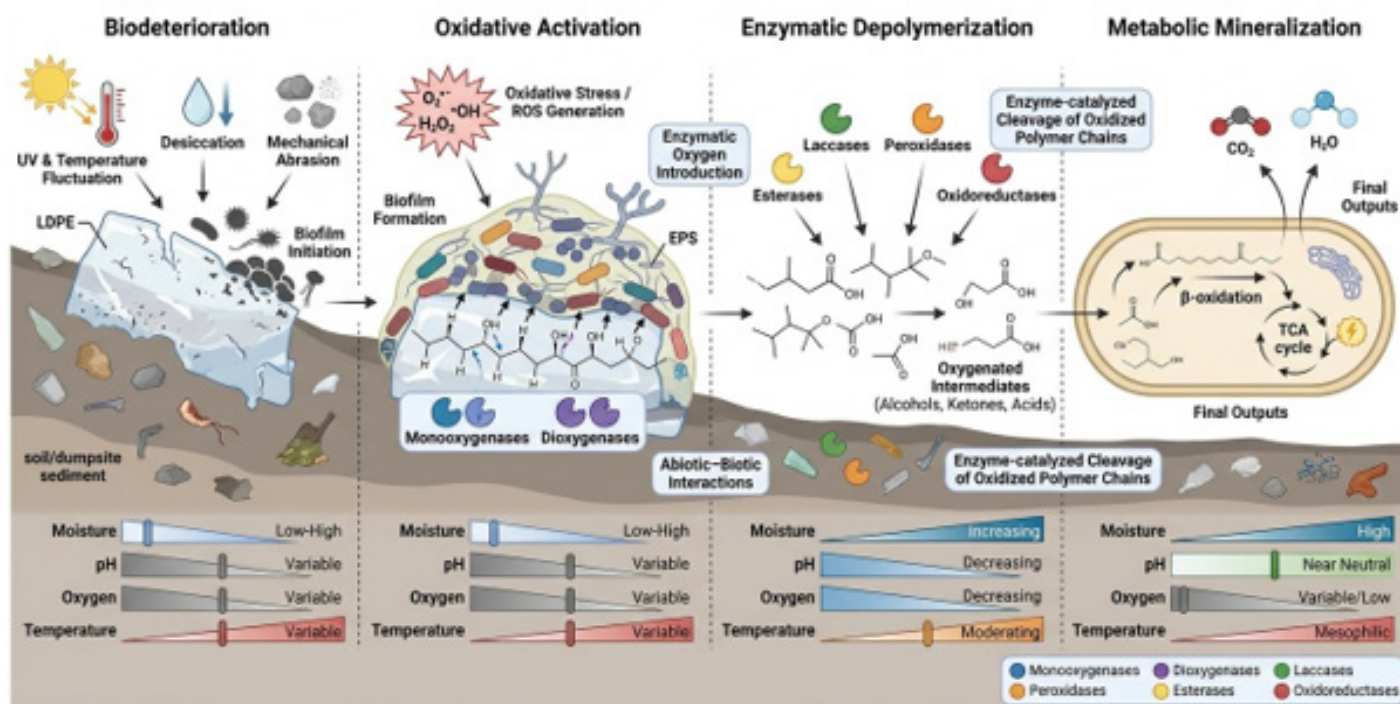


Figure 1: Conceptual overview of LDPE biodegradation pathways in dumpsite microbiota. Schematic representation of the multistage LDPE biodegradation process, illustrating biodeterioration, oxidative activation, enzymatic depolymerization, and metabolic mineralization. The figure highlights the roles of monooxygenases, dioxygenases, laccases, peroxidases, esterases, and oxidoreductases in generating oxygenated intermediates that enter microbial metabolic pathways. Biofilm formation, abiotic-biotic interactions, and environmental gradients typical of Nigerian dumpsites are integrated to contextualize mechanistic relevance.

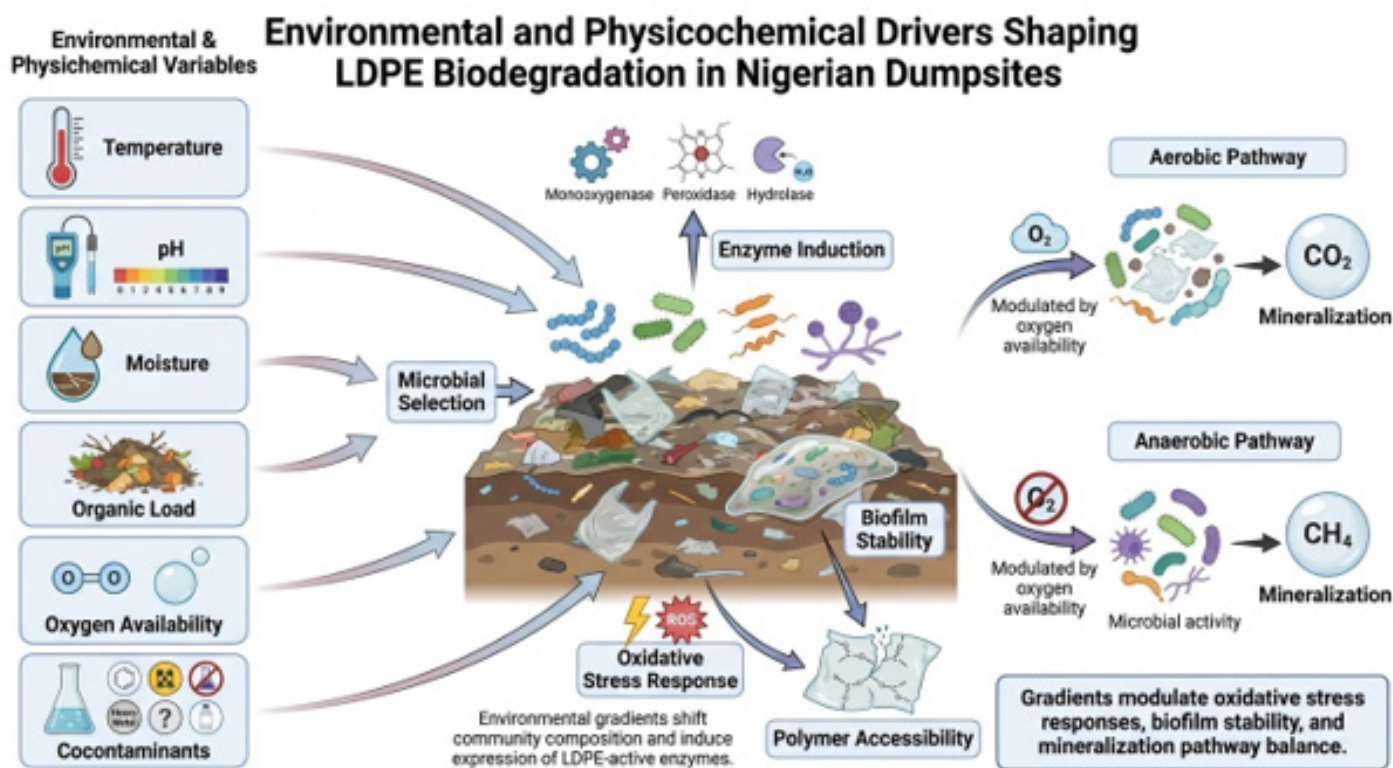


Figure 2: Environmental and physicochemical drivers shaping LDPE biodegradation in Nigerian dumpsites. Diagram summarizing key environmental variables, including temperature, pH, moisture, organic load, oxygen availability, and cocontaminants and their influence on microbial selection, enzyme induction, and polymer accessibility. The figure emphasizes how these gradients modulate oxidative stress responses, biofilm stability, and the balance between aerobic and anaerobic mineralization pathways.

therefore remains one of the least substantiated aspects of LDPE biodegradation, particularly in Nigerian research.

The integration of oxidative, hydrolytic, and metabolic pathways reflects the synergistic nature of LDPE biodegradation, yet the mechanistic coherence of these pathways is often assumed rather than demonstrated. Many studies present linear degradation models without accounting for the complexity of microbial consortia, the heterogeneity of dumpsite environments, or the physicochemical constraints imposed by the polymer itself. The absence of pathway-level validation, such as isotopic tracing, metabolomics, or transcriptomic profiling limits the ability to construct accurate mechanistic models. As a result, current understanding of LDPE biodegradation remains fragmented, with significant gaps in biochemical evidence and mechanistic clarity.

The enzymatic processes described above, from initial oxidative activation through hydrolytic fragmentation, oligomer transport, and intracellular β -oxidation collectively define the biochemical framework through which microorganisms transform LDPE into metabolically accessible intermediates. These pathways also highlight the substantial evidence gaps that currently limit mechanistic certainty, including the absence of purified enzymes, missing kinetic parameters, and the lack of structural data for key catalytic proteins. To consolidate these mechanistic insights, Figure 3 provides an integrated schematic of the enzymatic

systems implicated in LDPE depolymerization and metabolic assimilation, illustrating both the proposed biochemical sequence and the unresolved experimental limitations that constrain current understanding.

CHALLENGES, LIMITATIONS, AND KNOWLEDGE GAPS IN LDPE BIODEGRADATION RESEARCH IN NIGERIA

Research on LDPE biodegradation in Nigeria has expanded considerably in recent years, yet significant challenges continue to constrain the reliability, reproducibility, and mechanistic clarity of reported findings. One of the most persistent limitations is the heavy reliance on indirect indicators of degradation, such as weight loss, FTIR spectral shifts, and SEM imaging, which cannot distinguish between abiotic oxidation, microbial colonization, and true enzymatic cleavage.⁴² These methods often overestimate biodegradation and may misattribute physical weathering or environmental exposure to microbial activity. Without direct biochemical assays, purified enzymes, or metabolite profiling, it remains difficult to confirm whether observed changes reflect genuine polymer breakdown or superficial surface modification.

Methodological inconsistencies further complicate interpretation across studies. Variability in sampling depth, soil type, waste composition, and seasonal timing introduces substantial heterogeneity into microbial isolation outcomes.⁴³ Differences

in enrichment media, incubation conditions, and polymer pretreatment, particularly the use of UV-irradiated or thermally oxidized LDPE make cross-study comparison challenging and often lead to inflated degradation efficiencies. Many studies also lack appropriate abiotic controls, making it difficult to separate microbial contributions from environmental oxidation. The absence of standardized protocols for biodegradation assays undermines reproducibility and limits the ability to benchmark Nigerian findings against global research.

A major knowledge gap lies in the limited biochemical characterization of enzymes implicated in LDPE degradation. Although oxidative, hydrolytic, and metabolic enzymes are frequently cited, few studies have isolated, purified, or kinetically characterized these proteins.⁴⁴ Without enzyme purification, substrate specificity and catalytic mechanisms remain speculative. The absence of structural biology whether crystallographic, cryo-EM, or computational further restricts mechanistic insight and prevents rational enzyme engineering. This gap is particularly striking given the potential of dumpsite microorganisms to yield novel biocatalysts with unique oxidative capabilities.

Another critical limitation is the near absence of metabolite-level evidence. Very few studies have identified or quantified LDPE-derived intermediates using GC-MS, LC-MS, NMR, or isotopic tracing.⁴⁵ As a result, the metabolic fate of polymer-derived

carbon remains largely unknown. Without confirmation of mineralization products such as CO₂ or CH₄, it is impossible to determine whether LDPE is fully degraded or merely fragmented into smaller, potentially persistent microplastic intermediates. This lack of metabolic resolution represents one of the most significant barriers to validating LDPE biodegradation claims.

The limited use of omics-based approaches further constrains mechanistic understanding. Genomic, transcriptomic, and proteomic analyses are rarely employed in Nigerian studies, leaving enzyme-encoding genes unidentified and metabolic pathways uncharacterized.⁴⁶ Without omics data, it is difficult to determine whether LDPE exposure induces specific enzymatic pathways or whether degradation is merely a by-product of general stress responses. The absence of metagenomic profiling also limits the discovery of unculturable taxa that may play critical roles in polymer degradation but remain overlooked due to culture-based biases.

Finally, the ecological complexity of dumpsites is often oversimplified in laboratory studies. Many investigations rely on single isolates grown under controlled conditions, yet LDPE degradation *in situ* is likely driven by synergistic microbial consortia operating within biofilms and heterogeneous microenvironments.⁴⁷ The lack of controlled co-culture experiments, metatranscriptomic analyses, or functional

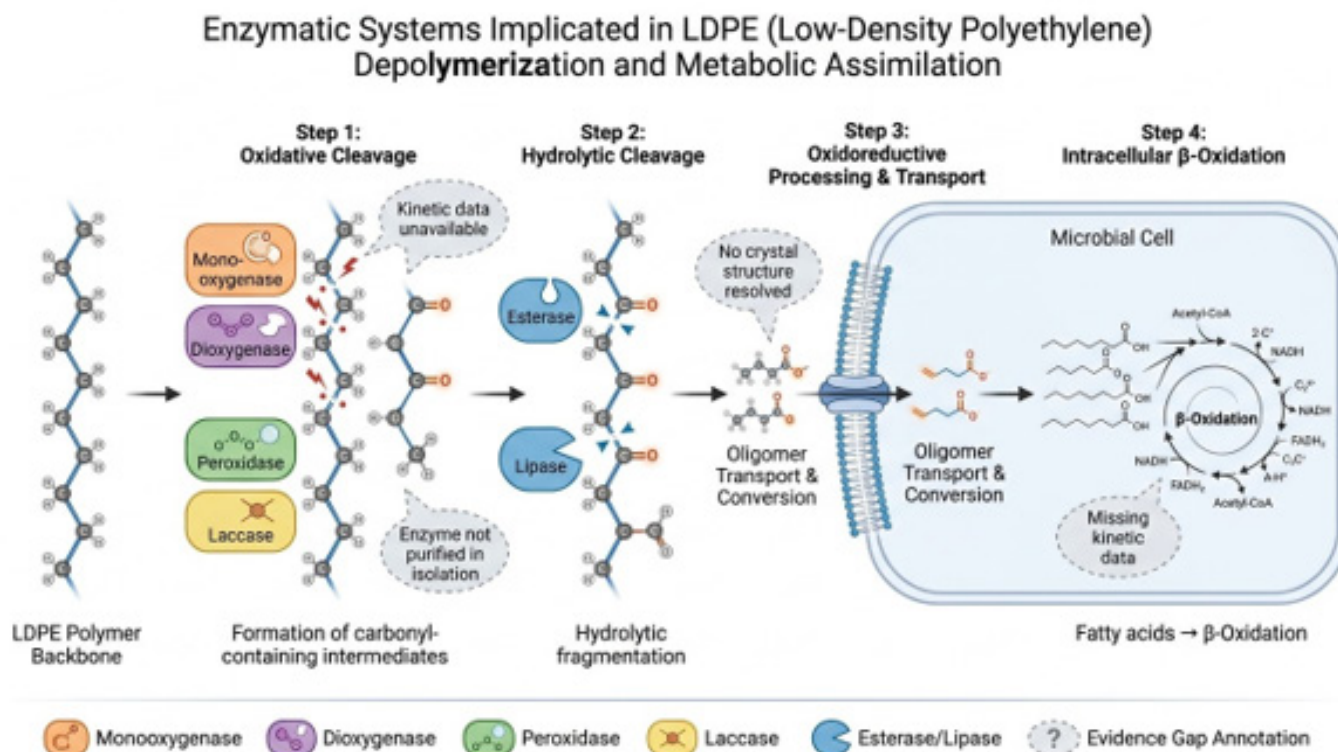


Figure 3: Enzymatic systems implicated in LDPE depolymerization and metabolic assimilation. Mechanistic illustration of oxidative, hydrolytic, and oxidoreductive enzyme classes involved in LDPE degradation. The figure depicts oxidative cleavage of the polyethylene backbone, formation of carbonyl-containing intermediates, hydrolysis of oxidized fragments, and intracellular conversion of oligomers into fatty acids entering β-oxidation. Evidence gaps, such as missing kinetic data, lack of purified enzymes, and absence of structural biology are visually annotated.

partitioning studies limits understanding of how microbial interactions shape degradation pathways. This gap is particularly important given the recurring observation that consortia often outperform individual strains, suggesting that LDPE biodegradation is an emergent property of microbial community dynamics rather than the activity of isolated taxa.

The cooperative dynamics described above highlight the central role of microbial consortia in driving LDPE biodegradation, where primary colonizers initiate oxidative surface modification, secondary degraders metabolize oxidized intermediates, and biofilm-forming taxa coordinate enzyme secretion through quorum-regulated signaling. These interactions create spatially stratified microenvironments that enhance enzyme concentration at the polymer interface and enable emergent biodegradative pathways not achievable by single isolates. To illustrate these synergistic processes, Figure 4 presents a detailed schematic of consortium-level interactions, highlighting the spatial organization, metabolic exchange, and coordinated enzymatic activities that collectively underpin LDPE degradation in dumpsite ecosystems.

Biotechnological and pharmacognostic implications

The microbial enzymes implicated in LDPE degradation hold considerable promise as natural biocatalysts with broad biotechnological relevance. Dumpsite microorganisms are

continually exposed to chemically complex and stress-laden environments, conditions that select for enzymes with exceptional oxidative and hydrolytic capabilities.⁴⁸ These enzymes, particularly monooxygenases, dioxygenases, laccases, peroxidases, esterases, and oxidoreductases exhibit catalytic properties that extend far beyond polymer degradation. Their ability to mediate difficult oxidative transformations positions them as valuable tools for green chemistry, bioremediation, and industrial bioprocessing. The catalytic versatility of these enzymes suggests potential applications in the detoxification of xenobiotics, the synthesis of fine chemicals, and the biotransformation of hydrophobic substrates that are otherwise challenging to modify using conventional chemical methods.

From a pharmacognostic perspective, dumpsite-derived microbial enzymes can be conceptualized as natural products, analogous to plant-, fungal-, or marine-derived metabolites traditionally studied in natural-product chemistry. Their ecological origin, structural diversity, and catalytic specificity align with the broader pharmacognostic mission of identifying biologically active compounds from natural sources.⁴⁹ The oxidative enzymes associated with LDPE degradation, for example, share mechanistic similarities with enzymes involved in drug metabolism, aromatic ring cleavage, and oxidative detoxification. This parallel highlights their potential utility in biocatalytic drug synthesis, metabolic engineering, and the

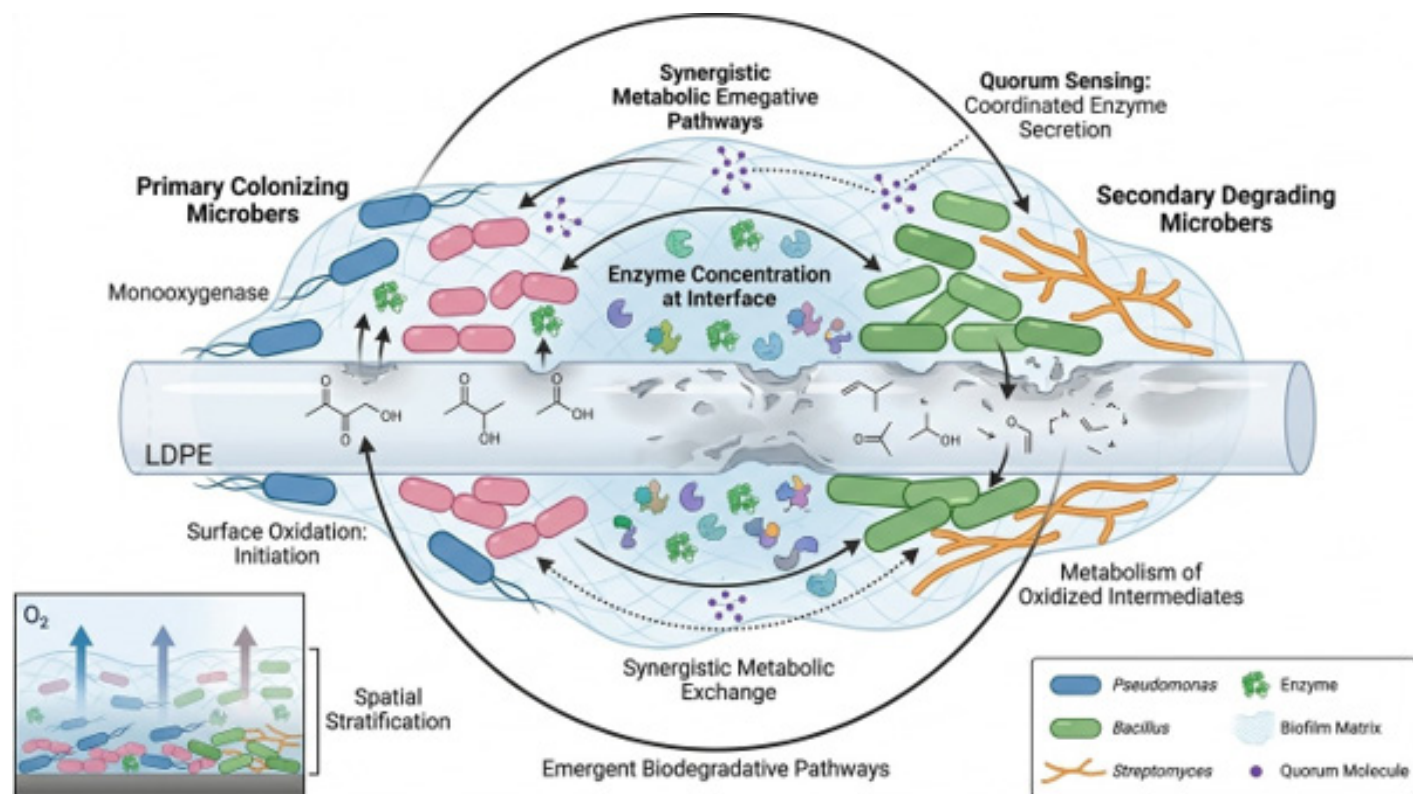


Figure 4: Microbial consortia and synergistic interactions driving LDPE biodegradation. Visualization of primary colonizers (e.g., *Pseudomonas*, *Rhodococcus*) initiating surface oxidation, secondary degraders (e.g., *Bacillus*, *Streptomyces*) metabolizing oxidized intermediates, and biofilm-forming taxa enhancing enzyme concentration at the polymer interface. Cooperative metabolic networks, quorum-regulated enzyme secretion, and spatial organization within biofilms are highlighted to illustrate emergent biodegradation capabilities.

development of environmentally benign synthetic pathways. By reframing these enzymes as pharmacognostically relevant natural products, the field expands its scope to include microbial biocatalysts from unconventional ecological niches.

The biotechnological potential of these enzymes is further highlighted by their relevance to the circular bioeconomy. As global interest in sustainable materials and waste valorization grows, microbial enzymes capable of transforming recalcitrant polymers into value-added products represent a promising frontier.⁵⁰ Oxidized LDPE intermediates could, in principle, be converted into biodegradable polymers, biosurfactants, or metabolic precursors through engineered microbial pathways. Although such applications remain speculative in the Nigerian context, they illustrate the transformative potential of enzyme-driven polymer valorization. Harnessing these capabilities will require advances in enzyme engineering, synthetic biology, and metabolic pathway optimization, areas where Nigerian research is still in its infancy.

Despite this promise, significant barriers limit the translation of dumpsite-derived enzymes into practical biotechnological applications. The absence of purified enzymes, structural data, and kinetic characterization restricts the ability to evaluate catalytic efficiency or engineer improved variants.⁵¹ Without genomic or proteomic data, enzyme-encoding genes remain unidentified, hindering heterologous expression and large-scale production. These limitations highlight the need for integrative

research approaches that combine classical microbiology with modern omics, structural biology, and protein engineering. Such approaches would not only clarify the mechanistic basis of LDPE degradation but also unlock the full biotechnological potential of these enzymes.

Pharmacognostically, the lack of biochemical and structural characterization represents a missed opportunity. Natural-product research traditionally relies on detailed structural elucidation, activity profiling, and mechanistic analysis, elements largely absent from current LDPE biodegradation studies in Nigeria.⁵² Incorporating these methodologies would elevate microbial enzyme research to the standards expected in natural-product chemistry and facilitate the discovery of novel catalytic motifs with therapeutic or industrial relevance. Moreover, the exploration of dumpsite microbiota aligns with the growing recognition that extreme or polluted environments can yield unique bioactive compounds, expanding the pharmacognostic landscape beyond conventional ecological sources.

Ultimately, the biotechnological and pharmacognostic implications of LDPE-degrading microbial enzymes hinge on the development of rigorous, mechanistically informed research frameworks. By integrating enzyme purification, structural biology, omics-driven discovery, and metabolic engineering, future studies could transform these enzymes from poorly characterized environmental curiosities into well-defined natural

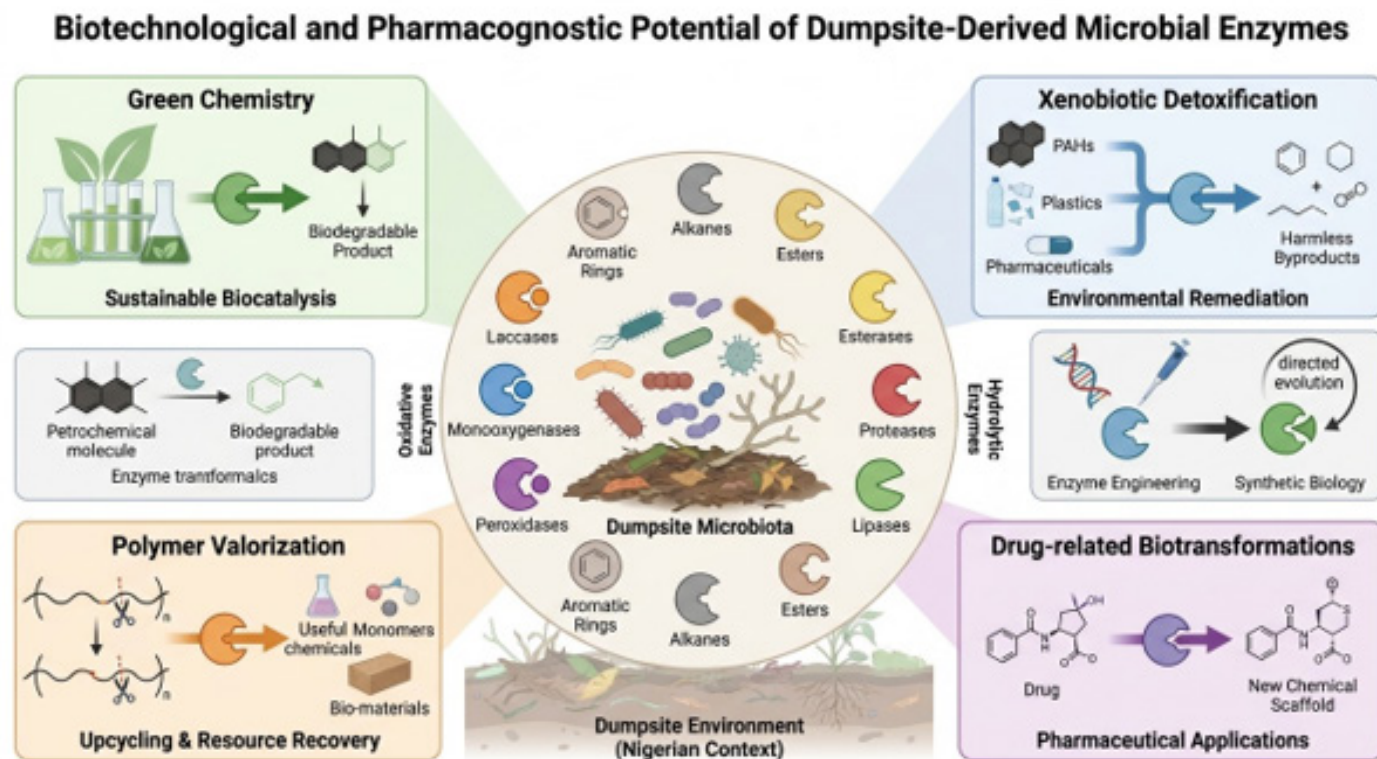


Figure 5: Biotechnological and pharmacognostic potential of dumpsite-derived microbial enzymes. Framework illustrating how oxidative and hydrolytic enzymes from dumpsite microbiota can be leveraged as natural biocatalysts for green chemistry, xenobiotic detoxification, polymer valorization, and drug-related biotransformations. The figure positions these enzymes within the broader pharmacognostic landscape, emphasizing their ecological origin, catalytic diversity, and potential for enzyme engineering and synthetic-biology applications.

biocatalysts with significant scientific and industrial value. Such advancements would not only enhance understanding of polymer biodegradation but also position Nigerian dumpsites as reservoirs of untapped biochemical innovation.

The biotechnological and pharmacognostic relevance of dumpsite-derived microbial enzymes extends far beyond their putative roles in LDPE degradation, positioning these biocatalysts as valuable natural resources for green chemistry, xenobiotic detoxification, polymer valorization, and drug-related biotransformations. Their catalytic diversity, ecological origin, and potential for engineering through synthetic-biology frameworks underscore their broader industrial and therapeutic significance. To consolidate these translational opportunities, Figure 5 provides an integrated overview of the biotechnological and pharmacognostic potential of these enzymes, illustrating their roles in sustainable bioprocessing, pollutant remediation, enzyme engineering, and the generation of novel chemical scaffolds.

CRITICAL KNOWLEDGE GAPS AND FUTURE RESEARCH PRIORITIES

Despite growing interest in LDPE biodegradation across Nigerian research institutions, substantial knowledge gaps continue to limit mechanistic understanding and hinder the development of robust, evidence-driven biodegradation frameworks. One of the most significant gaps is the absence of purified enzymes capable of acting directly on LDPE or its oxidized intermediates. Although oxidative and hydrolytic enzymes are frequently implicated, their catalytic roles remain largely speculative because no studies have isolated these proteins, demonstrated substrate specificity, or established kinetic parameters under physiologically relevant conditions.⁵³ Without purified enzymes, it is impossible to confirm whether observed polymer modifications arise from true enzymatic cleavage or from abiotic oxidation and microbial colonization.

A second major gap lies in the complete lack of structural biology. No crystallographic, cryo-EM, or high-resolution computational models exist for enzymes purported to degrade LDPE, leaving active-site architecture, substrate-binding pockets, and catalytic residues entirely undefined.⁵⁴ Structural insights are essential for understanding reaction mechanisms, guiding protein engineering, and identifying novel catalytic motifs. The absence of such data severely limits the translational potential of dumpsite-derived enzymes and prevents the field from advancing beyond descriptive microbiology.

Another critical limitation is the over-reliance on indirect assays such as weight-loss measurements, FTIR spectral shifts, and SEM imaging. These methods cannot differentiate between abiotic weathering, biofilm-mediated surface modification, and true enzymatic depolymerization, yet they remain the

dominant tools in Nigerian studies.⁵⁵ Without direct biochemical assays, metabolite profiling, or isotopic tracing, claims of LDPE degradation remain tentative. This methodological gap is compounded by the scarcity of quantitative mineralization data; CO₂ evolution is rarely measured, CH₄ detection is virtually absent, and no studies have traced polymer-derived carbon into microbial biomass. As a result, the completeness of LDPE degradation remains unknown.

Omics-driven discovery represents another major frontier that remains largely unexplored. Genomic, transcriptomic, and proteomic analyses are essential for identifying enzyme-encoding genes, reconstructing metabolic pathways, and determining whether LDPE exposure induces specific biochemical responses.⁵⁶ The absence of omics data limits the discovery of novel enzymes, obscures the roles of unculturable taxa, and prevents the development of mechanistic models that integrate microbial ecology with enzymatic function. Metagenomic profiling could reveal the functional potential of microbial consortia that outperform individual isolates, yet such approaches have not been applied in Nigerian LDPE biodegradation research.

The ecological complexity of dumpsites introduces additional challenges that remain insufficiently addressed. Most studies rely on single isolates grown under controlled laboratory conditions, yet LDPE degradation *in situ* is likely driven by synergistic microbial communities operating within biofilms and heterogeneous microenvironments.⁵⁷ The absence of controlled co-culture experiments, metatranscriptomic analyses, or functional partitioning studies limits understanding of how microbial interactions shape degradation pathways. Future research must therefore prioritize community-level investigations that capture the emergent properties of microbial consortia.

Finally, the lack of standardized protocols for sampling, polymer pretreatment, incubation conditions, and analytical methods undermines reproducibility and comparability across studies. Without harmonized methodologies, it is difficult to benchmark degradation efficiencies, evaluate enzyme performance, or integrate findings into global LDPE biodegradation frameworks.⁵⁸⁻⁶¹ Establishing standardized, mechanistically informed protocols is essential for advancing the field and ensuring that Nigerian research contributes meaningfully to international efforts in polymer biodegradation.

Collectively, these knowledge gaps highlight the need for a paradigm shift from descriptive, assay-driven studies toward mechanistically rigorous, enzyme-centric research. Future priorities must include enzyme purification and characterization, structural biology, omics-driven pathway discovery, metabolite-level validation, and community-scale mechanistic studies. By addressing these gaps, researchers can transform LDPE biodegradation from a loosely defined phenomenon into a

scientifically grounded process with significant biotechnological and pharmacognostic potential.

CONCLUSION

The current body of research on LDPE biodegradation in Nigeria reveals a field rich in ecological potential yet constrained by methodological and mechanistic limitations. Dumpsite microbiota clearly possesses metabolic versatility and enzymatic capabilities shaped by chronic exposure to complex waste streams, suggesting that these environments may serve as reservoirs of potent oxidative and hydrolytic enzymes with significant biotechnological value. However, the evidence supporting true enzymatic depolymerization and mineralization of LDPE remains largely inferential, relying heavily on indirect analytical methods that cannot distinguish between abiotic deterioration, microbial colonization, and genuine biochemical cleavage.

A recurring theme across the literature is the disconnect between observed surface modifications and the mechanistic processes required for complete polymer breakdown. While oxidative, hydrolytic, and metabolic enzymes are frequently invoked, their roles remain speculative due to the absence of purified proteins, kinetic characterization, structural data, and metabolite-level validation. This gap underscores the need for a paradigm shift from descriptive microbiology toward mechanistically rigorous, enzyme-centric research frameworks that integrate biochemical assays, omics-driven discovery, and structural biology.

The ecological complexity of Nigerian dumpsites further complicates interpretation, as LDPE degradation *in situ* is likely driven by synergistic microbial consortia operating within biofilms and heterogeneous microenvironments. Yet, most studies rely on single isolates and simplified laboratory conditions that fail to capture the emergent properties of microbial communities. Future research must therefore embrace community-level analyses, controlled co-culture experiments, and meta-transcriptomic profiling to elucidate the functional dynamics underlying polymer degradation.

Despite these limitations, the biotechnological and pharmacognostic implications of dumpsite-derived microbial enzymes remain compelling. Their catalytic diversity, ecological origin, and potential for oxidative biotransformations position them as promising natural biocatalysts for green chemistry, environmental remediation, and industrial bioprocessing. Realizing this potential will require coordinated efforts to standardize methodologies, validate mechanistic pathways, and develop robust biochemical and structural datasets.

In summary, LDPE biodegradation research in Nigeria stands at a critical juncture. The field has demonstrated ecological promise and generated valuable preliminary insights, yet substantial knowledge gaps must be addressed before claims of enzymatic LDPE degradation can be fully substantiated. By

adopting rigorous, interdisciplinary approaches that integrate microbiology, enzymology, structural biology, and systems-level analyses, future studies can transform this emerging field into a scientifically grounded and globally relevant domain with significant environmental and biotechnological impact.

ABBREVIATIONS

LDPE: Low-Density Polyethylene; **FTIR:** Fourier Transform Infrared Spectroscopy; **SEM:** Scanning Electron Microscopy; **GC-MS:** Gas Chromatography-Mass Spectrometry; **LC-MS:** Liquid Chromatography-Mass Spectrometry; **NMR:** Nuclear Magnetic Resonance; **PET:** Polyethylene Terephthalate; **PETase:** Polyethylene Terephthalate Hydrolase; **MHEase:** Mono(2-hydroxyethyl) Terephthalate Hydrolase; **K_m:** Michaelis Constant; **V_{max}:** Maximum Reaction Velocity; **DNA:** Deoxyribonucleic Acid; **RNA:** Ribonucleic Acid.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

Conceptualization and initial drafts were carried out by T.A.N and D.D. V.A. and I.E.C. transformed manuscript draft into a comprehensive review manuscript. Image software support provided by V.A. Validation was performed by T.A.N., V.A. and I.E.C. Formal analysis and investigation were conducted by D.D. Resources and data curation were provided by T.A.N and V.A. Subsequent review and editing undertaken by T.A.N., V.A. and I.E.C. Visualization was completed by V.A. and I.E.C, while supervision was provided by V.A. and I.E.C. Project administration was managed by V.A. All authors have read and approved the final version of the manuscript.

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