

A Mini Review on Recent Insight Into Degradation of Environmental Plastics

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Abstract

Plastic trash is inadvertently released into the environment, where it deteriorates in mechanical and physicochemical qualities and forms plastic particles that are referred to as microplastics when their size is less than 5 mm. Microplastic pollution has been documented in a variety of environments recently and is now thought to pose a risk to both human and environmental health. There is a perception that plastics are a threat to the environment due to their difficulty in degrading. However, little is yet known about how plastics degrade in the environment and how microplastics originate. The purpose of this review is to summarize the environmental degradation of plastics and identified mechanisms of plastic degradation. Efforts has been put on to understand the recent development in the field of MP degradation. Future studies should pinpoint the most important environmental factors and properties of MP that influence the degradation rate of MPs.

Key Words: Microplastic, Degradation, Enzymes, assimilation, Photo thermal degradation

Introduction

Widely used in agriculture, construction, health care and consumer goods, plastics play an important role in all areas of the world economy. Henceforth production of synthetic plastics has become fastest growing sectors in the world industry. Unique properties of plastic superior the other material which has resulted in 20-fold increase in the production of plastics since from 1964 and expected to be tripled by 2050(Muñoz, Morales et al. 2021). The whopping global demand for such polymers and no effective strategy applied to tackle the disposal issues brought on by plastic waste has resulted in significant plastic waste contamination, particularly in the marine environment (Chia, Tang et al. 2020). According to research, approximately 40 % of global plastics waste are being processed and recycled, while the remaining 60% is left untreated(Markl and Lackner 2020). According to current report, around 8300 million metric ton of plastic was manufacture, generating 6300 mt of plastic wastes up to 2015(Geyer, Jambeck et al. 2017). In addition, these untreated plastics are not biodegradable. Significate parts of unprocessed plastics which include ethylene, propylene, and polystyrene derived from fossil

hydrocarbons, natural gets degraded but few are left behind for an extended period of time and accumulates in marine bodies, elevated risk of environmental pollution and climate change(Dharmaraj, Ashokkumar et al. 2021).

Micro plastics, defined as microscopic plastic particles ranging in size from 0.1mm to 5mm⁷, contribute to plastic bioavailability. Micro plastics are divided as primary plastics which are produced for application including cosmetics, drug vectors, facial scrubbers, air-blasting media *ect*. Secondary micro plastic otherwise called as macro fragments which are formed because of biological and chemical degradation of plastic (Vazquez, Rahman et al. 2021). The concern of micro plastic is that it cannot only transfer toxic pollutants into water, but also leach plasticizers into the food chain, potentially leading to bioaccumulation. Research through light on impact of trophic level transfer of micro plastic in Marine ecosystem eventually ingestion by humans(Huang, Song et al. 2021). Apart of biomagnification of microplastics, recent research highlight's on microplastic biofilm as an important vector for microbes which results in new microbial niches in the aquatic system(Di Cesare, Pinnell et al. 2021). Below figure (Fig1) give comprehensive degradation methods of MP.

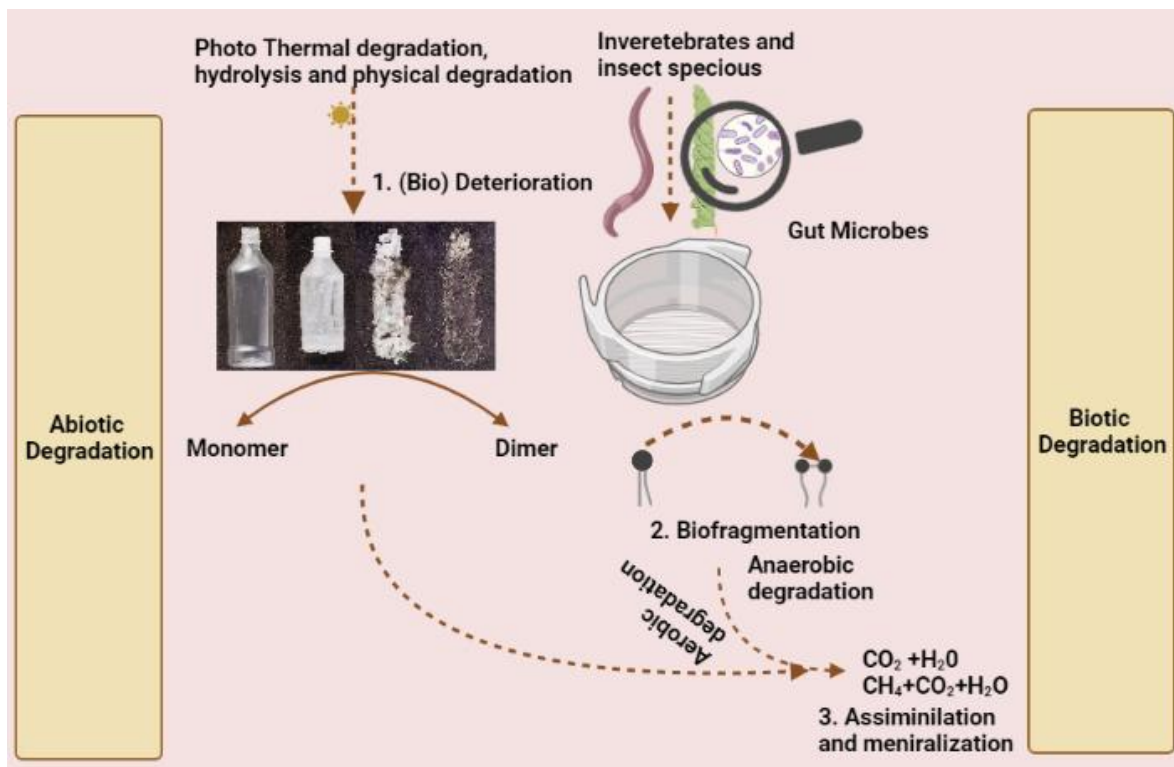


Fig1: Methods for degrading MPs presented in a comprehensive manner

Influence of microplastics on environment- a survey

Chemicals commonly employed in the manufacture of plastics are hazardous. Bisphenol A (BPA), phthalates, and several brominated flame retardants used in household items and food packaging have all been found to be endocrine disruptors that can harm human health if consumed or inhaled (Niu, Li et al. 2021). BPA is a common plasticizer used in industry, particularly in the production of polycarbonate plastics and food packaging.

BPA was discovered to be estrogenic in the early 1930s by Dodds and Lawson, and the General Court of the EU has confirmed that it is a 'substance of considerable concern' due to its hormone disruptive qualities on the human body (Toussaint and Raffael 2019). The European Chemicals Agency (ECHA) had previously decided to identify the compounds used in the manufacture of plastic products such as water bottles, food containers, and receipts, and the Court had supported that judgement. It has been linked to obesity, cardiovascular illness, reproductive disorders, and breast cancer in various studies, and as a result, it has gotten a lot of attention in the recent decade, especially in terms of human safety (Cox, Covernton et al. 2019).

In 2008, it was projected that BPA contamination of food was responsible for 12,404 incidences of paediatric obesity and 33,863 cases of newly diagnosed coronary heart disease. According to another study, BPA in food contact materials and thermal paper is to blame for 42,400 obese four-year-olds in Europe (with health costs of 1.54 billion euros per year) (Smith, Love et al. 2018) (Ebere, Wirnkör et al. 2019) (Campanale, Massarelli et al. 2019). Even though studies on the degree of bisphenol A adhered on microplastics surface are limited, it is still debated whether microplastics constitute relevant pollutant vectors for uptake into organisms in comparison to other uptake channels, such as water or sediment particles.

The first investigation to look for BPA in microplastics collected from remote, open ocean and metropolitan beaches in America and Europe found amounts ranging from 1 to 729.9 ng/g. Only minimal quantities of BPA (less than 1 ng/g) were found in most areas, including urban beaches. The sorption of large amounts of BPA to marine plastics is improbable due to its decreased hydrophobicity (\log n-Octanol/Water Partition Coefficient (K_{ow}) = 3.40). BPA was found at rare high amounts in plastic pieces from far beaches (730 ng/g) and open ocean fragments (283 ng/g). Because it is a component of plastic items and an addition, its use explains the greater BPA amount (Schwabl, Köppel et al. 2019). Indeed, BPA is a component monomer of polycarbonate plastic and epoxy resin, and unreacted monomers in the plastics and resin, as well as polymer degradation products, can leach into the environment. Furthermore, BPA is employed as a plastic additive, and BPA leaching from

commercial plastic goods and disposed plastics is possible. Phthalates are esters of phthalic acid (1,2-benzene dicarboxylic acid) with two distinct length carbon chains. Phthalates are a class of compounds that are created in huge amounts; in terms of manufacturing volume, they are the largest class of synthetic chemicals. Phthalates are created throughout the world at a rate of about 6,000,000 t/year. For the past 20 years, this production has remained quite consistent. Since 2007, di(2-Ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and butyl-benzyl-phthalate (BBP) have been banned in all toys and childcare articles in concentrations greater than 0.1 percent (entry 51 of Annex XVII of the Regulation of the European Union (REACH), as well as diisononyl phthalate (DINP), diisodecyl phthalate etc (Gasperi, Wright et al. 2018).

According to the European Union's rapid alert system for product safety (RAPEX), 1591 cases of dangerous phthalates were detected in various products over the course of 14 years (from 2005 to 2018), with most of them being toys (94%). There were 206-recorded cases of toys containing hazardous phthalates in 2018. When we look at the cases that were related to food containers (detected by the Rapid Alert System for Food and Feed (RASFF), which is similar to RAPEX but only for the food industry), we find that there were 108 cases of phthalate contamination in food containers between 2007 and 2018, an issue that came with the risk of ingestion through food products. A 2011 study in Harbin and Shanghai (China) looked at the presence of nine phthalate esters in eight different food categories. The main component detected in majority of the food samples was DEHP, which had values ranging from below the limit of quantification (LOQ) to 762 ng/g wet weight (Vianello, Jensen et al. 2019). Early investigations looked into the potential of virgin and aged microplastics to adsorb metals in this regard. Plastic manufacture pellets were recovered from beaches and sediment flats in south-west England, revealing varying trace metal concentrations (Cr, Co, Ni, Cu, Zn, Cd, and Pb) that, in some cases, exceeded those found in surrounding estuarine sediments. In a laboratory-scale experiment, the same authors investigated the rates and processes of metals linked with virgin and beached polyethylene pellets. Both virgin and beached pellets adsorb trace metals, whereas older pellets adsorb at a higher rate.

Metal adsorption is thought to occur via non-specific interactions between neutral metalorganic complexes and the hydrophobic surface of the bulk plastic medium, as well as interactions between divalent cations (e.g., Cu^{2+} , Cd^{2+} , and Pb^{2+}) and oxyanions (e.g., $\text{Cr}_2\text{O}_4^{2-}$) with charged or polar regions of the plastic surface (affected by imperfections and the presence of charged contaminants and additives, for example). Trace metals accumulate substantially more in aged, beached pellets, with equilibrium partition coefficients ranging from around 4 mL/g (Co) to 220 mL/g (Zn) (Cr). Changes

to the polymer, as well as the presence of biofilms and chemical precipitates, increase its reactivity, enhancing the crucial role of plastic as a vehicle for metal transport in the marine environment.

PLASTIC DEGRADATION BY PHYSICAL METHODS.

Plastics are synthetic organic polymers that are used in a wide range of industries, including the manufacturing industry, which uses a million tons of plastic per year to produce textiles and bres, and the food industry, which uses plastic for packaging products to reduce food waste and transportation costs(Ibrahim, Shahar et al. 2021). Over 250000 tons of plastic have been discovered floating at sea in the marine environment around the world. Estimated a minimum of 5.25 trillion particles weighing 268,940 tons using an oceanographic model of floating debris distribution calibrated by the data and corrected for wind-driven vertical mixing(Eriksen, Lebreton et al. 2014). Long chain polymers contain properties such as large molecular weight, hydrophobicity, and crystallinity that make it difficult for bacteria to cross their membranes. With the help of metabolism, the monomers can flow through the cell membrane. In water, visible light triggered heterogeneous zinc oxide photocatalysts successfully degraded low-density polyethylene (LDPE), as well as polyethylene (PE) plastic with polypyrrole/TiO₂ (PPy/TiO₂) nanocomposite as photocatalyst(Li, Xu et al. 2010).

The process which depletes the chemical and physical properties of the polymer, as well as its appearance. Various forms of polymer degradation methods have been utilised in the past, including thermal, photooxidative, mechanical, biological, irradiation, and chemical. Because of their unique qualities and structural interactions for degradation, ionic liquids have been used as chemicals and solvents (Kulkarni and Dasari 2018).

Photodegradation is caused by UV light and oxygen exposure. These photodegradation processes occur to a depth of 50–100 m, resulting in molecular weight decrease and cracking, which aids in the creation of microplastics. Furthermore, as C–H bonds oxidise, the resultant carbonyl groups, such as aldehydes and ketones, aid in "biofilm coverage."(Veerasingam, Ranjani et al. 2020).

Saba Sadaqat Ali, Ishtiaq A. Quazi et al(Ali, Qazi et al. 2016) 2016 worked on degradation of LDPE (low density polymer) Under visible light exposure, photocatalytic degradation of BG sensitised TNT composites PE films. The dye sensitization of nanotubes has boosted the breakdown rate of LDPE films under visible light, and such films can degrade with a good rate under sunlight, making them more cost effective.

Backhorn, 2005 reported on this reactor functions as a heat transfer agent, it is used in a cycled form reactor. The extruder was held at 190 degrees Celsius, and polymer mixes containing any polymer and catalyst were fed to the reactor(Ali, Qazi et al. 2016). The temperature was kept at 330°C. The temperature was raised after dechlorination, and the mixture was kept at 440°C for 60 minutes. From the

bottom, residue was collected. Then tests such as TGA and liquid analysis were performed, revealing that CaCO₃ was the best choice for HCl fixation, resulting in a liquid product. And for HCl fixation and reduction, RM was the most effective.

At around 300°C some polymers degrade almost completely in less than an hour, as measured by weight loss through volatilization, whilst others lose relatively little weight in the same time frame, even at 450°C (Du, Xie et al. 2021).

When a polymer is heated, the chemical processes that occur are dependent on the heating temperature, heating rate, and the environment in which the heating occurs. Various features of synthetic polymer thermal degradation processes are thoroughly explored in various publications. The reactions that occur when the polymer is heated at temperatures between 500°C and 800°C are of special interest (considered the typical range for pyrolysis). Analytical pyrolysis also entails a rapid temperature rise, on the order of 10,000°C per second.

According to Jellinek et al., 1949, a more or less fast decline in the molecular weight of the polymer occurs during the first few percentage losses at temperatures where volatilization of the breakdown products occurs, followed by a steadier drop. The presence of weak links induced by foreign atoms or groups of elements, such as O, O₂, and OH, which were absorbed in the chain during polymerization, could explain the first fall in molecular weight under the impact of heat (Urbanek, Rymowicz et al. 2018).

Plastic degradation by Enzymatic Degradation

Anthropogenic pollution by micro plastic is one of the major environmental stress factors behind ecotoxicology. Technologies and methodologies along with its advantages and disadvantages for the removal of micro plastics from the environment is critically reviewed by many researches. This section mainly discusses about removal of micro plastic by microbes which get adapted with microplastic ecosystem. Persistence of Microbes in such environment has evolved them to overcome the nerve-racking effects of these Anthropogenic microplastic. In respond to these stresses, new macromolecules (enzymes) which regulates cell function for cellular defense are produced (Campanale, Massarelli et al. 2020). These enzymes are important not just in modulating cellular function and decomposing anthropogenic pollutants such as microplastic (Zhang, Xu et al. 2016). These enzymes target micro plastic as its carbon source by mineralizing into carbon, nitrogen, methane, and water. Able to utilize the plastic as their energy source shows that they can grow and flourish on micro plastic waste. Even though each enzyme has its own unique mechanism by degrading microplastic, this remains the most challenging aspect. According to the recent research on this area claims that majority of microplastic

degrading enzymes belongs to hydrolase family(Othman, Hasan et al. 2021). Most commonly, plastic degrades with the help of Lipase, PETase (an Esterase) and Cutinase. Degrading ability of these enzyme either changing the functional group of these microplastic or by degrading the building block of these fibers are the main focus of the researchers in effort to deal with truly ever swelling MPs pollutants withinside the environment(Shah, Patel et al. 2013).It's reported that Lipase from fungus and cutinase from *Aspergillus oryzae* has ability to increase the hydrophobicity of fabrics(Wang, Lu et al. 2008). Furthermore, Degradation of polymers can also be accelerated by the surface-to-volume ratio, i.e., the higher the ratio or the smaller the polymer size, the greater the possibility of degradation than for fibers or films. Likewise, enzyme-based degradation, several biodegradable plastics have been evaluated and reported(Ghosal, Ghosh et al. 2016). For example, PHB depolymerization by PHB depolymerase has been documented in several publications(Garcia-Hidalgo, Hormigo et al. 2013). Despite this, 5 critical aspects must be considered for understanding biodegrading ability of these enzymatic which includes 1. Crystallinity 2. Polymer chain orientation 3. Surface topology 4. Water absorbency 5. Reaction temperature(Chamas, Moon et al. 2020).Most amazing fact is that with these types of enzymes, many types of plastics, including, PU, PBS, PLA, PET, and PE, have been reported todeteriorate slowly. In the succeeding section, enzymatic mechanism by which MPs get decomposed is depicted.

Enzymatic Mechanism

Several reports have claimed that hydrolase, a third class of enzyme,is the principal enzymes responsible for debasing the MPs waste in the ecosystem. In general, degrading occurs in 2 stags. 1. Extracellular Deploymentsation of polymers units. In this stage polymers are broken down into short chains such as Monomer, dimer, or oligomer. Depolymerized polymers are then engulfed intercellular for the mineralization. Through permeable membranes, deployment of a polymer facilitates absorption into cells. 2. Mineralization of the shorter chain leads to the formation of CO₂, CH₄ and H₂O as by product which then used as carbon source for bacterial metabolic reaction in general(Othman, Hasan et al. 2021). Detail mechanisms are reviewed with the help of Laccase and alkane hydrolase are from the AlkB family enzyme. The researchers pay more attention to alkane hydrolase due to its novelty in MP degradation(Zurier and Goddard 2021). By oxidative cleavage of the amorphous region of HDPE, Laccase degrades MP especially HDPE which contributes 46% to total MP waste, thus providing access to the carbonyl part of the polymer chain(Bacha, Nabi et al. 2021). As first step of degradation, Microbes gets colonization on the surface of polymer and modify the surface thus facilitate the colony and biofilm growth. This involves secretion of surfactants or adhesive for rapid adaptation to MP niches quickly. This phase of process is called biodeterioration. In second phase, extracellular enzymes

secreted by attached microbes get adhered on hydrophobic region of plastic thus creating apolymer-enzyme interaction. The presence of hydrophobic cleft near active site in these types of enzymes increases the enzymes accessibility to polymer that contain the hydrophobic groups. Further, active sites of these enzymes involves in the breakage of long polymer chain into small monomer or dimers. This process is also known as biofragmentation. In third phase of reaction, these monomers get assimilate intracellular thus utilizing these monomer and dimer as carbon sources (Miri, Saini et al. 2022, Tang, Lock et al. 2022). Below is the diagrammatic illustration of the same (fig:2).

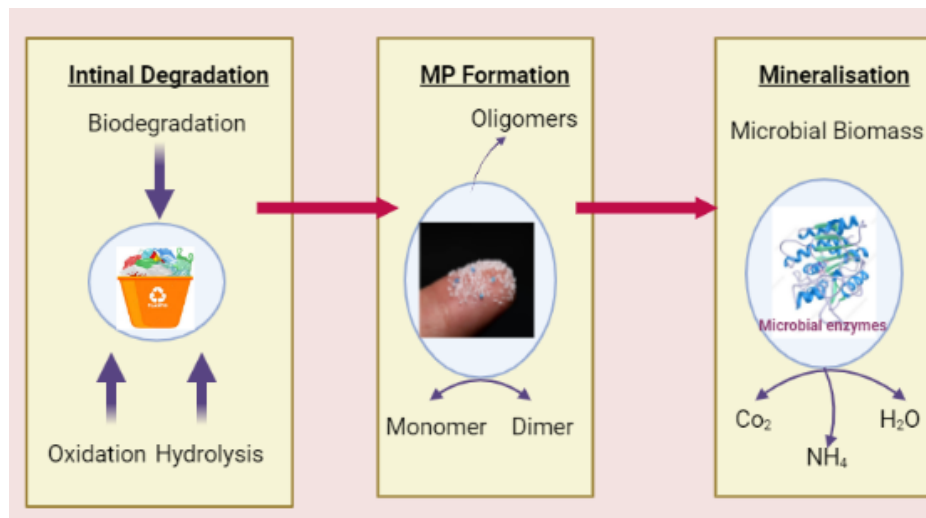


Fig 2: Figure illustrating the steps involved in degradation of MP by microbial biomass.

Enzyme mediated degradation- Recent advance

The literature has become more focused on the microbial life on the surface of MPs with limited knowledge about microbial ecotoxicology esp in the aspects of ability of these microbes to degrade MPs (Urso and Pumera 2022). The degrading mechanisms of microorganisms have been recently updated in many papers. The key microorganisms capable of using plastic as an energy source and carbon source are *Arthrobacter*, *Corynebacterium*, *Micrococcus*, *Pseudomonas*, *Rhodococcus*, and *Streptomyces*. Among them Bacteria and Fungi are key interest for the research to understand the degradation of both synthetic and natural polymer (Urbanek, Rymowicz et al. 2018). In recent publication done by Closaset *al.*, 2016, *Pseudozyma antarctica* showed an accelerated degradation of plastic mulch under laboratorial condition. When the strain was grown in the presence of xylose on mulch films a high degradation rate was seen. The result of this study gave a way for a new combinatorial approach to increasing degradation rates, thereby reducing the duration (Urbanek, Rymowicz et al. 2018).

Several studies have dealt with microbial degradation of plastic materials in recent years, focusing on microorganisms isolated from natural environments both from terrestrial and marine ecosystem (Shah, Patel et al. 2013). The degradation potential of microplastics is higher when organisms living in microplastic-contaminated environments where they have an already adapted metabolism, so their polymer degrading potential is higher. As a result, microorganisms can be used in bioremediation without having any negative consequences. In recent study, *Bacillus cereus* and *Bacillus gottheili* was able to degrade the UV pretreated MPs by altering the functional groups and other properties. Pretreated with UV results in decreased hydrophobicity therefore increasing compatibility of microbes with surfaces of MPs. According to report of Auta et al., 2017 *Bacillus gottheili* has broad range of degrading capacity when compared with *Bacillus cereus*. On other side. Butbunchu and Pathom-aree, 2019 has reported the ability of actinomycetes to degrade the PLA. This biopolymer can be degraded by MPLA-degrading actinomycetes either in a laboratory or in the field. The *Kibdelosporangium aridum* strain was likewise shown to have a significant biodegradation capacity, lowering the original polymer by roughly 97 percent. As the degradation progressed, multiple pits appeared on the PLA surface, and most of these were enlarged as the surface was attacked by the strain. It was assumed earlier that polyethylene terephthalate (PET) plastic, the most commonly used disposable plastic, was not biodegradable. Recently, Scientists in Japan have isolated *Ideonella sakaiensis*, bacterial strain grown on PET bottles utilizing the PET as carbon source thus was able to degrade the PET in useful monomer (20). Summary of recently identified organism which potentially degrades broad spectrum of the MP is illustrated in Fig 3.

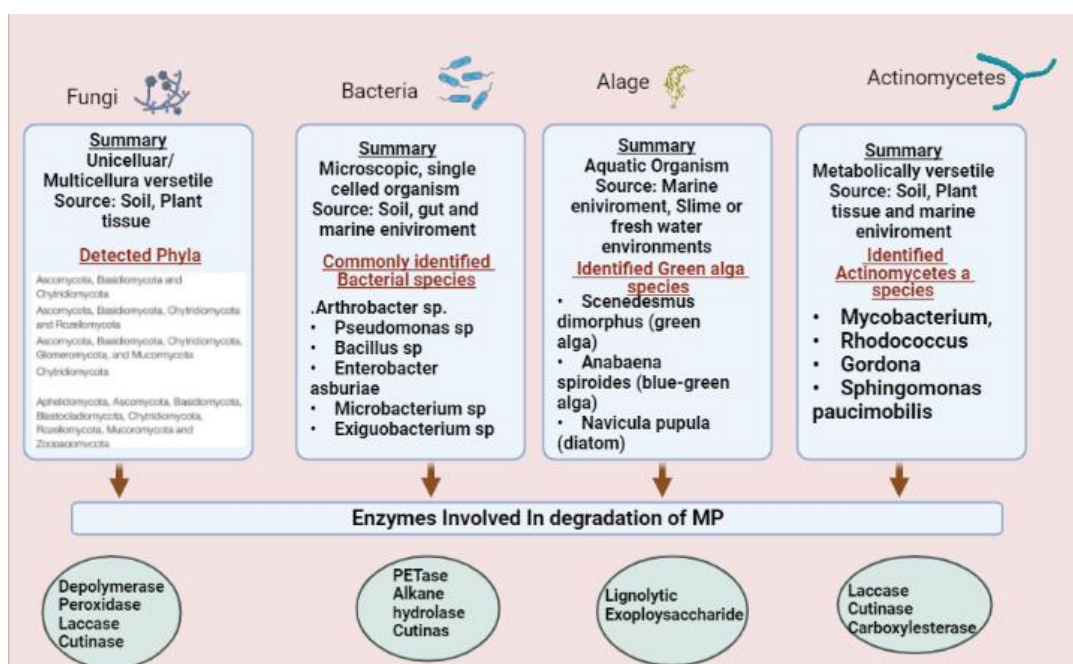


Fig 3: An overview of several microbial enzymes involved in degradation MPs.

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