



Review

Degradation of conventional plastic wastes in the environment: A review on current status of knowledge and future perspectives of disposal



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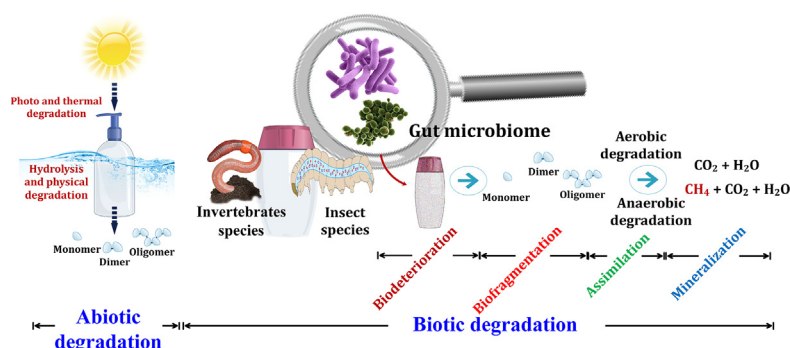
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HIGHLIGHTS

- The main hazardous effect of plastic is its accumulation in the environment.
- An effective eco-friendly management practice for plastic wastes is still absent.
- Invertebrates gut microbiota could play an important role in plastic degradation.
- Plastic degradation can improve by combining various degradation techniques.
- Plastic degradation calls for future studies to develop biodegradation processes.

GRAPHICAL ABSTRACT



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ABSTRACT

Accumulation of plastic wastes has been recently recognized as one of the most critical environmental challenges, affecting all life forms, natural ecosystems and economy, worldwide. Under this threat, finding alternative environmentally-friendly solutions, such as biodegradation instead of traditional disposal, is of utmost importance. However, up to date, there is limited knowledge on plastic biodegradation mechanisms and efficiency. From this point of view, the purpose of this review is to highlight the negative effects of the accumulation of the most conventional plastic waste (polyethylene, polypropylene, polystyrene, polyvinylchloride, polyethylene terephthalate and polyurethane) on the environment and to present their degradability potential through abiotic and biotic processes. Furthermore, the ability of different microbial species for degradation of these polymers is thoroughly discussed. The present review also addresses the contribution of invertebrates, such as insects, in plastic degradation process, highlighting the vital role that they could play in the future. In total, a schematic pathway of an innovative approach to improve the disposal of plastic wastes is proposed, with view to establishing an effective and sustainable practice for plastic waste management.

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1. Introduction

Plastic represents one of the most essential and widely used materials in the world, owing to desired properties, including light weight, low maintenance requirements, weathering resistance, low toxicity, transparency, and low price, which facilitate plastic applications in various industrial, commercial and agricultural activities (Jenkins et al., 2020; Amobonye et al., 2021). Because of their stability and durability, emanating from their polymeric nature (Rivard et al., 1995), plastics have attracted huge attention compared to any other solid component. However, most plastic types are non-degradable and it takes centuries for complete degradation. As a result, plastics tend to accumulate rather than decompose in landfills or the natural environment (Barnes et al., 2009; Matjašič et al., 2021). Furthermore, the common monomers used for the synthesis of plastic polymers (e.g., ethylene and propylene) commonly derive from fossil hydrocarbons. Also, polymeric structure makes them resistant to microbial degradation, while their relatively short presence in nature hinders the appearance of new enzymes that could degrade conventional polymers (Mueller, 2006; Amobonye et al., 2021).

Currently, the most widely used plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), polyethylene terephthalate (PET) and polyurethane (PU) (Gewert et al., 2015), which are classified into two categories: C—C backbone polymers and heteroatomic polymers (Fig. 1). C—C backbone polymers, including PE, PVC, PS and PP, represent 77% of the total market share, while heteroatomic polymers, such as PET and PU, represent ~18% of the market share (Gewert et al., 2015; Danso et al., 2019). C—C backbone polymers are resistant to hydrolysis and biodegradation and susceptible to thermal oxidation (Krueger et al., 2015), while heteroatomic polymers may be processed through photo-oxidation, hydrolysis, and biological degradation (Gewert et al., 2015).

The global plastic production from 1950 to 2018 was estimated at 8.3 billion metric tonnes, with an increase of 5% (185 million tonnes) every year (Jambeck et al., 2015; Geyer et al., 2017; Amobonye et al., 2021). However, 76% of the total plastic production ends as wastes, which can be further divided into 14% recycled, 14% incinerated and 72% landfilled or released in the environment (Ellen MacArthur Foundation, 2015). Therefore, pollution from plastic wastes' accumulation in the environment constitutes an ever-increasing environmental threat to natural ecosystems and public health (Shah et al., 2008), while an environmentally friendly practice for effective treatment has

not been found yet. In this concern, several reports highlight the potential of the microbial degradation of plastic wastes (Yoshida et al., 2016; Sarkhel et al., 2020; Zhang et al., 2020). However, there is a gap in our knowledge on the available biodegradation mechanisms and their efficiency. Under this scope, the purpose of the present review is to address the effects of different plastic types on the environment and human health and to present in detail the biodegradation process of synthetic plastic, including the factors affecting the process. Also, the algal, fungal, bacterial and insects' contribution to plastic biodegradation is analyzed. Lastly, a strategy to improve the efficiency of biodegradation for biofuel production such as biogas, bioethanol and/or biodiesel is proposed.

2. Impacts of plastic wastes' accumulation

According to the United Nations, since 2020 over 400 Mt. of plastic wastes will be annually produced, while plastics production is expected to double by 2035 reaching 800 Mt., and 1600 Mt. by 2050 (Barra and Leonard, 2018). The plastic manufacturing process releases a huge quantity of harmful gaseous substances into the air, including carbon monoxide, dioxins, nitrogen oxides and hydrogen cyanide, which pose a serious threat to the environment and human health. For example, Royer et al. (2018) reported that the trace gases produced from low-density polyethylene (LDPE) increase with incubation time (212 days) and reached 5.8 nmol methane/g/day, 14.5 nmol ethylene/g/day, 3.9 nmol ethane/g/d and 9.7 nmol propylene/g/d. Also, LDPE's emission rates are ~2 and ~76 times higher for methane and ethylene, respectively, when incubated in air compared to water, highlighting that plastics could be an unrecognized source of climate change-relevant trace gases that are expected to increase as more plastic is produced and accumulated in the environment. Concerning plastic disposal (Fig. 2), 6.3 billion metric tonnes of the global plastic production from 1950 to 2018 ended as waste and more than 4 billion tonnes have been used just once prior to disposal (Geyer et al., 2017). Moreover, about 4.5 billion tonnes of total plastic wastes end up in landfills, or are released in the environment, negatively affecting microbial content of soil. Landfilling results in soil infertility, since more than 500 years are needed for complete decomposition (Chamas et al., 2020), while plastic degradation also releases toxins (Webb et al., 2013). In case of biodegradable plastics, there are many microorganisms which accelerate biodegradation in landfills, including bacteria such as *Pseudomonas* sp., nylon-eating bacteria, and flavobacteria, which break down nylon through the activity of the nylonase enzyme (Negoro, 2000).

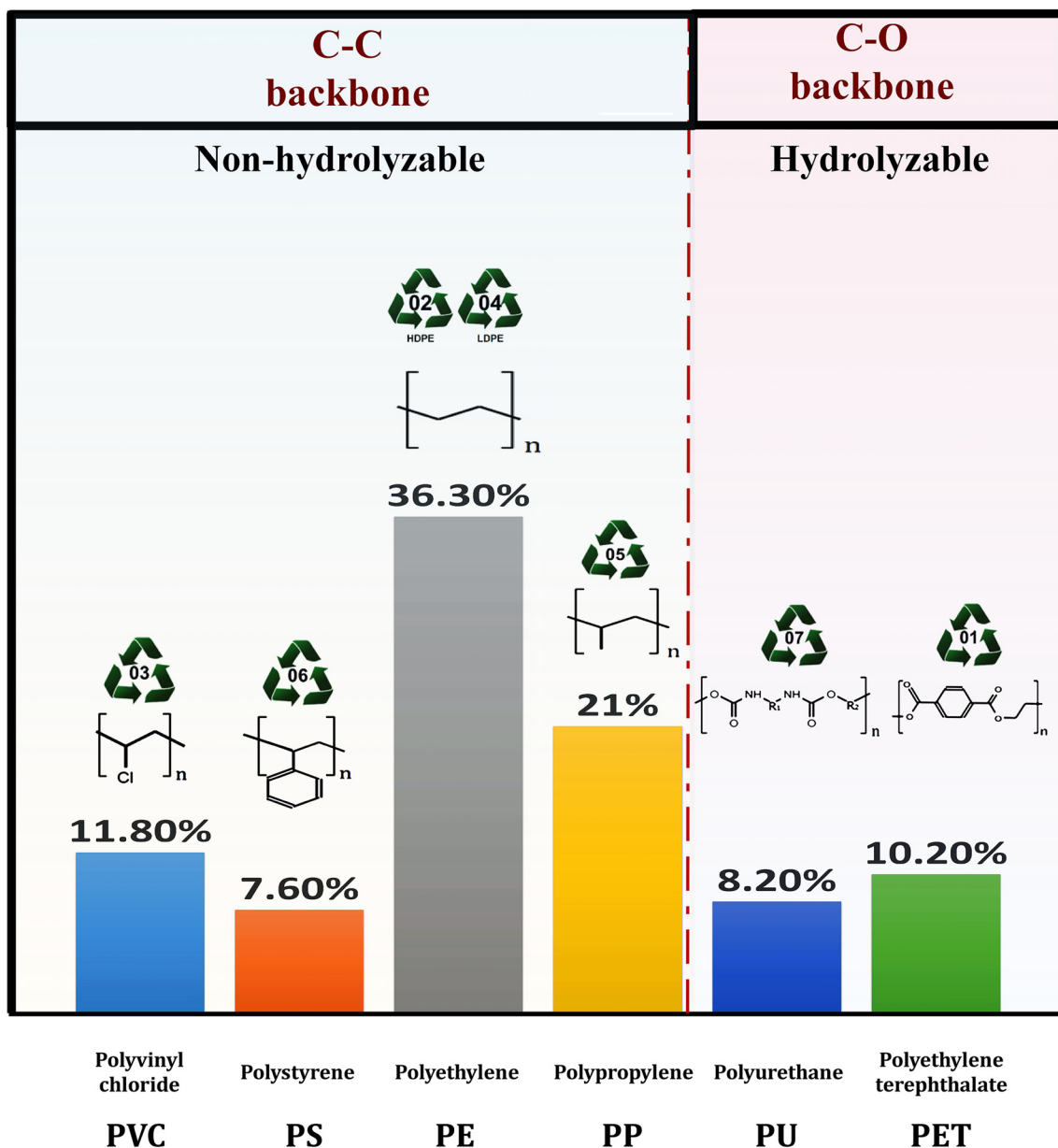


Fig. 1. The most used plastic types, their market share and classification based on chemical backbone structure.

2.1. Environmental impact

In 2020, 195 countries were estimated to produce about 400 Mt. of plastic waste, with about 8.8 Mt. entering the ocean (Koller and Braunneg, 2018; Serrano-Ruiz et al., 2021). Based on United Nations Centre for Regional Development (UNCRD) report, the southeastern countries of Asia (China, Indonesia, Philippines, Vietnam, Sri Lanka, Thailand, Malaysia, and Bangladesh) are ranked first in plastic wastes mismanagement, with 88% of plastic wastes ending up in water bodies (UNCRD, 2019). Plastic wastes can act as a carrier for organic pollutants, chemicals, heavy metals, and pathogens (Cregut et al., 2013; Galloway and Lewis, 2016; Chen et al., 2019; Chamas et al., 2020; Tang et al., 2021). Furthermore, abiotic degradation of plastic releases highly toxic compounds, deteriorating the quality of soil and water (Chen et al., 2019), with oceans loaded with 5.25 trillion nano-, macro-, and microplastic particles weighing 269 t (Eriksen et al., 2014). Several plastic-type wastes have a hydrophobic nature that enhances aggregation with other pollutants, such as polyaromatic hydrocarbons (PAHs),

organic pollutants and polychlorinated biphenyls (Liu et al., 2016). This reactivity depends on hydrophobicity and the ratio of the surface area to volume and makes plastic debris efficient sorbents. Additionally, the long-lasting accumulation of microplastic can affect the food chain, since microplastics can be ingested by animals (Frias et al., 2010). Li et al. (2020a) highlighted the histopathological damage in fish tissues in response to plastic pollution and showed that the abundance of microplastics in the guts of *Hemiculter leucisculus* ranged from <1 mm to 3 mm and was estimated by 2.3–15.8 items/g of digestive tissue.

Undoubtedly, biota face serious water pollution by plastic waste discarded in different water bodies including lakes, rivers, ponds, etc. The lakes in the megacity of Dhaka represent one of the best examples of pollution by plastic bottles, cans, bags and other plastic products frequently thrown by visitors. The presence of plastic wastes in water bodies disturbs natural flow, limits the ability of fish to reproduce and destroys vital organisms, while polymers in the oceans could contribute to global warming by creating a shaded canopy hindering plankton to grow (Proshad et al., 2018).

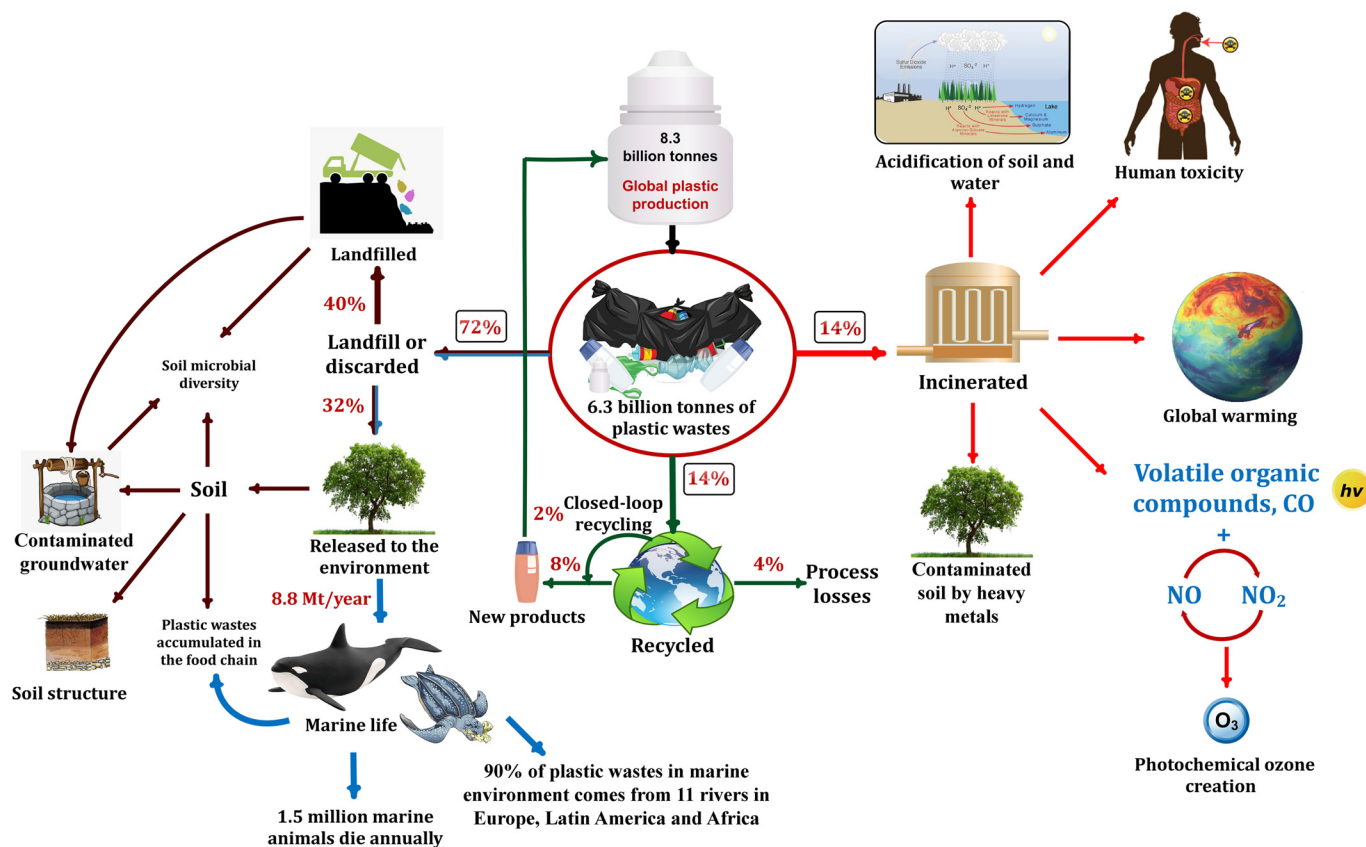


Fig. 2. Plastic wastes fate and their harmful impacts on the environment.

In terms of soil contamination, various types of plastic wastes contaminate the soil either by settling on the surface or penetrating the soil layers from different routes such as sludge, fertilizers, irrigation using wastewater, landfills, biosolids or from other sources (Horton et al., 2017; Darwesh et al., 2021). The fragmentation of plastics into

microplastics (MP) on the soil surface results from temperature and photo-oxidation (Horton et al., 2017). This fragmented MP can be translocated, as shown in Table 1, deeper into the soil by plants and the activity of soil organisms (Zhu et al., 2018), contaminating groundwater and deteriorating soil properties (Scheurer and Bigalke, 2018).

Table 1
Effect of plastic on soil invertebrates.

Plastic type ^a	Concentration	Size	Organism	Time (day)	Plastic effect	References
PES	Five concentrations ranging from 0.02–1.5% w/w	12 µm–2.87 mm and 4–24 mm	Enchytraeids (<i>Enchytraeus crypticus</i>), isopods (<i>Porcellio scaber</i>), oribatid mites (<i>Oppia nitens</i>), and springtails (<i>Folsomia candida</i>)	28	Insignificant effects on the soil invertebrates were observed. However, the energy reserves of the isopods were decreased. The reproduction decreased up to 30%, but only for long fibers in soil. The short fibers were clearly ingested. The authors' also showed that the plastic can enter terrestrial food chain.	Selonen et al., 2020
PVC	1–5% w/w	130 µm	Lugworm (<i>Arenicola marina</i>)	28	Reduction of feeding activity and energy reserves was depleted	Wright et al., 2013
PE	0.4% w/w	Plastic bag film (183 ± 93 µm) and facial cleanser (137 ± 51 µm)	Common rough woodlouse (<i>Porcellio scaber</i>)	14	No effect of plastic on <i>P. scaber</i>	Kokalj et al., 2018
	10% w/w	250–1000 µm	Earthworms (<i>Eisenia andrei</i>)	28	No effect on <i>E. andrei</i> , but histopathological alterations of the gut epithelium and immune response in coelomocytes were observed	Rodriguez-Seijo et al., 2017
	7% w/w	<150 µm to 1 mm	Earthworms (<i>Lumbricus terrestris</i>)	14	Earthworms can transport the smaller MP particles (<250 µm) from the soil surface and plastic can be leached into drainage.	Yu et al., 2019
	7, 28, 45, and 60% w/w	<150 µm	Earthworms (<i>Lumbricus terrestris</i>)	60	Worms's mortality increased and growth rate was reduced at 28, 45, and 60% of microplastics.	Huerta Lwanga et al., 2016
	0%, 0.005%, 0.02%, 0.1%, 0.5%, and 1% w/w	<500 µm	Springtails (<i>Folsomia candida</i>)	28	PE showed a significant toxic effect on springtails. Also, changed their gut microbial community.	Ju et al., 2019

^a PE, Polyethylene; PES, Polyester; and PVC, Polyvinyl chloride.

Many researchers have investigated the effects of macro- and microplastic wastes on soil organisms, demonstrating the accumulation of plastic in organisms' bodies causing histological damages (Bravo Rebolledo et al., 2013; Bråte et al., 2016; Diepens and Koelmans, 2018). Furthermore, Lozano and Rillig (2020) showed that microfibers added to the soil strongly affect soil community, in terms of biomass and biodiversity which could affect ecosystems equilibrium.

Lastly, plastic wastes incineration releases several pollutants into the atmosphere and is considered as one of the main sources of air pollution nowadays. The main pollutants released through incineration, as shown in Fig. 2, include particulate matters (PMs), metals, aldehyde (-CHO), methane (CH₄), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO₂), furan (C₄H₄O), polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and other substances such as solid material (i.e., ash, as residue) which increases the levels of heavy metals, inorganic salts, and organic compounds in the environment (Sabiha-Javied and Khalid, 2008; Sharma et al., 2013). PMs can be released as solids or aerosol and may contain heavy metals, acids, and/or trace organic compounds. Concerning the process of incineration, the level of PMs control and gas temperature affects the produced emissions. However, most incinerators operate without add-on air pollution control devices, which further leads to the release of harmful gases in the atmosphere (Sharma et al., 2013). Moreover, numerous chemical substances with unknown toxicity are emitted, while the entire range of the effects on human health caused by the exposure to the whole mixture of emitted substances through plastic incineration is still unknown (Sharma et al., 2013).

2.2. Effects on human health

Plastic disposal can have a significant impact on human health, either directly or indirectly through inhalation and digestion, respectively (Fig. 3). In particular, the persistence of microplastics may lead to several biological responses such as inflammation, genotoxicity, apoptosis, oxidative stress, and necrosis (Proshad et al., 2018; Prata et al., 2019), while a range of severe outcomes can ensue in case of continuous exposure, including tissue damage, fibrosis and carcinogenesis (Wright and Kelly, 2017). Polymers composition itself may have a series of chemical effects by the leaching of unbound chemicals and/or residual monomers; or the associated hydrophobic organic contaminants desorption, resulting in human health deterioration (Wright and Kelly, 2017).

Micro- and nano-plastics' uptake by human and animals could allow the cellular entry of adhered or endogenous contaminants (Khan et al., 2015; Wright and Kelly, 2017; Prata et al., 2019). The cellular response to micro- and nano-plastics vary from a few scattered cells to macrophages extensive aggregations (Urban et al., 2000). PE particles (0.5–50 μm), which can locate to neighboring vessels where transportation via the perivascular lymph spaces occurs (Willert et al., 1996), provoke a nonimmunological foreign body response (Doorn et al., 1996). Also, PMs can cause oxidative stress due to inhalation and subsequently result in inflammation and intestinal fibrosis (Nel et al., 2006). In this concern, Barabad et al. (2018) studied the PMs produced through vinyl or plastic incineration, reporting the release of high concentrations of harmful pollutants, fine and ultrafine particles, while acetone, benzene and other toxic compounds were also detected. At a heat flux of 25 kW/m², the production of PMs of 0.35 μm was highest at 63.0 μg/m³, while at fluxes of 35 and 50 kW/m², PMs production of 0.45 μm was highest at 67.8 and 87.7 μg/m³, respectively.

Moreover, all plastics contain reactive oxygen species (ROS), which concentration can significantly increase due to the interaction with light or the presence of transition metals (Wright and Kelly, 2017), leading to free radical formation by the dissociation of the C—H bonds (White and Turnbull, 1994; Gewert et al., 2015). In addition, Lithner et al. (2011) showed that certain types of plastic, such as PU, PVC, styrenic polymer (such as PS) and epoxy resin, can generate hazardous monomers, including mutagenic and/or carcinogenic resin monomers.

Concerning the transfer of micro- and macro-plastic wastes in the food chain (Fig. 3), Huerta Lwanga et al. (2017) studied the low-density polyethylene microparticles (LDPE-MPs) transfer via chickens and earthworms, demonstrating LDPE-MPs concentration of 129.8 MP/g feces in chickens and 10.2 MP/gizzard, respectively. Lastly, in contrast to seabirds, direct transfer of additives from plastic to human has not yet been confirmed (Tanaka et al., 2013). Overall, the plastics consumption per annum can be estimated as 840 plastic particles/person (Huerta Lwanga et al., 2017). Thus, by taking into consideration the mismanagement of plastic wastes and the global impacts of plastic on the environment, wildlife and human health, there is an urgent need for new technologies of plastic wastes treatment and disposal. Under this scope, physicochemical degradation and biodegradation could be considered as a promising environmentally friendly approach to overcome plastic pollution.

3. Degradation of plastic wastes

Plastic wastes can be processed through physicochemical degradation (abiotic) and biodegradation, which initially break down the physical forces of the polymeric materials (Kyrikou and Briassoulis, 2007). Photodegradation, thermo-oxidative degradation, hydrolytic degradation and biodegradation have been reported as the main mechanisms for plastic degradation in the environment (Andrady, 2011). In nature, degradation of plastic starts with photodegradation, followed by hydrolysis and thermo-oxidation process. These processes lead to plastic wastes breakage into low molecular weight (MW) compounds, which can subsequently be metabolized by microbial activity (Andrady, 2011; Webb et al., 2013). However, this process is very slow, and it can take centuries to complete (Chamas et al., 2020).

3.1. Plastic polymers' properties

The process of plastic degradation is determined by both environmental conditions and physicochemical properties of polymeric substances, as depicted in Fig. 4. The physicochemical properties of plastic play an important role in the degradation process. Plastic susceptibility to abiotic and biotic degradation depends on backbone composition and chain length, with long carbon chain such as PP, making polymers resistant to degradation (Huerta Lwanga et al., 2016; Fotopoulou and Karapanagioti, 2017). However, the incorporation of heteroatoms, such as in PET and PU (oxygen-containing polymers) constitutes plastic susceptible to biodegradation and thermal degradation (Singh and Sharma, 2008). Also, the polymer hydrophobicity affects the degradation efficiency, where the degradation rate increases with increasing hydrophilicity (Padsalgikar, 2017). Furthermore, the degradation rate depends on the polymer crystallinity (Jenkins and Harrison, 2008); the more crystalline the polymeric structure, more water and oxygen are needed for degradation. Therefore, an increase in either molecular weight or degree of crystallinity reduces degradation rate (Jenkins and Harrison, 2008). On the other hand, the amorphous polymeric structure can be attacked by water and oxygen. The polymer amorphous regions are also considered more suitable for thermal oxidation (Li et al., 2019). In this concern, the polymer MW can affect the degradation rate, while high MW polymers exhibit a slower degradation rate because of their lower relative surface area (Singh and Sharma, 2008).

Interestingly, plastic manufacturing, in terms of production techniques and the additives used, strongly affects degradation rate of the produced plastic. For instance, PP made by bulk (mass) polymerization or by Ziegler-Natta catalyst is characterized by higher susceptibility to photodegradation than the co-polymerized PP (Tang et al., 2005). Also, PS formed polymers through free radicals polymerization were less stable against photo-oxidation than the PS produced through the anionic polymerization technique, due to the presence of functionalizing group (peroxide residue) (Pospíšil et al., 2006). Furthermore, several additives such as stabilizers that are used

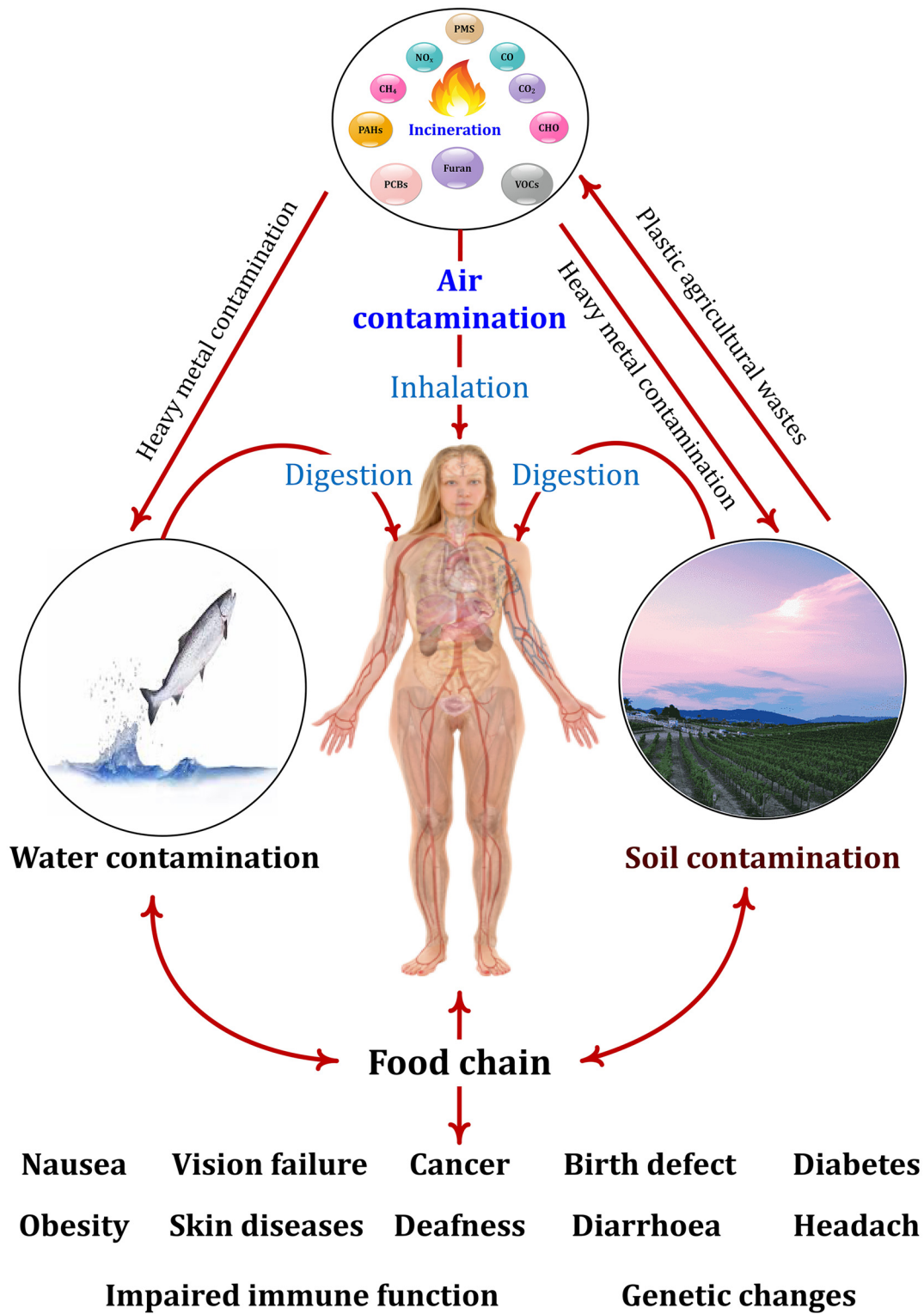


Fig. 3. The direct and indirect effect of plastics on human health.

tend to decrease degradation rate and chromophores (carbonyl and hydroperoxide groups) (Aldas et al., 2018). For instance, chromophores presence lead to photochemically generated radicals that initiate the photodegradation due to the presence of many available sites for photo-oxidation. Also, the presence of metal-metal bonds can improve the photodegradation process because of the homolytical bond cleavage upon irradiation (Daglen and Tyler, 2010). Likewise, the morphological features of plastic should be

taken into consideration, as the degradation rate tends to increase in case of rough surfaces that are more suitable for biofilm formation than smooth ones (Booth et al., 2017).

3.2. Environmental factors

The geographical location, climatic conditions, smog and pollutants among others, affect the mechanisms and rate of plastic degradation

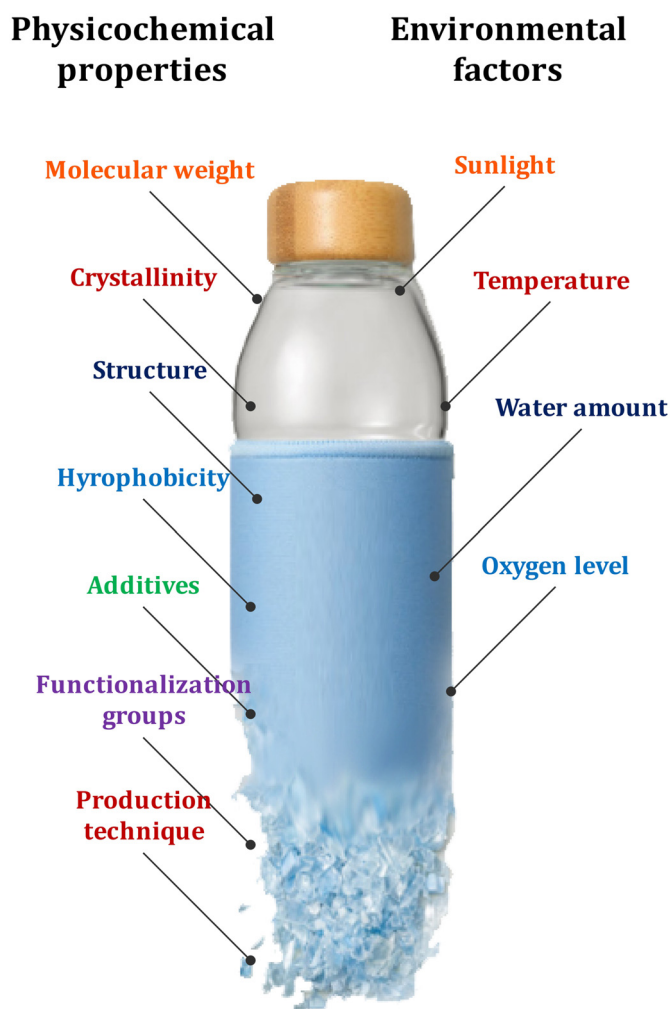


Fig. 4. Factors affecting the plastic abiotic degradation rate.

(Andrady et al., 2003). Sunlight is of utmost importance for plastic degradation, with light intensity increasing the photo-oxidation reaction rate and therefore the degradation rate of plastic (Kitamoto et al., 2011). Furthermore, the rate of abiotic degradation also increases along with an increase in temperature (Pischedda et al., 2019), where the reaction rate duplicates per 10 °C increase. Temperature also affects the polymer chain mobility, which subsequently affects the enzymatic activity during microbial degradation, as well as the hydrolysis process rate by affecting the formation of free radicals, the oxygen diffusion rate and humidity (Booth et al., 2017). PET chain scission was higher by 500% at 100% relative humidity and 60 °C, in comparison with 45% relative humidity (Edge et al., 1991). Also, humidity enhanced the photodegradation of PP (Fernando et al., 2009), PE (Jin et al., 2006), and PVC (James et al., 2013), by increasing the hydroxyl radicals concentration. However, a reduction of UV light intensity in the seawater leads to a decrease in the photodegradation rate. In contrast, a high level of humidity at the sea surface enhances the light degradation process because of the solubility of certain photo-stabilizers into the water, leading to effective degradation (Booth et al., 2017).

Oxygen availability also affects the degradation rate of plastic during photodegradation and biodegradation (Queste et al., 2013). Price and Horrocks (2013) reported that the polymeric degradation process is accelerated in the presence of high oxygen concentration, because of the fast reaction between oxygen and carbon-centered radicals released from the initial degradation products. Such

interactions cause an increased polymer alkyl radicals' concentration, leading to higher levels of scission and cross-linked products. In addition, water availability is an essential factor during biotic and abiotic process of degradation, because of the hydrolysis process that causes the cleavage of functional groups, leading to the cleavage of the polymeric chain (Pitt, 1992).

4. Physicochemical degradation

Abiotic degradation of plastic occurs naturally, as in case of mechanical degradation caused by the tidal forces, waves and abrasion by stones. This fragmentation process causes the formation of plastic debris. Naturally, the effect of photo-oxidation and hydrolysis process generate a brittle material and mechanical degradation can easily ensue leading to the formation of micro- and nano-plastic fragments. However, during chemical fragmentation, the polymer MW is decreased, in contrast to mechanical fragmentation, where no change in the MW is observed (Lambert and Wagner, 2016). This process is controlled by many factors, including polymer chain length, intramolecular forces between polymer chains, mechanical stability, polymer crystallinity and plastic weight.

4.1. Photodegradation

Photodegradation is considered as the most important abiotic degradation pathway in aerobic outdoor environments (Gijsman et al., 1999). Photo-oxidation causes plastic's surface oxygenation which increases the polymer hydrophilicity and enhances the microbial biofilm formation on the polymer surface. As illustrated in Fig. 5, PE, PP and PS are susceptible to photo-initiated oxidative degradation. The mechanism of plastic photodegradation includes three main stages; namely, initiation, propagation and termination. During the initiation stage, polymer chain chemical bonds are broken by light or heat to produce free radicals (Yousif and Haddad, 2013). However, the polymers must contain unsaturated chromophoric groups that absorb light energy (Gijsman et al., 1999; Gewert et al., 2015). Several plastic types, such as PE and PP do not contain any unsaturated double bonds in their polymeric backbone, therefore these compounds are expected to be resistant to photodegradation. However, small amounts of external impurities or structural abnormalities can allow the initiation step of photodegradation to occur (Gijsman et al., 1999; Scott, 2002). Subsequently, during the propagation stage the polymer radicals react with oxygen and form peroxy radicals. Besides the formation of hydroperoxides, further complex radical reactions take place and lead to auto-oxidation (Singh and Sharma, 2008). Propagation ultimately leads to chain scission or crosslinking (Tolinski, 2009). Termination of the radical reaction occurs when inert products are formed from the combination of two radicals (Peacock, 2000). Therefore, due to oxidation, random chain scission is performed to produce oxygen-containing functional groups such as olefin, ketone and aldehyde compounds (Scott, 2002). Due to the presence of unsaturated double bonds, these compounds are considered more susceptible to photo-initiated degradation. This process leads to a reduction in plastic MW. Therefore, the produced compounds surface area is increased, making them more susceptible to the fragmentation process. In this concern, Albertsson and Karlsson (1988) investigated PE photo-degradation in an inert system for more than 10 years, demonstrating that PE degradation rate was characterized by three stages, including a rapid CO₂ release and O₂ uptake during the 1st stage until the equilibrium phase, a decline of the degradation rate during the 2nd stage and lastly, a rapid deterioration of the surface structure and an increase in the degradation rate during the 3rd stage.

4.2. Hydrolysis

Hydrolysis of plastic represents one of the main steps during the abiotic degradation pathway. Hydrolysis is accelerated by the presence of

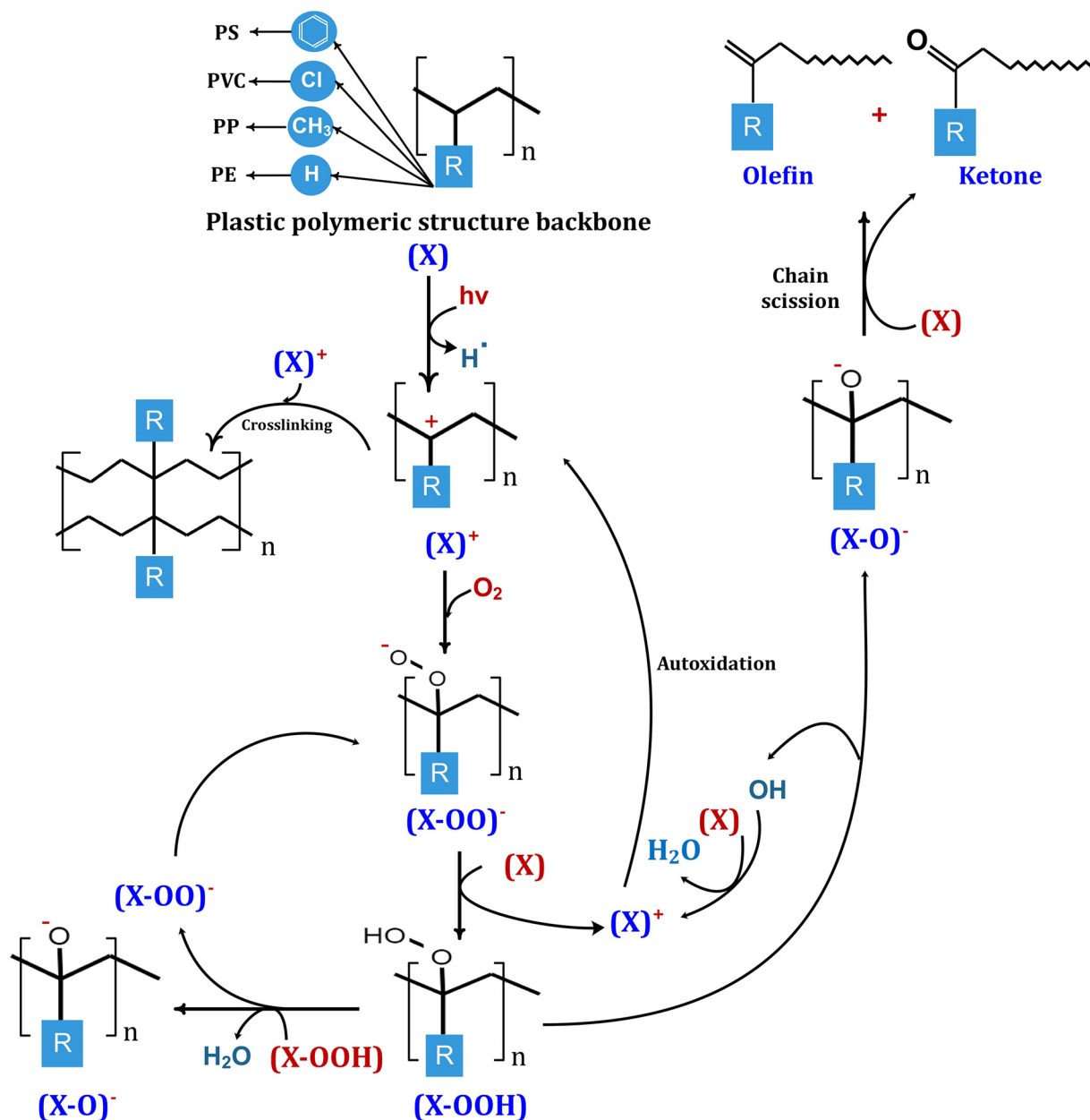


Fig. 5. Plastic photodegradation mechanism.

catalysts, such as ions released through this reaction (Baes and Mesmer, 1976). The hydrolysis rate depends on the susceptibility of polymeric chemical bonds to water attack and its concentration inside the material. Also, the rate of water diffusion in the polymeric material is a critical factor (Crawford et al., 1988; Padsalgikar, 2017). During hydrolysis, water reacts with the polymer causing physicochemical changes and this process is chemically or biologically catalyzed, as illustrated in Fig. 6(A). In the acid-base catalyzed reactions, the mechanism involves a nucleophilic attack on the carbonyl group in esters or amides bonds (Hosseini et al., 2007). Also, there are several factors affecting the hydrolysis rate, including polymeric molecules MW, where the hydrolysis rate decreases by increasing the molecular weight. Likewise, reaction rate is affected by the molecules mobility and hydrophobicity or hydrophilicity (Booth et al., 2017). Moreover, based on the experimental rule (Newman's rule of six), the hydrolysis rate depends on the chain's stereochemical composition, where hydrogen, oxygen and carbon atoms

interfere sterically with rotations of other groups which limit the number of conformations that allow attack by OH or H ions. Polyesters (PES) are particularly stable with a large number of atoms in the sixth position (Lopalco et al., 2016).

4.3. Thermal degradation

Plastic's thermal degradation can be performed at high temperatures, usually higher than 100 °C, depending on the plastic polymer type and characteristics. The antioxidant additives incorporated through plastic manufacture prevents thermal oxidation at low temperatures. In contrast, the degradation due to heat oxidation is accelerated by stress and exposure to other reactive compounds, like ozone. In general, the resistance to degradation depends on the chemical composition of the polymer, with PP, PVC and polybutadiene (PBD) being susceptible to thermal degradation. In contrast, polymers such as

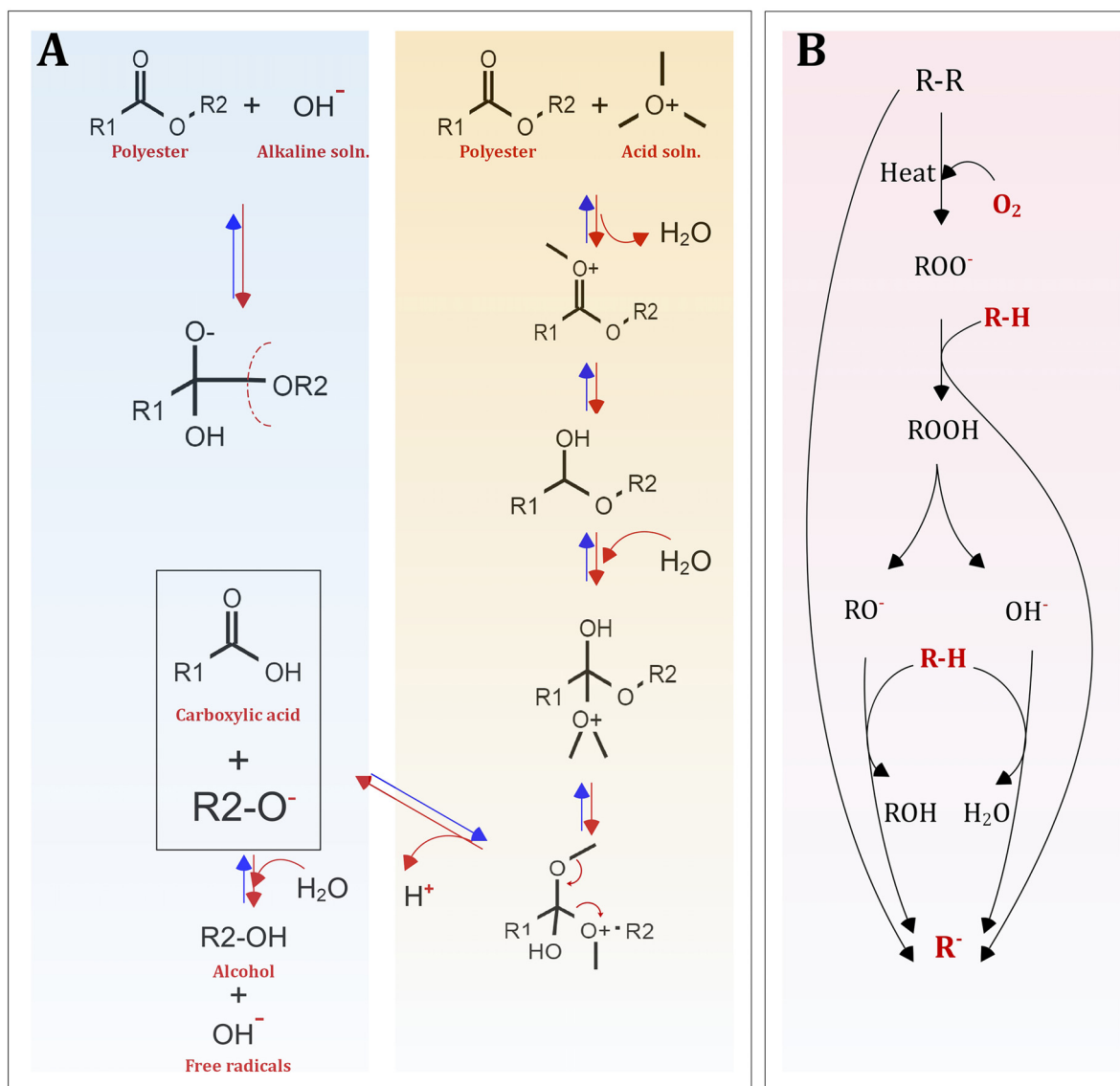


Fig. 6. Abiotic degradation of polyester. A, hydrolysis process and B, thermal degradation process.

polysulfone, polyether ketone, and polysiloxanes are thermally resistant owing to the strong bonds in their backbone. Overall, the contribution of thermal degradation under normal environmental conditions globally is considered negligible, particularly in cold, marine environments (Kitamoto et al., 2011; Booth et al., 2017). The mechanism and factors affecting thermal degradation are presented in Fig. 6(B), as previously reported (Van Krevelen and Te Nijenhuis, 2009).

5. Microbial degradation

The biodegradation process refers to the conversion of organic compounds into biogas and residual biomass, as a result of microbial activity (Ali and Sun, 2019; Ali et al., 2019a, 2019b), that can utilize plastic as carbon source (Shah et al., 2008; Magnin et al., 2020). Synthetic plastics, including PES, polyvinyl, polyamide (PA) and PU, represent the most widely used materials around the globe. However, only a small fraction of their wastes can be biodegraded due to the nature of plastic and its physicochemical properties, since plastic is a weak growth substrate for microorganisms (Biffinger et al., 2014). The enzymatic degradation of plastic through hydrolysis can be performed by binding the enzyme to the polymer to catalyze the hydrolytic cleavage of polymers into

oligomers, dimers, and monomers, and finally to be mineralized to CO_2 and H_2O . The ability of fungi, bacteria and algae as polymer degrading microorganisms has been previously highlighted and several species have been reported to grow on easily degradable polymers, such as cellulose and lignin (Ali and Sun, 2015) or resistant to degradation polymers such as PE and PU (Shah et al., 2008; Raghavendra et al., 2016; Zhang et al., 2020; Cassone et al., 2020).

5.1. Microbial potential for plastic biodegradation

The extensive surface area of the fungal mycelial can penetrate the polymeric substance surface in order to effectively access and degrade the conventional plastic polymers (Sánchez, 2020). Also, extracellular enzymes (e.g., depolymerase) can be secreted by the mycelia and breakdown polymers into oligomers, dimers and monomers (Ameen et al., 2015; Ali et al., 2021), while compared to bacteria, the concentration of enzymes secreted by a fungus is significantly higher (Gangola et al., 2019). Subsequently, the produced monomers can be assimilated and mineralized by fungal intracellular enzymes. White-rot and brown-rot fungi can significantly contribute to plastic and other polymeric substances

Table 2
The efficiency of fungal species in plastic polymers degradation.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE	• <i>Mucor rouxii</i> NRRL 1835	Freshwater	28	A slight weight reduction	El-Shafei et al., 1998
	• <i>Aspergillus flavus</i>	Soil and leaves	90	A reduction in molecular weight was recorded	Yamada-Onodera et al., 2001
	• <i>Penicillium simplicissimum</i>		100		
	• <i>Aspergillus terreus</i>	Soil	126	A degradation percentage of 29 and 16% for the UV and non-UV treated films, respectively.	Esmaeili et al., 2013
	• <i>Aspergillus fumigatus</i>	Soil			
	• <i>Fusarium solani</i>				
	• <i>Aspergillus niger</i>				
	• <i>Lysinibacillus xylanilyticus</i>				
	• <i>Aspergillus japonicas</i>	Soil	30	These strains degraded 30–36% of LDPE substrate weight.	Singh and Gupta, 2014
	• <i>Fusarium sp.</i>	Soil	30	Biofilm formation, weight loss, and HDPE surface modification	Sangeetha Devi et al., 2015
	• <i>Aspergillus flavus</i>				
	• <i>Aspergillus tubingensis</i>				
	• <i>Aspergillus caespitosus</i>	Seawater	28	Biodegradation of the films was revealed by SEM, CO ₂ emission, and enzymatic activity (Laccase, MnP, and LiP)	Ameen et al., 2015
	• <i>Aspergillus terreus</i>	Soil	90	Morphological damages on PE sheets	Ojha et al., 2017
	• <i>Alternaria alternata</i>				
• <i>Eupenicillium hirayamae</i>					
• <i>Phialophora alba</i>					
• <i>Paecilomyces variotii</i>					
• <i>Penicillium oxalicum</i>					
• <i>Penicillium chrysogenum</i>					
• <i>Zalerion maritimum</i>					
• <i>Aspergillus oryzae</i>					
• <i>Aspergillus oryzae</i>	Seawater				
• <i>Aspergillus oryzae</i>	Soil	120	A reduction in LDPE sheets weight was reported	Muhonja et al., 2018	

*PE, Polyethylene; LDPE, Low-density polyethylene; HDPE, High-density polyethylene.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE	• <i>Trichoderma viride</i>	Soil	45	A reduction in LDPE film's weight	Munir et al., 2018
	• <i>Aspergillus nomius</i>	Soil	60	Weight reduction	Sangale et al., 2019
	• <i>Aspergillus terreus</i> MANGF1/WL				
	• <i>Aspergillus sydowii</i> PNP15/TS	<i>Galleria mellonella</i> gut	28	A reduction in the molecular weight was observed	Zhang et al., 2020
	• <i>Aspergillus flavus</i> PEDX3				
• <i>Penicillium citrinum</i>					
PET	• <i>Penicillium funiculosum</i>	Cutinase- and polyesterase-producing fungi.	21	Proved that polyesterase could hydrolyze PET	Liebming et al., 2007
	• <i>Penicillium sp.</i>	Soil	84	Chemical changes in polymeric chains were observed	Nowak et al., 2011
	• <i>Penicillium sp.</i>	The plastic wastes dumped soil	28	Morphological changes were detected	Sepperumal et al., 2013
	• <i>Pichia pastoris</i>	Engineered yeast strain	18 h	PETase-displaying a promising route for efficient biological recycling of PET	Chen et al., 2020
	• <i>Aspergillus sp.</i>	Seawater	42	A reduction in plastic weight by 22%	Sarkhel et al., 2020
PBS and PBSA	• <i>Pseudozyma spp.</i>	Leaves and husks of paddy rice	42	A degradation activity on PBS and PBSA. <i>P. antarctica</i> produced two lipases (A and B) on media containing oil	Kitamoto et al., 2011
	• <i>Aspergillus sp.</i>	Endophytic fungi from endemic plants	90	Only <i>L. theobromae</i> could degrade irradiated PP film	Sheik et al., 2015

*PE, Polyethylene; PET, Polyethylene terephthalate; PBS, poly-butylene succinate; PBSA, poly-butylene succinate-co-adipate; PP, Polypropylene.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PCL	• <i>Alternaria alternata</i> -ST01	NA	15	High growth and enzymatic activity (cutinase). The degradation rate reached 93.3%. Also, SEM showed cracks on the PCL film surface	Abdel-Motaal et al., 2020
	• <i>Aspergillus brasiliensis</i> (ATCC 9642)	Standard strains	28	Visible growth was observed. <i>C. globosum</i> was a pioneer in PCL degradation	Vivi et al., 2019
• <i>Trichoderma virens</i> (ATCC 9645)					
• <i>Chaetomium globosum</i> (ATCC 16021)					
• <i>Penicillium funiculosum</i> (ATCC 11797)					
• <i>Paecilomyces variotii</i> (ATCC 16023)					
PPU	• <i>Pestalotiopsis microspora</i>	Plastic-degrading fungi	16	A clearance of the medium was observed	Russell et al., 2011
	• <i>Aspergillus tubingensis</i>	Soil	60	A complete degradation into smaller pieces was reported	Khan et al., 2017
	• <i>Cladosporium cladosporioides</i>	Plastic debris floating in shoreline	6–14	A visible halo zone on agar plates was observed	Brunner et al., 2018
• <i>Leptosphaeria sp.</i>					
• <i>Penicillium griseofulvum</i>					
• <i>Xepiculopsis graminea</i>					
PVC	• <i>Phanerochaete chrysosporium</i> PV1	PVC films buried in the soil	300	A morphological deterioration was observed	Ali et al., 2013
	• <i>Lentinus tigrinus</i> PV2				
	• <i>Aspergillus niger</i> PV3				
	• <i>Aspergillus sydowii</i> PV4				
	• <i>Aspergillus sydowii</i> PV4				

Table 2 (continued)

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PP (MI-PP; ST-PP)	<ul style="list-style-type: none"> • <i>Phanerochaete chrysosporium</i> NCIM 1170 • <i>Engyodontium album</i> MTP091 	Soil	360	18.8 and 9.42% gravimetric weight loss, TGA weight loss estimated by 79% and 57% with UV pretreated MI-PP	Jeyakumar et al., 2013
*PCL, Poly (ϵ -caprolactone); PPU, Polyester polyurethane; PVC, Polyvinylchloride; PP, Polypropylene; MI-PP, pro-oxidant blended polypropylene; ST-PP, starch blended polypropylenes; NA, not available.					
Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
P4	• <i>Fusarium</i> sp.	Soil	60	Morphological damages were observed	Tachibana et al., 2010
PSS	• <i>Gloeophyllum trabeum</i> DSM 1398	Fruit bodies on rotting oak wood	20	A reduction in molecular mass by 50% was reported	Krueger et al., 2015
PE and PU	<ul style="list-style-type: none"> • <i>Aspergillus fumigatus</i> • <i>Aspergillus niger</i> • <i>Fusarium oxysporum</i> • <i>Penicillium</i> sp. • <i>Lasiodiplodia crassispota</i> • <i>Trichoderma harzianum</i> 	Soil	90	Morphological degradation and a halo zone was observed on the growing culture on both LDPE and PU media	Raghavendra et al., 2016
*P4, Polyamide 4; PSS, Polystyrene sulfonate; PE, Polyethylene; PU, Polyurethane.					

biodegradation, due to their ability to produce several extracellular enzymes such as lignin peroxidase, manganese peroxidase, versatile peroxidase and multi-copper oxidase laccase to decompose lignin and convert it into CO₂ and H₂O (Ameen et al., 2015; Ali et al., 2020a). Interestingly, lignin is similar to plastic, in terms of certain physical properties such as hydrophobicity and chemical structure, including non-phenolic aromatic rings and presence of ether bonds and carbon skeleton which are oxidized during the degradation of lignin (Kim et al., 2011; Ali et al., 2020b). Such similarities enable certain lignin-modifying enzymes, like laccase and manganese peroxidase to degrade certain plastic polymers such as PE and PP (Jeyakumar et al., 2013). In Table 2, effective fungal strains for degradation of plastic wastes are listed. Our investigation revealed that *Aspergillus* spp. and *Penicillium* spp. have been highlighted as promising strains for plastic biodegradation, while *Aspergillus flavus* represents the most commonly used and the most effective strain in plastic degradation. Concerning the isolation source, contaminated soil and seawater have been the predominant sources of plastic-degrading fungal strains. Currently, most studies have been focused on PE as a fungal substrate, however more plastic types and different fungal strains should be investigated.

Similarly, bacterial strains can inhabit the plastic contaminated soil or water and metabolize plastic substances. Several studies indicated that biodegradation of plastic by specialized bacteria could be an effective bioremediation strategy (Yoshida et al., 2016). In this respect, our literature review showed that among all tested bacterial strains, *Bacillus* spp., *Pseudomonas* spp. and *Streptomyces* spp. show high efficiency against different plastic polymers, as shown in Table 3. However, the predominant species was by far *Bacillus cereus* and the plastic contaminated soil was the main source of isolation. Although the fungal degradation rate is higher than the bacterial rate (Muhonja et al., 2018), plastic degradation by fungi requires more stable conditions than in case of bacteria (Artigas, 2008). However, further research is needed to fully unravel bacterial potential and prove the effectiveness of bacterial consortia in plastic degradation.

Recently, a limited number of studies have revealed the ability of algal species to degrade plastic polymers, as presented in Table 4. Interestingly, the filamentous blue-green algae, such as *Anabaena spiroides*, are able to grow on the surface of PE wastes because of the availability of critical factors, including sunlight, water, and nutrients (Kumar et al., 2017), showing the potential of microalgae to colonize plastic surfaces. Furthermore, several species of diatoms and cyanobacteria have shown efficiency against PE biodegradation (Kumar et al., 2017; Moog et al., 2019). However, the effectiveness of microalgae as plastic degraders needs further investigation.

5.2. Mechanism of microbial degradation of plastic wastes

The microbial degradation of plastic wastes is carried out via five main steps, including colonization, biodeterioration, biofragmentation, assimilation and mineralization, as shown in Fig. 7. The first stage of microbial degradation mechanism is the colonization of microbial species on the plastic surface, during which the microorganisms involved form consortia leading to biofilm formation, which provokes severe damages on the polymer surface (Gu, 2003). Microbial adhesion to the polymer surface is performed by the production of various proteins and polysaccharides (Capitelli et al., 2006), which infiltrate into the material pores leading to an alteration in pores' size. Consequently, the biodeterioration step is carried out as a result of the microbial adhesion and activity on the plastic surface. During this stage, surface degradation occurs that alters the physicochemical properties of the plastic polymer.

Concerning the activity of various microorganisms, filamentous fungi use their mycelia to penetrate into the polymeric material to increase the size of the pores and induce the formation of cracks, leading to decreased polymer resistance and durability (Bonhomme et al., 2003). Also, the microbial penetration rate can be enhanced by the microbial secretion of extracellular substances that affect hydrophobic and hydrophilic phases. These extracellular substances enhance the accumulation of pollutants, which enhance microbial growth and also biodeterioration rate (Zanardini et al., 2000). Furthermore, microbial deterioration is more effective when is carried out by consortia instead of sole strains (Skariyachan et al., 2016). More specifically, chemolithotrophic microorganisms, such as *Nitrosomonas* spp., *Nitrobacter* spp., and *Thiobacillus* spp., can release active chemicals, including sulphuric and nitric acid (Ranalli et al., 2009). Also, microorganisms that use chemical bonds in organic substrates and/or oxygen as an energy source (chemo-organotrophic) can release organic acids (e.g., gluconic, oxalic, glyoxylic, citric, oxaloacetic, glutaric, etc.) (Jenings and Lysek, 1996). Concomitantly, the medium pH is modified because of the formation of acids and bases during the microbial metabolic activity, which can lead to increased surface erosion (Lugauskas et al., 2003). Also, it is worth noting, that the efficiency of mineral acids in biodeterioration by fixing cations is lower than that of organic acids that are necessary for process completion (Warscheid and Braams, 2000).

Physical biodeterioration may be carried out by filamentous microorganisms (bacteria and fungi) that can invade the polymer material and subsequently increase the pores and cracks (Hakkarainen et al., 2000). However, some microbial species can also perform oxidation-

Table 3
The efficiency of bacterial species in plastic polymers degradation.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE	• <i>Streptomyces viridosporus</i> T7A	Standard lignocellulose-degrading strains	20	<i>Streptomyces</i> spp. demonstrated a further reduction in percent elongation and PE molecular weight average	Lee et al., 1991
	• <i>Streptomyces badius</i> 252				
	• <i>Streptomyces setonii</i> 75Vi2	Freshwater	28	A slight weight reduction was observed	El-Shafei et al., 1998
	• <i>Streptomyces</i> spp.				
	• <i>Bacillus pumilus</i>	Bacterial strains adopted with PE as carbon source	14	The abiotic treatment and biological pretreatment reduced plastic weight by 8.4%	Roy et al., 2008
	• <i>Bacillus haldenitrificans</i>				
	• <i>Bacillus cereus</i>				
	• <i>Pseudomonas</i> sp.	Soil	45	Degraded LDPE up to 5.0%.	Tribedi and Sil, 2013
	• <i>Enterobacter asburiae</i>		60		
	• <i>Bacillus</i> sp.				
	• <i>Streptomyces</i> spp.	Soil	180	Reduction of 46.7 and 24.2% in weight with <i>Streptomyces</i> spp. and <i>Pseudomonas</i> spp., respectively	Deepika and Jaya, 2015
	• <i>Pseudomonas</i> spp.				
	• <i>Lysinibacillus fusiformis</i>	Seawater and Soil	60	The maximum percentage in weight reduction (21.9%) was recorded with <i>L. fusiformis</i> at pH 3.5 at 25 °C	Shahnawaz et al., 2016
• <i>Bacillus cereus</i>					
• <i>Ideonella sakaiensis</i>	Screening strains exposed to PET in the environment	70	Detected the production of two enzymes capable of hydrolyzing PET and the reaction intermediate.	Yoshida et al., 2016	
• <i>Pantoea</i> sp.	Soil	120	81 and 38% of weight reduction for LDPE strips and LDPE pellets, respectively.	Skariyachan et al., 2016	
• <i>Enterobacter</i> sp.					
• <i>Rhodococcus ruber</i> C208	NA	7	Degraded LDPE at a rate of 0.86% per week.	Sivan et al., 2006	
• <i>Sphingobacterium multivorum</i>	Soil		Bacterial growth on pretreated LDPE surface	Montazer et al., 2018	
• <i>Pseudomonas</i> spp.	Water and soil	90	The plastic weight reduction was assessed by 35–40% and production of extracellular lipase was observed	Skariyachan et al., 2015	
• <i>Brevibacillus borstelensis</i>	Coastal regions	30	Weight reduction was evaluated by 11.4%	Mohanrasu et al., 2018	

*PE, Polyethylene; LDPE, Low-density polyethylene; HDPE, High-density polyethylene; NA, not available.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE	• <i>Acinetobacter</i> spp.	<i>Galleria mellonella</i>	3	The intestinal microbiome of <i>G. mellonella</i> is intricately associated with PE biodegradation	Cassone et al., 2020
	• <i>Microbulbifer hydrolyticus</i> IRE-31	Marine pulp mill wastes rich in lignin	30	Polymer surface morphological changes were observed and ketone group was formed	Li et al., 2020b
	• <i>Lysinibacillus macrolides</i>	Soil	120	A reduction in LDPE sheets weight was reported. Also, the highest degradation activity for bacteria was 36% and 20% attributed to <i>B. cereus</i> and <i>B. borstelensis</i> , respectively	Muhonja et al., 2018
• <i>Pseudomonas putida</i>					
• <i>Bacillus subtilis</i>					
• <i>Brevibacillus borstelensis</i>					
• <i>Cellulosimicrobium funkei</i>					
PE and PS	• <i>Citrobacter</i> sp.	<i>Tenebrio molitor</i>	32	Mass conversion estimated by 49.0% and the MW decreased by 40% in PE-fed worms and by 13% in PS-fed worms	Brandon et al., 2018
	• <i>Kosakonia</i> sp.				
PU	• <i>Serratia</i> spp.	<i>Galleria mellonella</i>	21	Loss of plastic mass using 150 larvae fed on either PS or PE	Lou et al., 2020
	• <i>Bacillus</i> sp.				
	• <i>Corynebacterium</i> sp.	Soil	28	Zones of hydrolysis were observed besides the release of CO ₂	Shah et al., 2008
	• <i>Bacillus</i> sp.				
	• <i>Pseudomonas</i> sp.				
• <i>Micrococcus</i> sp.					
• <i>Arthrobacter</i> sp.					
PET	• <i>Vibrio</i> sp.	Seawater	42	The weight reduction of plastic polymer by 35% was recorded	Sarkhel et al., 2020
P4	• <i>Stenotrophomonas</i> sp.	Soil	60	Morphological damages were observed	Tachibana et al., 2010

*PE, Polyethylene; PU, Polyurethane; P4, Polyamide 4; LDPE, Low-density polyethylene; PET, Polyethylene terephthalate.

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE and PVC	• <i>Acanthopleurobacter pedis</i>	Soil	70	Morphological damages were observed.	Sah et al., 2011
	• <i>Microbacterium</i> sp.				
	• <i>Pseudomonas putida</i>				
	• <i>Pseudomonas aeruginosa</i>				
	• <i>Pseudomonas otitidis</i>				
	• <i>Bacterium</i> Te68R				
	• <i>Bacillus aerius</i>				
	• <i>Bacillus cereus</i>				
	• <i>Acanthopleurobacter pedis</i>				
	• <i>Pseudomonas otitidis</i>				
	The bacterial strains were selected based on their potential to	70	A relatively better biodegradation potential of developed consortium for PVC	Anwar et al., 2013	

Table 3 (continued)

Polymer type*	Microorganism	Isolation source	Time (day)	Conclusions	References
PE and PP	• <i>Bacillus aerius</i>	degrade PVC	140	The loss of weight for plastic pellets was 45.7, 37.2, and 44.2%, respectively.	Skariyachan et al., 2018
	• <i>Bacillus cereus</i>				
	• <i>Aneurinibacillus</i> spp. • <i>Brevibacillus</i> spp.				

*PE, Polyethylene; PVC, Polyvinylchloride; LDPE, Low-density polyethylene; PP, Polypropylene.

reductions and chemical biodeterioration, such as chemolithotrophic microorganisms that can uptake manganese and/or iron (Fe^{3+}) cations, through specific proteins in the microbial cell membrane (Pelmont, 2005). In case of enzymatic biodeterioration, several extracellular enzymes are involved in this process, such as peroxidases (Otsuka et al., 2003). However, certain plastic polymers are resistant to degradation, such as PU and PVC (Shah et al., 2008). Under this scope, microorganisms tend to produce some enzymatic groups, such as lipases, esterases, ureases and proteases to overcome these polymers' crystallinity (Ameen et al., 2015; Yoshida et al., 2016).

Fragmentation is a lytic process, essential for the degradation of polymers into monomers, dimers, and/or oligomers, as shown in Fig. 7. Through this process, microorganisms use different mechanisms to cleave polymers, including secretion of specific enzymes such as oxidoreductases and hydrolases and/or free radicals. The chemical bonds linking the plastic forming monomers are similar to those found in natural polymers such as lignocellulosic compounds. Therefore, it is reasonable to assume that most of the lignocelluloses degrading enzymes can degrade plastic polymers as well (Chen et al., 2020). The microbial *endo*- and *exo*-enzymes involved in this process are not synthesized immediately. Instead, it takes time to start up the cell machinery for specific enzymes synthesis (Lucasa et al., 2008). Moreover, enzymes concentration increases as a function of time and the activity terminates with substrate exhaustion, explaining the long time that microorganisms need to degrade plastic (Tables 2–4). Furthermore, the hydrolysis stage is strongly determined by the activity of various enzymes. For instance, the depolymerase enzyme and its reaction mechanism is based on the reaction between aspartate, histidine, and serine. This catalytic triad generates a nucleophilic alkoxide group attacking the ester bond to form alcohol and acyl-enzyme complex (Gewert et al., 2015; Austin et al., 2018). Because of the polymer hydrophobic

crystalline nature, the polymer chain scission reactions can be complicated. Thus, the reaction needs the implication of more enzymes to transform polymer structure. For example, mono and dioxygenases that form alcohol and/or peroxy groups can increase polymer structure polarity that makes the biodegradation process more effective. Furthermore, peroxidases catalyze reactions between peroxy molecules, such as hydrogen peroxide (H_2O_2), organic peroxide, phenol, and/or aliphatic unsaturation (Hofrichter, 2002). Also, oxidases containing copper atoms (metalloproteins) are secreted by most lignolytic microbial cells to catalyze hydroxylation and/or oxidation reactions (Chiellini et al., 2006).

On the other hand, the free radical oxidation aims at increasing the molecule polarity by the addition and/or formation of a hydroxyl function and carbonyl or carboxyl group. The increased hygroscopic properties increase microbial attack. Furthermore, several oxidation reactions can be catalyzed by several enzymes that can generate free radicals inducing oxidative stress that lead to chain reactions and induce the polymeric structure conversion and degradation. However, linear polymeric compounds degradation through enzymatic reactions is extremely constrained since the enzymes cannot interact with the internal part of these structures (Lucasa et al., 2008; Phaniendra et al., 2014). Furthermore, several microbial degraders, including bacteria, fungi, and algae, can produce H_2O_2 (Diaz et al., 2018). Concerning the oxidation ability of algal species, Diaz et al. (2018) demonstrated that extracellular superoxide and H_2O_2 were produced by five marine harmful bloom-forming algae (HBA) species, including *Aureococcus anophagefferens*, *Pseudonitzschia* sp., *Heterosigma akashiwo*, *Chattonella marina*, and *Karenia brevis*.

Concerning the assimilation of the produced monomers, the microbial cell obtains the energy sources from these integrated monomers, allowing the microbial cell to grow. Some monomers penetrate the cell through individual-specific membrane carriers. However, other molecules cannot be assimilated due to cell membrane permeability.

Table 4

The efficiency of algal species in plastic polymers degradation.

Polymer type ^a	Microorganism	Isolation source	Time (day)	Conclusions	References
PE	• <i>Navicula pupula</i> (diatom)	PE bags and water samples	45	Growth of microalgae on the polyethylene sheet and the erosion cum degradation was observed	Kumar et al., 2017
	• <i>Scenedesmus dimorphus</i> (green microalgae)				
	• <i>Anabaena spiroides</i> (cyanobacteria)				
PET and PETG	• <i>Phormidium lucidum</i>	Domestic sewage water	42	A rapid growth of cyanobacterial species on the PE surface and a reduction in crystallinity thickness and weight of the LDPE film was observed	Sarmah and Rout, 2018
	• <i>Oscillatoria subbrevis</i>	Domestic sewage water	42		
	• <i>Nostoc carneum</i> (cyanobacteria)	Domestic sewage water	42		
PET and PETG	• <i>Phaeodactylum tricorutum</i> (diatom)	Genetically modified diatom species	7	FT-IR and NMR spectroscopy indicated the presence of ethanol and ethyl propanoate as a result of the biodegradation of PE. Also, the growth of <i>N. carneum</i> was inversely proportional to plastic thickness and weight loss	Moog et al., 2019
PET and PP	• <i>Spirulina</i> sp. (cyanobacteria)	NA	112	Tensile strength and PE carbon decreased	Khoironi et al., 2019

^a LDPE, Low-density polyethylene; PE, Polyethylene; PETG, polyethylene terephthalate glycol; PET, Polyethylene terephthalate; PP, polypropylene; NA, not available.

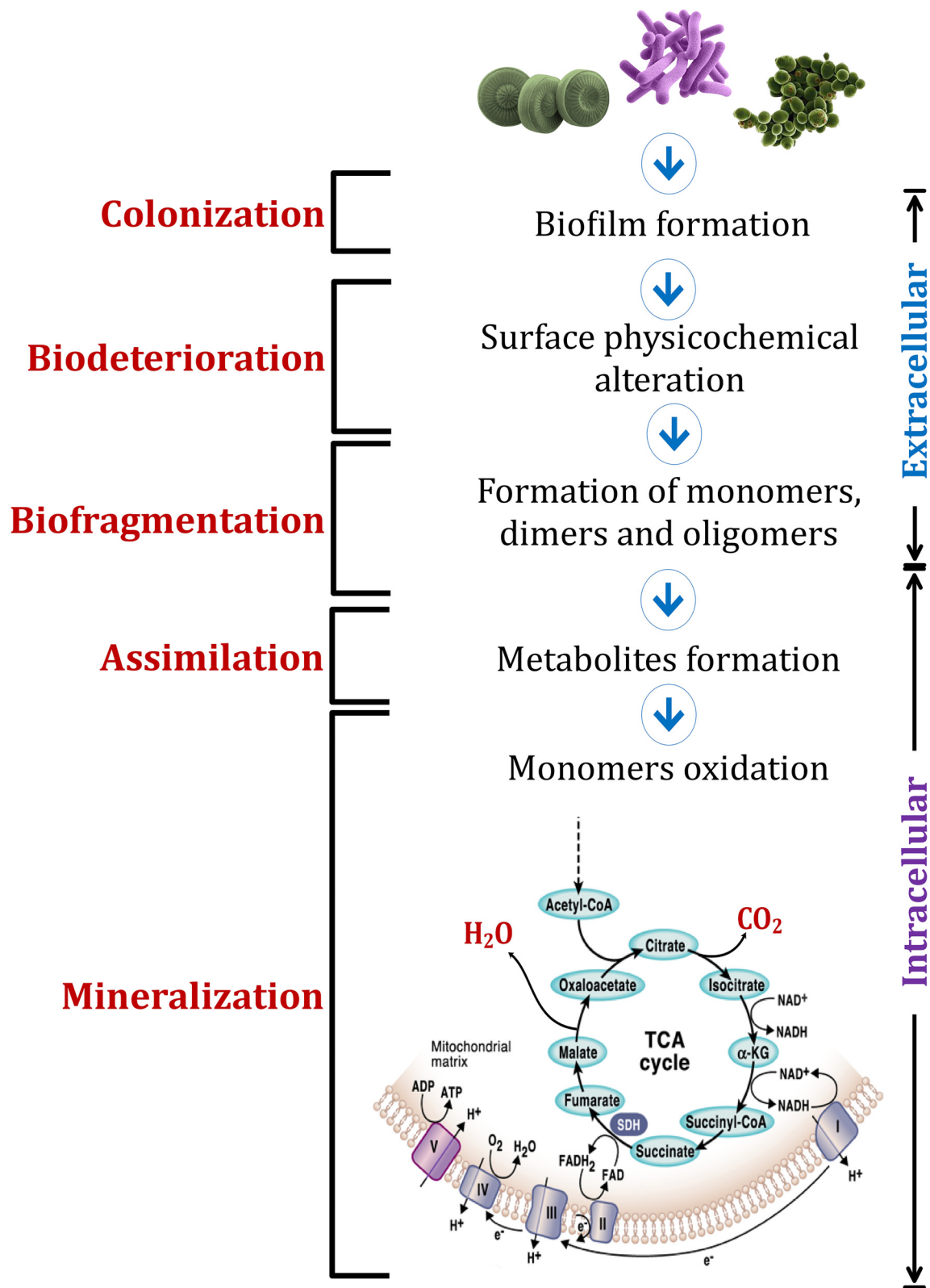


Fig. 7. Microbial degradation stages of plastic polymers.

Subsequently, the microbial cell may use the non-assimilated monomers via the biotransformation process including enzyme-catalyzed conversion (Lucasa et al., 2008; Al-Tohamy et al., 2020a), as shown in Fig. 8. Inside the microbial cell, the degraded monomers are oxidized

using the microbial catabolic pathways to produce cell organelles and energy-carrying molecules such as adenosine triphosphate (ATP), which is carried out through three pathways (aerobic respiration, anaerobic respiration, and fermentation), in both aerobic and/or anaerobic

environment (Hong and Gu, 2009; Al-Tohamy et al., 2020b; Ali et al., 2020c, 2020d).

6. Invertebrates as effective plastic biodegraders

Invertebrates' digestive tract has inspired many researchers, due to their ability to feed on wood, plastic wastes or other polymeric compounds. Such species include waxworms (*Plodia interpunctella*), superworms (*Zophobas atratus*), mealworm (*Tenebrio molitor*) and wood-feeding termite (*Reticulitermes chinensis*), the greater wax moth (*Galleria mellonella*), land snail (*Achatina fulica*) and other invertebrates (Yang et al., 2014; Ali et al., 2017a; Ali et al., 2018; Song et al., 2020; Yang et al., 2020). Also, social insect species that live in colonies and are characterized by group integration, labour division and generation's overlap, such as bees, waxworms, and termites that have the most specific and harmonious gut communities, with significant and beneficial functions in nutrition may provide an opportunity for plastic biodegradation. Therefore, the question arises about which bacterial or fungal species contained in invertebrates and especially insects have the ability to degrade plastic polymers and which mechanism is applied for this biodegradation process?

In this concern, Dowd and Shen (1990) found that the *Lasioderma serricorne* digestive tract is inhabited by symbiotic yeasts, which can produce hydrolytic enzymes that degrade alkaloid esters and phenolic

compounds. Also, according to Yang et al. (2014), the insect's digestive tract provides an ideal environment for microbial colonization and displays a broad platform of specific microbial consortia for particular functions that provide several benefits to the hosts. Under this scope, Riudavets et al. (2007) investigated the degradation activity of the cigarette beetle (*L. serricorne*), the rice weevil (*Sitophilus oryzae*) and lesser grain borer (*Rhyzopertha dominica*) on packaging and multilayer films of PP, PE, and PES. Also, Yang et al. (2014) reported the ability of *P. interpunctella* to digest PE films owing to the insect's digestive tract that could be an outstanding source for the isolation of PE-degrading microorganisms, such as *Enterobacter asburiae* and *Bacillus* sp. In addition, Yang et al. (2015) investigated *Bacillus* sp. YP1 genome and found 182 genes responsible for the xenobiotic's catabolic activity and biodegradation pathway. Subsequently, Brandon et al. (2018) studied the ability of *T. molitor* for PE and PS digestion and estimated 49% of PE mass conversion to CO₂, while the MW of polymer residues decreased by 40% and 13% in PE-fed mealworms and PS-fed mealworms, respectively, due to the catabolic activity of *Citrobacter* sp. and *Kosakonia* sp. Also, Yang et al. (2020) found that PS foam-fed *Z. atratus* digested 0.58 mg/day/superworm, which was four times higher than *T. molitor*. Also, PS foam-fed superworm could live normally for 28 days with styrofoam as the carbon source, showing the ability of superworm as an effective plastic waste biodegrader. Between the most remarkable results currently reported, Bombelli et al. (2017) investigated the ability of

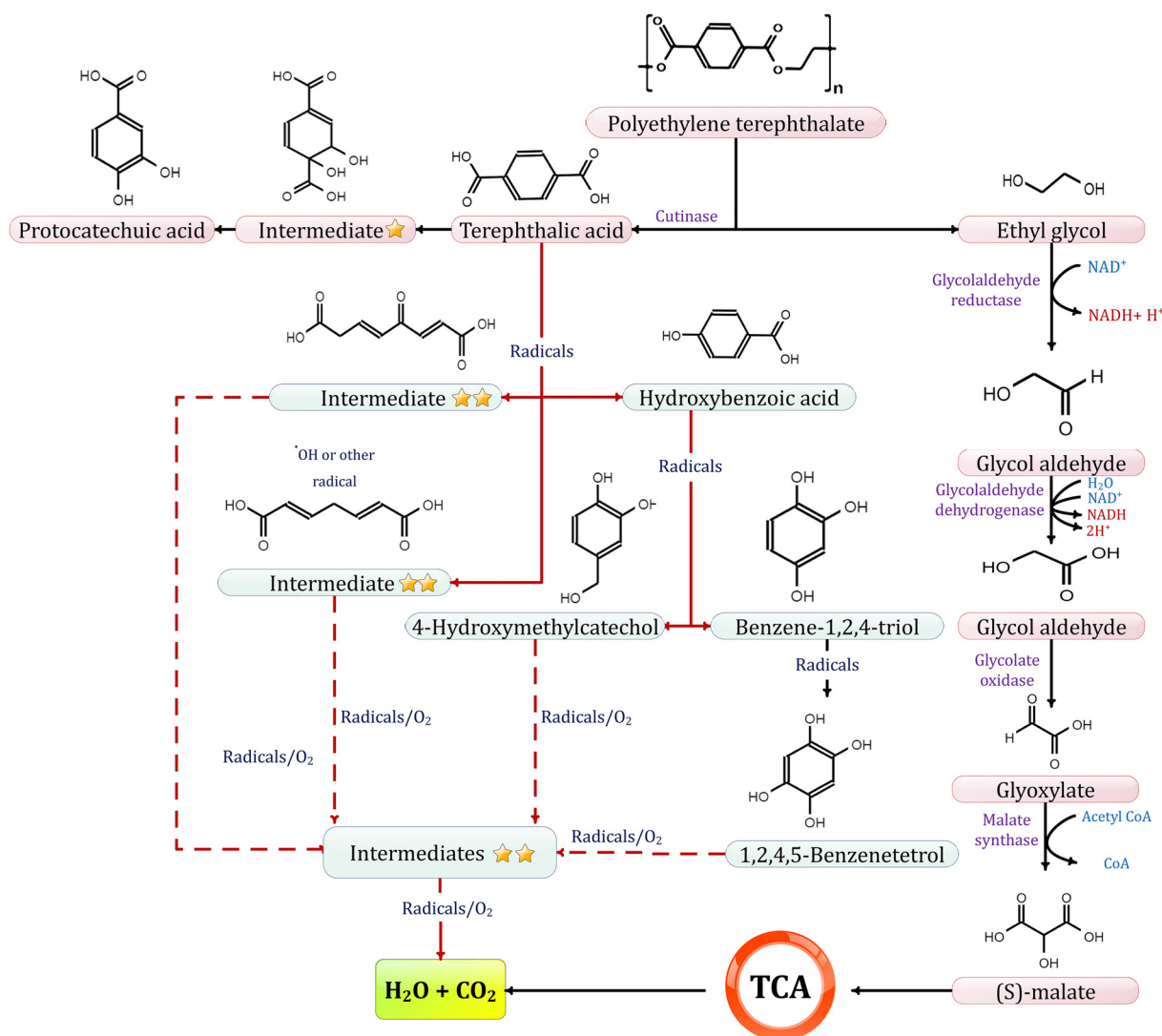


Fig. 8. Enzymatic reactions and mechanisms involved in PET degradation.

G. mellonella against PE and PP and found that they could degrade 1.84 mg/day/worm, which stands for degradation of 92% of total plastic.

Downs et al. (2002) reported that *G. mellonella* can degrade long-chain fatty acids in beeswax by breaking ester bonds, owing to its ability to produce esterase and lipase enzymes. In addition, Kong et al. (2019) stated that beeswax-fed *G. mellonella* can produce lipase, carboxylesterase and fatty-acid degrading enzymes. Zhang et al. (2020) explained that the outstanding activity of *G. mellonella* in plastic biodegradation derives from the presence of *Aspergillus flavus* in their gut, as well as the production of laccases and laccase-like multi-copper oxidases. In contrast, Cassone et al. (2020) attributed this performance to the activity of *Acinetobacter* sp. that plays an important role for lepidopterans regarding PE biodegradation. In this context, the insect's role in plastic waste biodegradation is anticipated to prevail in the future, however further investigation is needed, since insects' intestinal microbiome still remains poorly understood. In Fig. 9 the predominant microbial species in the plastic degrading insects' gut are presented, including fungal species (*Aspergillus* spp.) and bacterial species (*Bacillus* spp., *Enterobacter* spp., *Pseudomonas* spp., and *Staphylococcus* spp.). Lastly, in vitro studies revealed the ability of the Antarctic krill (*Euphausia superba*) to degrade micro-plastics into nano-plastics through digestive fragmentation (Dawson et al., 2018). Hence, it is highly recommended to investigate more species, either insects or invertebrates such as enchytraeids (*Enchytraeus crypticus*), isopods (*Porcellio scaber*), oribatid mites (*Oppia nitens*) and springtails (*Folsomia candida*), that can degrade and digest short fiber PE (Ali et al., 2017b; Selonen et al., 2020).

7. Recommendations for future research

Plastic is one of the most widespread materials globally and one of the main pollutants in the environment. On the other hand, the microbial consortia in the contaminated environment play an important role in plastic degradation through their enzymatic activity. The occurrence of polymer-degrading microbes varies depending on the environment. Therefore,

1. Further study on the harmful effects of accumulated plastic wastes in the marine and soil environments is needed, along with their impact on fauna and flora, in order to protect human health and natural environment.
2. It is necessary to investigate polymer-degrading microbes' mechanisms, including the abiotic and biotic factors affecting plastic degradation in various ecosystems.
3. Single microbial species lack the ability to degrade all plastic types because of the lack of a suitable or specific enzyme. From this point of view, we recommend the exploitation of the synergisms between different microbial species that would enlighten the way toward plastics biodegradation improvement. In parallel, the use of molecular techniques to determine effective consortia involved in polymers chain degradation will be critical. Thus, researchers should focus on the field of genomics and proteomics.

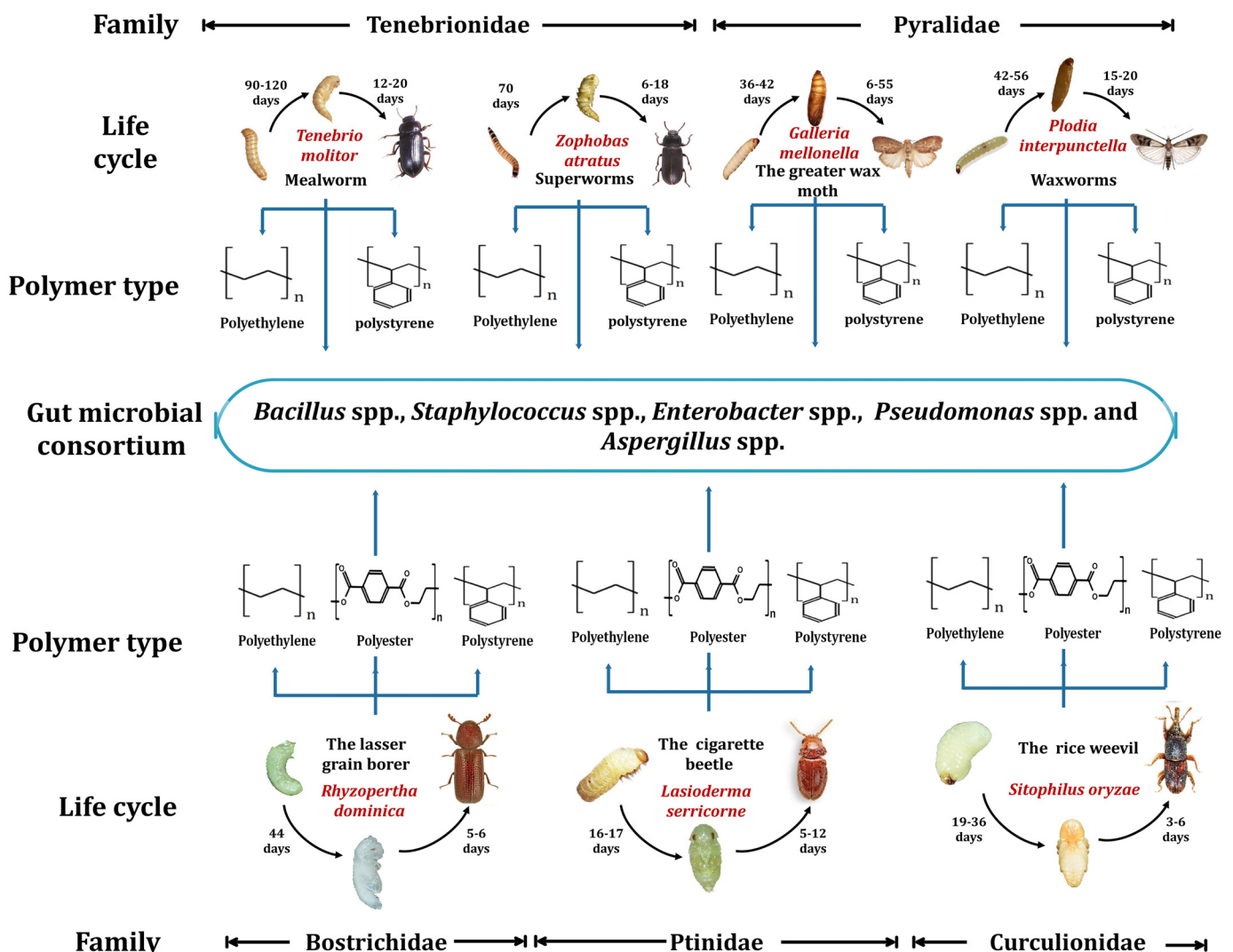


Fig. 9. Insects species involved in the plastic polymer degradation process.

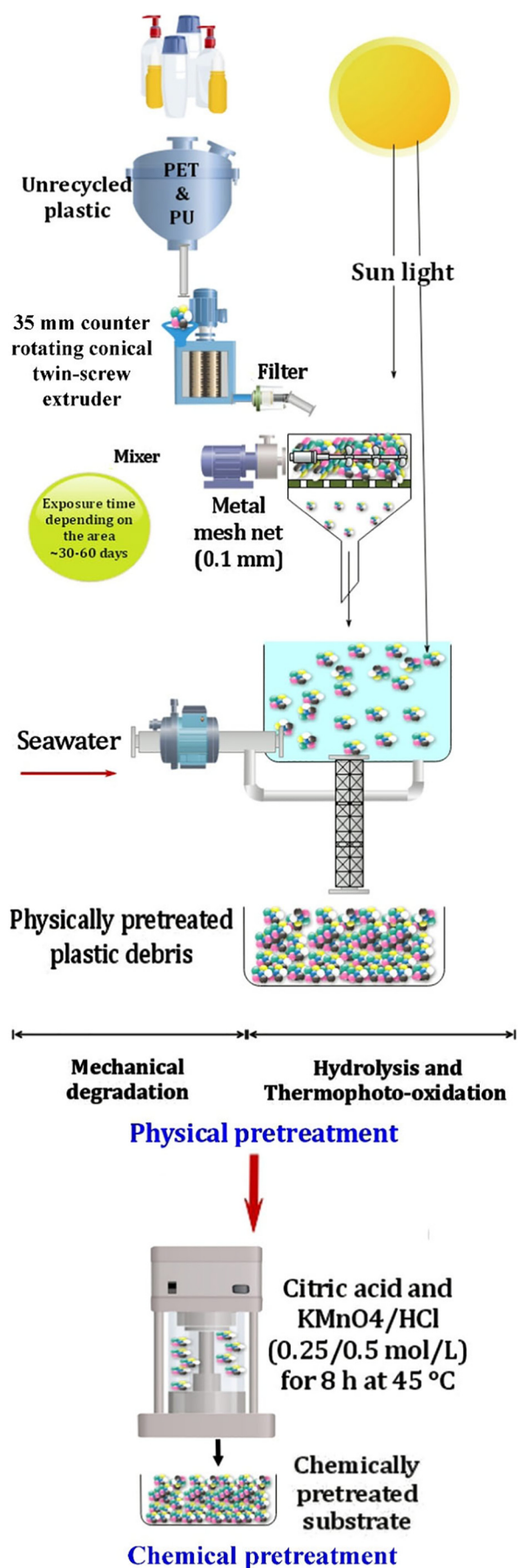


Fig. 10. Physical and chemical pretreatment of plastic wastes.

- We recommend the wider use and more intense research on cyanobacterial species that can produce free radicals, as promising microbial species for polymer biodegradation.
- The plastic-eating insects, such as *G. mellonella*, has been reported that could degrade ~92% of total plastic production, and their outstanding abilities should provide a wide platform for scientific research and, even more for industrial applications. In general, further advanced studies should be performed, aiming at investigating new species and developing new promising technologies able to utilize plastic wastes for recycling or production of biofuels.

In total, the challenge of plastics biodegradation lies in their polymeric structure that limits the polymer breakdown into monomers. However, the microbial enzymes are ineffective when attacking non-hydrolyzable synthetic plastic polymers. Thus, it is recommended to replace these polymers with biodegradable polymers, known as bioplastics. Hence, the newly formed polymer such as polylactide or polyhydroxyalkanoates, PHAs which are industrially used for packaging can enhance the biodegradation rate.

Furthermore, in Fig. 10 we illustrate our proposal for a simple industrial-scale reactor with view to enhance the biodegradation process and link the physical and chemical pretreatment techniques that are currently available, and degrade most of the synthetic plastic types. Initially, abiotic degradation occurs to degrade the plastic polymer into monomers, dimers, and oligomers, while the pretreatment is based on several techniques using UV or chemical methods, in order to subsequently enable microbial growth on the produced compounds. These compounds mixed with organic materials such as lignocellulosic wastes through the biological pretreatment stage will provide the optimum medium for microbial growth (Fig. 11). Afterwards, the hydrolysate of the hydrolysis and biological pretreatment stage will be subjected to anaerobic digestion in the presence of methanogens and ultimately the degraded plastic polymer will result in methane gas (bio-fuel) production.

8. Conclusion

Plastics are between the most indispensable materials in our daily life, because of their unique properties. However, plastic utilization and accumulation tend to continuously increase, posing a serious environmental and health threat. Our review article demonstrated the harmful effects of mismanaged plastic wastes on the environment and human health, concurrently addressing the need for an environmentally friendly processing practice, including biodegradation. However, the physicochemical characteristics of plastics challenge the microbial degradation. Nevertheless, in nature several microorganisms significantly contribute to plastic biodegradation. Correspondingly, the importance of insects' gut microorganisms in biodegradation process cannot be neglected. Our review also highlights the vital role of pretreatment, either physical and/or chemical as a main step to enhance the degradation of all polymeric materials. Under this scope, it is necessary to cope with and possibly alter the polymer nature and composition before the biological treatment in order to apply suitable physicochemical pretreatment techniques, such as gamma- or UV-irradiation and chemical pretreatment using acidic or alkaline solutions. However, an effective environmentally friendly, economical and widely used plastic-degrading process is still unavailable and further investigation is needed to develop new technologies to degrade plastic wastes.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

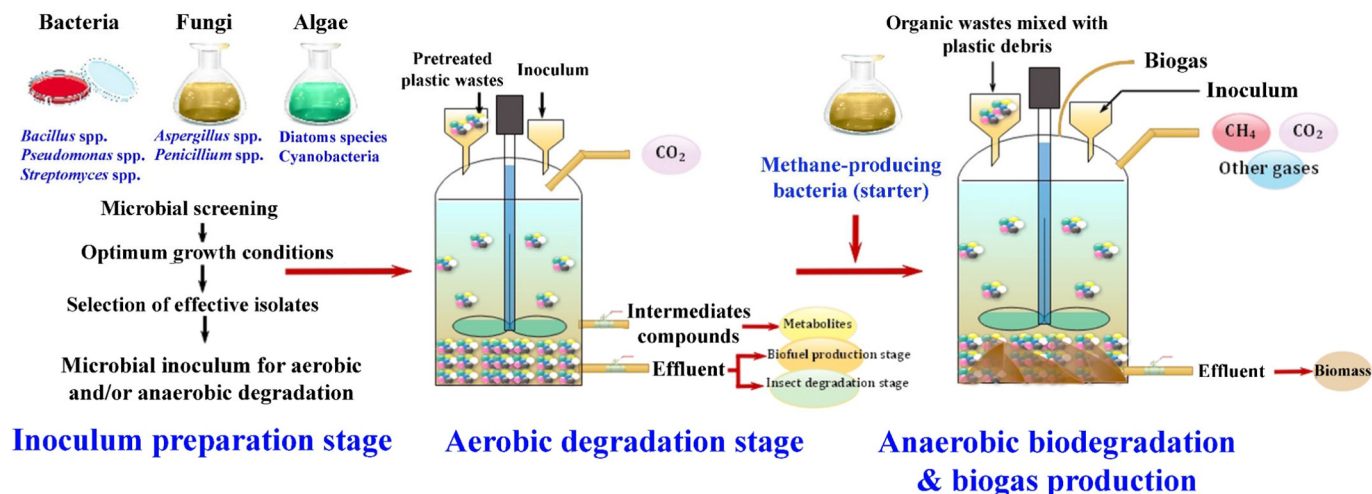


Fig. 11. Biogas production using anaerobic co-digestion of plastic and organic wastes.

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