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Environmental impact and mitigation of micro(nano)plastics pollution using green catalytic tools and green analytical methods

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ABSTRACT

The exponential utilization of plastics and their recalcitrant nature results in their extensive environmental accumulation, a pressing environmental problem that modern societies are currently facing. The presence of plastic waste in different environmental matrices can seriously affect life forms, ecosystems, and the economy. Furthermore, plastic wastes can break down into smaller pieces called microplastics (MPs) and nanoplastics (NPs), leading to new interactions with the environment and living organisms. Therefore, there is an urgent need to provide sustainable and cost-effective solutions for their mitigation. The first half of this review discusses the characteristics, sources, distribution, and adverse consequences of MPs and NPs. The latter half discusses mitigation strategies based on the utilization of enzymes as green catalytic tools. Enzymatic approaches outstand as effective sustainable strategies for microplastic degradation since plastic-degrading enzymes can specifically target the polymer structure for their further degradation. In addition, we have also discussed the novel approaches to enhance the performances and stability of natural enzymes including immobilization methods onto different materials and nanomaterials. Finally, possible key directions are also provided for future research considerations to find a practical, feasible, and environmentally friendly strategy to tackle the current crisis of plastic pollution.

1. Introduction

Plastics are polymeric materials used extensively due to their excellent physicochemical properties and industrial viability [1]. Approximately, 367 million tons of plastics were produced and distributed worldwide [2]. Plastics are low-cost, lightweight, versatile, durable, formable, corrosion, and heat-resistant materials that have contributed to the industrial development of society [3]. These plastics are categorized based on their physical and chemical properties into thermoplastics and thermosets that include polyvinyl chloride (PVC-U), polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephthalate (PET), and others [4]. Plastic is widely used in the food industry as a common material for food packaging; however more sustainable biodegradable alternatives have been reported to reduce the harmful effects of conventional polymeric substances [5]. Similarly, it has been reported the use of biodegradable polymers for different applications such as coating for fertilizers [6] and the preparation of membranes for biogas upgrading [7,8].

Despite its world usage and high value to economics, plastic has a slow degradation rate, which represents a serious social, environmental, and economic threat [9]. The lack of effective waste management, disposal measures, and sustainable recycling and elimination methods of plastic has led to its accumulation in the environment [3]. These issues and the unrestrained production and consumption of plastics contribute rapidly to climate change [10]. Greenhouse gas emissions occur at every stage of the plastic lifecycle (extraction, transportation, refining, and manufacturing), with estimations such as 1.7 gigatons of CO_2 in 2015 [11]. Furthermore, poor management and disposal of plastic have led to accumulation in ecosystem matrices such as oceans, landfills, and dumps. Marine plastic pollution destabilizes ecosystems and is detrimental to aquatic species and habitats [12], representing a major concern for

Abbreviations: COVID-19, Coronavirus disease 2019; FTIR, Fourier-transform infrared spectroscopy; GC-MS, Gas chromatography–mass spectrometry; GI, Gastrointestinal; HDPE, High-density polyethylene; LDPE, Low-density polyethylene; MNPs, Micro- and nano-plastics; MPs, Microplastics; NPs, Nanoplastics; PA, Polyamides; PAC, Polyacrylic; PE, Polyethylene; PET, Polyethylene terephthalate; PP, Polypropylene; PS, Polystyrene; PVC-U, Polyvinyl chloride; SEM, Scanning electron microscope.

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biodiversity. Large plastic entanglements for marine animals are widely reported, with registries of over 350 species entangled in plastic debris [13]. Almost 284 million metric tons of plastic garbage were generated in 2020 and it is estimated that 12000 million tons of plastic residues will be generated by 2050 [14]. This uncontrolled waste generation was notable during coronavirus disease 2019 (COVID-19) pandemic, with an overflow of plastic-based packaging and medical product responsible for a 44.8 and 13.2% increase in plastic waste [15].

During their degradation period, plastics lose their integrity and break down into smaller pieces and particles, raising another environmental concern. These tiny particles are called microplastics (MPs) and nanoplastics (NPs). The presence of micro and nanoplastics (MNPs) results in new interactions with the environment and living organisms. MPs are ingested by multiple organisms, from phytoplankton to higher tropic levels, including mammals, birds, and fish, increasing their toxic potential and impacting the biosphere [14]. MPs also have deep implications for terrestrial ecosystems. Terrestrial soils show toxicity and environmental effects due to the contamination of soil, flora, and fauna [16]. MPs are exposed to organisms such as earthworms, responsible for shaping the physical properties of soils, resulting in deep implications for the terrestrial ecosystems [17]. On the other hand, NPs represent a higher hazard due to their size range and permeability, allowing cells and tissues to enter more easily [16]. NPs such as polystyrene can produce DNA damage, mutagenesis, and cytotoxicity [18]. In contrast with MPs and macroplastics, the size of NPs penetrates the circulatory system of species such as juvenile carps, bursting biochemical responses, and tissue lessons [19].

The need for public awareness regarding MNPs is crucial, and remediation techniques are yet to be studied and implemented. Techniques to manage macroplastic debris have been established, such as recycling, incineration, bioremediation, and landfills [4]. Nonetheless, there is an opportunity area in remediation techniques for MNPs and new strategies need to be addressed to overcome their limitations. Some common remediation methods for MNPs include membrane technology, phytoremediation, biodegradation, biotechnology, and photocatalysis [18]. Physical processes such as membrane, disc, sand, or granulated filter technologies involve filtration, adsorption, or sedimentation of MNPs. These methods show high efficiency and can be used on a large scale with excellent results [18,20]. Biological degradation techniques are also suitable for treating MNPs waste due to their low energy input, eco-friendliness, and low carbon emission [21]. In these methods, invertebrates, and microorganisms such as bacteria, algae, and fungi break down MNPs' long carbon chains into simpler monomers through enzymatic degradation [22]. Biological catalysts or enzymes promote the biodegradation of complex plastic polymers into harmless end products, such as carbon dioxide, water, and biomass [23]. However, the efficiency of these plastic degrading enzymes is much lower than other remediation techniques and new green catalysts technologies need further exploration [22].

Understanding the characteristics, sources, pathways, environmental distribution, and harmful effects of MNPs is of great importance and the first approach to solving the scope of this environmental concern. At the same time, it is worth exploring contemporary and sustainable remediation techniques such as biodegradation which can mitigate MNPs pollution. Therefore, this review seeks to analyze the characteristics of micro and nano-plastics and present recent advances in green catalytic tools and enzymatic technologies for the degradation of plastic polluting particles.

2. Sources, characteristics, and distribution of micro- and nano-plastics

2.1. Classification, characteristics, and emission sources of micro- and nano-plastics

Microplastics are defined as plastics smaller than 5 mm in diameter. Fragmentation of MPs results in the formation NPs, which encompass sizes of 1–100 nm. MNPs are produced due to the low degradability rate of macroplastics and other weathering conditions and pathways (Fig. 1). During its lifetime, plastics encounter physical, chemical, and biological transformations that produce micro and nano-plastics, such as hydrolysis, photooxidation, chemical oxidation, thermal effects, and biodegradation [24].

MNPs can be divided into primary MNPs, which are processed plastic particles, and secondary MNPs, which are plastic debris that degrades from large pieces of plastics. Primary MNPs originate from plastic pellets and microbeads found in personal care products to function as film-forming agents, functionalized polymers, hydrophilic agents, and silicones [25]. When plastics enter the environment, they weaken due to exposure to UV radiation, weathering, and physical abrasion which eventually turns large pieces of debris into MNPs. For instance, MNPs are formed and released from the surface of the plastic through delamination, which occurs when the plastic interacts with wind, waves, and other abrasive interactions like exposure to salt [26,27]. Even mechanical recycling of plastic wastes unintentionally generates secondary MNPs, leading to a greater pollution emission to the aquatic environment [28]. In addition, the photodisintegration caused by intense UV radiation induces the oxidation of the polymeric matrix resulting in serious fragmentations [22]. These oxidative processes depend on environmental factors (e.g., UV exposure, temperature, soil composition, moisture) and plastic characteristics (e.g., chemical structure, morphology, crystallinity) [29].

Plastic chemical structures and stability will determine their pathway to the environment as MNPs. Plastics like PS, PET and PVC are least stable to photodegradation and outdoor wearing due to their atomic structure. PET is highly susceptible to biodegradation and has a more elevated chance of turning into MPs and NPs [26]. Physical characteristics such as shape, density, and composition of MNPs will determine the distribution in water bodies and terrestrial ecosystems [24]. MPs with a lower density than water bodies such as PE, PP, and expanded PS are more prone to appear on open water bodies (surface waters and shores) than more dense polymers such as PVC and PET; on the other hand, higher density MPs such as PVC and PET tend to rest in sediments, beaches, subsurface and deep-sea waters [26].

2.2. Occurrence of micro- and nano-plastics

The presence of MNPs has been identified in the hydrosphere, lithosphere, atmosphere, and biosphere. This includes all major rivers, oceans, and urban areas [14]. MNPs can be detected in most water bodies, sediments, and soils and are absorbed by different aquatic and terrestrial organisms [22]. Most studies regarding MNPs pollution are concentrated on aquatic environments [25,30]. Due to human industrialization and urbanization, plastic waste ends up in the marine environment through hydric cycles, urban waterways, sewage, and industrial wastewater connected to all oceans and coastal areas [14,31]. Consequently, MNPs are mostly distributed in all types of water bodies. According to recent studies, urban streams and glaciers have the highest concentrations of MPs among all water bodies as a result of transport processes that start in urban areas [32].

MNPs in water bodies are mainly composed of types of plastic such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVU-CU), which can be detected on coastal water bodies such as beaches and rivers and deep-water bodies such as oceans, reefs, and lakes. However, MNPs can be found throughout aquatic environments all around the world, with different compositions and particle sizes across various recent studies (Table 1) [33–37]. For example, during a recent study conducted during an Antarctic expedition, concentrations with an average of 0.10 ± 0.14 and 1.66 ± 1.20 items/m^3 were detected in surface and subsurface water samples respectively [33]. MNPs are likely to have existed for a long time on these waters, which is attributed to the accumulation of particles during snow depositions with limitations to be washed off [32]. These samples contained varied com-

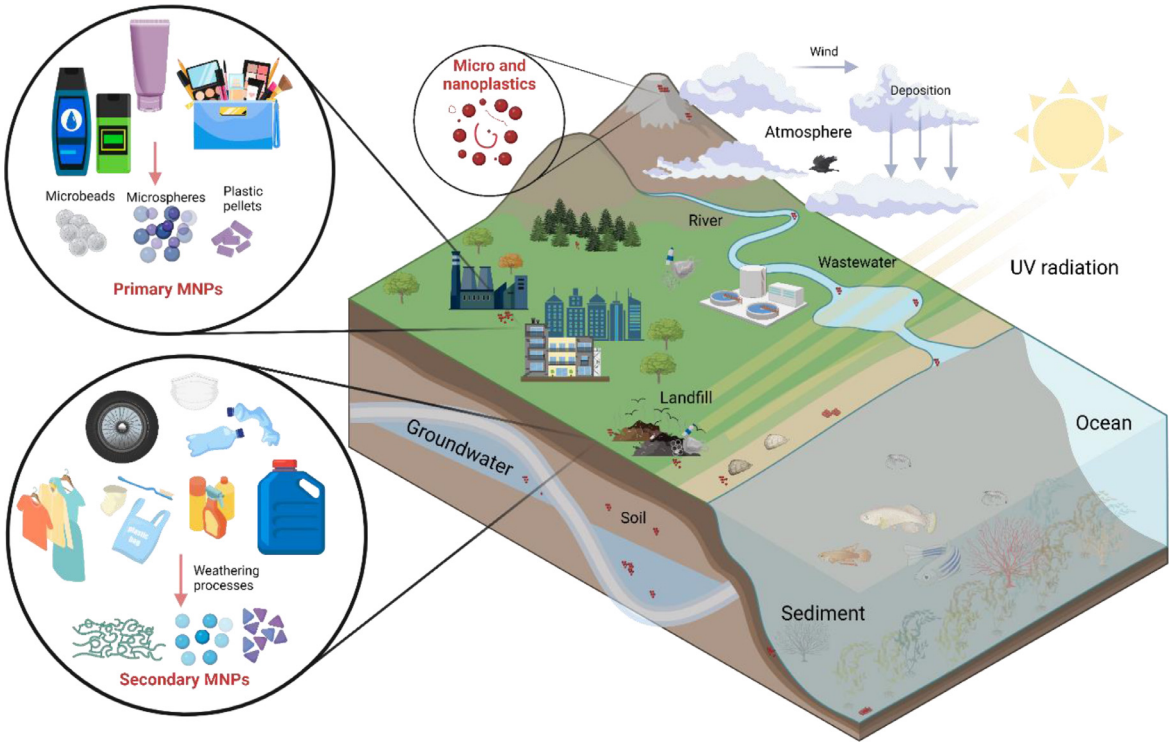

Fig. 1. Sources of micro(nano)plastics waste and their pathway to the environment. Created with BioRender.com and extracted under premium membership.

Table 1
Occurrence of micro(nano)plastics in aquatic environments.

Location	Sample type	Concentration	Plastic size range	Composition	Ref.
Antarctica	Surface waters	0.10 ± 0.14 particles/m^3	0.18–4.97 mm	PET, PP, PE, AC	[33]
Antarctica	Subsurface	1.69 ± 1.21 particles/m^3	0.14–4.99 mm	PP, PET, PE, PAN, PS, PA, PVC	[33]
Caspian Sea, Iran	River	40 – 460 particles kg^{-1}	200–5000 μm	PP, PA, PS	[34]
Zhuhai, China	Seawater	10.00 ± 27.50 particles/L	101–500 μm	PE, PP, PS, PVC	[36]
Faafu Atoll, Maldives	Reef	0.26 particles/m^3	50 μm – 1 mm	PE, PET, PVC	[35]
Fuerteventura, Spain	Wastewater	4.4–40 items/L	200–400 μm	PES, PP, PE	[37]

Abbreviations: PE (Polyethylene); PP (Polypropylene); PS (Polystyrene); PAC (Polyacrylic); PVC-U (Polyvinyl chloride); PET (Polyethylene terephthalate).

positions that included PET, PE, and PP in their majority. Furthermore, studies have been conducted on the occurrence of MNPs in freshwater on continental landmasses and transitional ecosystems. These types of water bodies are the source of plastic particles in marine ecosystems. For example, ding a study on the Qarasu River in Iran, samples were performed to study the excess of MPs near pollution sources [34]. The mean abundance of MPs of 10 sampling stations was 40 – 460 particles/kg, ranging from 200 to 5000 μm. There was a high occurrence of plastic fibers and particles composed of PP, PE, and PA.

New information regarding MNPs, and marine wildlife has also been found. MNPs may deeply affect marine fauna from zooplankton, invertebrates, and larval fish to sea turtles, marine birds, and bigger fish species [18]. Therefore, studies of marine ecosystems are crucial and coral reefs are valuable sample locations. In a study conducted in a Maldivian coral reef in Faafu Atoll, samples were collected from sediments and seawater samples. Despite the remote location from local urbanization, an average concentration of 0.26 particles/m^3 was found [35]. Another study was conducted to investigate MPs in seawater and oysters along the coastline of Zhuhai, China. This study showed the relation between the presence of MPs and their harmful effects on the aquatic fauna. The abundance of MPs was in the range of 0.14–7.90 particles/g and 10–27.50 particles/L in seawater [36]. The analysis of marine species and water samples is a promising form of study to determine the level of pollution in different aquatic environments.

Pollution in agroecosystems with MNPs is also of great interest due to the alteration of biological, chemical, and physical processes and soil ecosystems caused by MNPs. The use of wastewater, sewage sludge, and biosolids in agriculture leads to a high microplastic loading [29,37]. One of the latest contributions to these studies was performed by Pérez-Reverón et al. [37] who studied wastewater and soil samples on the volcanic island of Fuerteventura in Spain. After the physicochemical analysis of the wastewater samples, different MPs, such as fibers, fragments, microbeads, and films were found, establishing a relationship between MPs and wastewater irrigated soils.

2.3. Environmental distribution of micro- and nano-plastics

The environmental distribution of MNPs is influenced by many ecosystem components and transporting agents. The degree of MNPs pollution is distributed between environmental systems such as air, soil, sediments, marine water, and freshwater [38]. MNPs have spread around the world's oceans, from surface water to deep trenches. Freshwater is also a source of MNPs, as it functions as the transport medium to all types of marine ecosystems (lakes, rivers, oceans). Tons of MNPs circulate in the atmosphere, allowing them to reach distant locations such as mountains, plateaus, polar regions, and even the troposphere [3].

MNPs are accumulated in the soil, and they persist affecting biodiversity and organisms. Plastic particles are distributed from farmlands, landfills, littering, atmospheric deposition, and surface runoff to soil ecosystems [39]. Leachate and landfills are important sources of MNPs with a high abundance of MNPs in many samples. About 99.4% of MPs in landfill sites are related to plastic waste buried in landfills [40]. Other inputs such as agricultural, urban, recreational, and industrial land contribute significantly to MNPs loads in soils and other ecosystems such as freshwater bodies and oceans [16]. Once MNPs enter the surface soil, they can migrate to lower and deeper soils through leaching, bioturbation, dry-wet cycles, root water movements, and agricultural activities [3].

Plastic debris transported from land sources enter the ocean. Land-based debris contributes 80% of ocean plastic waste with MNPs distributed around shorelines, beaches, bottom sediments, and seawater [39]. Accumulation of plastic particles has been detected in the open ocean from the Atlantic and the Pacific Ocean and the Caribbean and Mediterranean Sea [38]. It is estimated that 4.85 trillion microplastics are accumulated on the global ocean surface [3]. Wastewater is a distribution source for MNPs and most importantly for NPs. Wastewater treatment plants receive tons of waste from municipal, industrial, domestic, and stormwater sources. These wastes are not correctly treated before they are released into fresh and sea water bodies. Not all NPs are removed efficiently at wastewater treatment stages, so they pass through and may be released into marine environments [41].

Atmospheric transport is another form of distribution of MNPs that can pose a threat to fragile areas and ecosystems due to its versatility. Human-linked activities like road traffic, vehicle movement, tire friction, and road surface are major sources of atmospheric MNPs [14]. At the same time, MNPs' abundance is dependent on meteorological factors and dry and wet depositions that cause long-range dispersion and transport to the surrounding environments [3]. Microplastics suspended in the air could represent a serious human health issue and detections of MNPs in the atmosphere of metropolitan areas show very high concentrations. For instance, an annual estimation of 120.7 kg of MPs is suspended through Shanghai air currents [16]. MNPs have also been found during interactions between the atmosphere and other interfaces, such as glacial, snow, or urban dust. High concentrations of MPs have been found in the Arctic and European snow with ranges from 0 to 154,000 particles/L [25].

3. Harmful effects of micro- and nano-plastics

MNPs on the different ecosystems, such as water, air, and land, has received attention from the scientific community because their persistence can cause serious harmful effects to the environment and human health directly and indirectly (Fig. 2).

3.1. Effects on the environment

The main sources of MNPs in the ocean are river transportation and coastal discharge. Lately, atmospheric deposition seems to be a potential source of MNPS as well. Over the years, it has been estimated that freshwater transports between 70% and 80% of MNPs from the terrestrial to the marine environment [42]. On the surface of water bodies, MNPs can become habitats for viruses and bacteria due to their low density, easy suspension, and strong hydrophobicity. When MNPS accumulate microbial populations, they form microbial films that later transfer to the deep ocean. Several studies analyze the ecological toxicity of MNPs that are frequently ingested by marine organisms. A study on crustaceans from China demonstrated that the ingestion of these MNPs can cause severe risks including acute poisoning symptoms, endocrine disruption, and reproductive toxicity [43,44]. Bivalves, including oysters, clams, shellfish, and mussels, have also been used as research models because they are a key food source for humans and the food they ingest goes directly to their digestive system. Studies on a group of blue mussel larvae exposed to MNPs showed that their growth was not affected but developed abnormal and malformed. Another investigation reported that oysters at an exposure of 50 nm NPs decrease their fertilization rates and embryo-larval development. Freshwater organisms also have attracted substantial interest since humans have much more contact with this environment. Diverse research has reported the influence of MNPs on their growth, development, and behavior. A study exposed Zebrafish (*Danio rerio*) to all four common MNPs, such as polyamides (PA), PE, PP, and PVC and the results revealed intestinal damage and splitting of enterocytes [44]. Plastic particles with color are commonly used to increase the attractiveness and longevity of plastics. Numerous studies on colored MNPs proved that specific colors are more ingested by specific marine organisms. For example, blue-colored PP and PE MNPs were the most common color found in the stomachs of bluegill (*Lepomismacrochirus*) and longear sunfish (*Lepomis megalotis*). White and uncolored MNPs were mostly found in Asian clams (*Corbicula fluminea*). This ingestion of MNPs caused adverse effects that inevitably lead to a decrease in their growth and reproduction, such as blocked digestive tracts, lacerations, inflammatory responses, respiration problems, false sense of satiation or/and deficient predator avoidance [42].

MNPs are released into the atmosphere by several sources, such as synthetic textiles (e.g., clothing, furnishings, carpeting), abrasion of materials, and resuspension of MNPs from waste, landfills, and emissions [45,46]. Due to their small size and low density, plastic particles can easily be suspended in the air. Thus, they perform as good carriers of different organic pollutants in the air and transport them over long distances, followed by their wet or dry deposition on oceans, freshwater systems, and land [16,44]. Comparing this migration process of MNPs to aquatic transportation, airborne transportation has fewer topographic limitations. Airborne MNPs are easily transported in multiple directions and exhibit a long persistence. Recently, a trajectory analysis indicated that approximately 218 MPs are transported for a distance up to 95 km. An estimation of the standard daily average MPs fallout in Greater Paris reported 118 particles/m^2 per day. An evaluation of Shanghai's air reported an amount of transportation of 120.7 kg of suspended MPs per year. A research group reported a count of 44 fibers, 249 fragments, and 73 films m^{-2} deposited per day in the pristine French Pyrenees catchment. Another study revealed an important amount transported via the atmosphere and deposited via wet deposition on the Arctic and European snow of 0–14.4 $\times$ 10^3 N liter^{-1} and 0.19 $\times$ 10^3 0.19 $\times$ 10^3–154 $\times$ 10^3 N liter^{-1} $\times$ 10^3 N liter^{-1}, respectively [16]. In addition, evidence has proved the presence of MNPs in high elevated glaciers of the Tibetan Plateau. Although outdoor exposures are a major issue, indoor exposure measures revealed daily deposition rates of 1600 – 11000 microfibers/mm^2, depending on the indoor type and lifestyle [46].

MNPs, as a result of fragmentation of plastic due to temperature and photo-oxidation, contaminates soil by penetrating soil layers and mainly come from different sources including recycling of sludge, wastewater irrigation, fertilizers, landfilling, biosolids, or other [44,45]. Recently, the amount of MNPs that are transferred to soil exceeds the amount of MNPs present in the ocean. The presence of MNPs affects the physicochemical properties of the soil such as porosity, soil structure, water holding capacity, soil bulk, and others. A study revealed that PP MNPs stimulate enzyme activity and increase the amount of dissolved organic carbon, nitrogen, and phosphorus. A similar study reported that PE and PVC-U reduce the diversity of the bacterial community and increase the activity of urease and phosphatase. Another research also proved that LDPE affects the microbial communities depending on the exposure time. MNPs also influence the physiological activities of organisms in the soil habitat and reflect in growth inhibition and damage to the intestinal and immune systems, among other adverse effects. Scientists found that nematodes easily ingest MNPs and accumulate them in the middle and then in other parts of the gut. Also, evidence showed that earthworms exposed to 0.2–1.2% of PE MPs suffer from inhibition in their growth and die when exposed to a concentration of 1–2%. In addi-

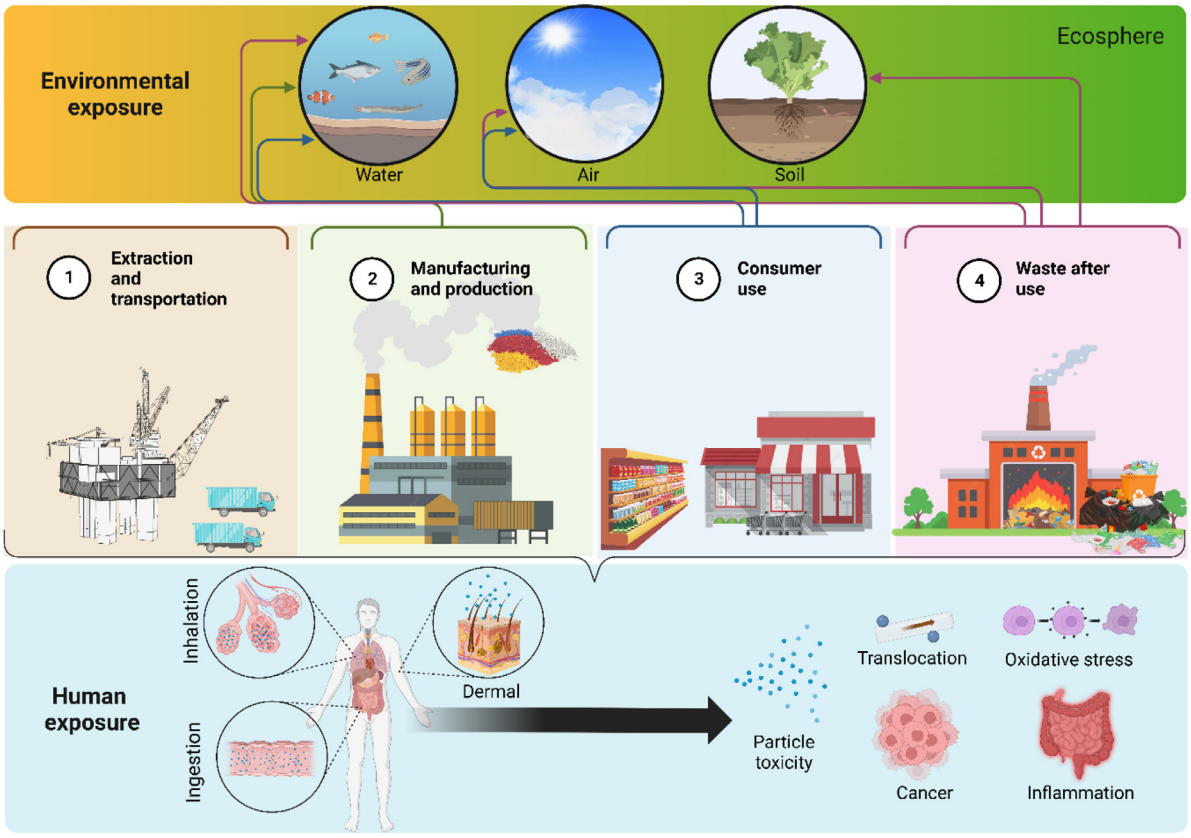

Fig. 2. Harmful effects of plastics on the environment and human health across their life cycle. Created with BioRender.com and extracted under premium membership.

tion, MNPs affect plant growth and germination, interfering with plant roots' uptake of water and nutrient [44].

To get a better perspective on the impact of MNPs pollution there are some key parameters to focus on. MNPs with a smaller size show a greater biological impact than those have a larger size. Similarly, the shape is also a key factor, irregular particles seem to induce more physical impact in comparison to round particles. Finally, concentration has substantial importance in toxicological studies since in vivo and in vitro research uses higher concentrations of MNPs than those that are in the environment [16]. However, the distribution of MNPs on all components of the environment and the harmful effects on living organisms need to be further studied to accurately estimate the impact of MNPs pollution.

3.2. *Effects on human health*

Humans are constantly exposed to sources of MNPs, including food, medicine, clothing, dust, and cosmetics [47]. Three primary entry routes contribute to the total amount of MNPs present in the human body: Ingestion, inhalation, and skin contact. Recently, direct ingestion of plastic particles, especially PET, PS, and PP MNPs, has gained substantial scientific and public attention because it is the most significant way in which humans consume MNPs [25,48]. An estimation of the number of MNPs consumed from the average intake of food revealed that the average annual consumption is in the range of 39 000 to 52 000 particles and including a water intake from a bottled source and tap water, one person could be ingesting 90 000 particles and 40 000 particles per year, respectively [49]. A recent study analyzed water samples from popular brands of mineral bottled water and showed that nine of the eleven brands investigated contained different amounts of MNPs [50]. Similar studies have also shown direct ingestion of MNPs via the consumption of alcohol, salt, sugar, honey, milk, and other food or drink items regularly consumed by humans [25,51]. An extensive and increasing body of evidence suggests that MNPs end in diverse consumed items via animals ingesting MNPs in the environment, contamination during production, and/or plastic packaging [49]. Plastic particles can reach the gastrointestinal system through contaminated food products or after inhalation through mucociliary clearance, a mechanism that involves the movement of particles from the respiratory system. Consequently, several biological responses can be observed, such as inflammation, increased permeability, and a change in the gut microbe composition and metabolism [47]. After ingestion, particles could be absorbed through phagocytosis or endocytosis and infiltrate the microfold cells (M-cells) in the Peyer's patches. Many negative health concerns derive from the absorption of MNPs, such as particle toxicity, chemical toxicity, and the introduction of pathogens and parasite vectors. The interaction between NPs and molecules within the gastrointestinal (GI) tract, such as proteins, lipids, carbohydrates, nucleic acids, ions, and water, results in the encompass of NPs by a collection of proteins known as a 'corona'. PS NPs may develop in different forms of complex coronas, depending on the conditions they are in. Additionally, studies have demonstrated that protein corona changes within an in vitro model representing human digestion, improving the translocation of NPs [48]. The same mechanisms could apply to MPs as their translocation to the circulatory system after ingestion has been proved in vivo [47]. However, the risk of direct ingesting MNPs is not entirely known since there is very little research reported. Most use PS nanoparticle models, excluding other main polymeric materials present in the environment.

The second major route of human exposure to MNPs is via inhalation. Plastic particles in the atmosphere are in direct and continuous contact with humans. An evaluation of MPs in the air estimated an individual inhalation of 26–130 airborne MPs per day [47]. Even though some MNPs inhaled may be removed by immune mechanisms such as sneezing, cilia

floating, etc., the small-sized fibers are extremely difficult to remove due to their high surface area and high penetration potential [42,44]. In addition, the pollutants act as oxidants, causing oxidative stress, inflammation, and carcinogenesis [51]. A large body of evidence proves that synthetic textile workers that are constantly exposed to small plastic fibers, such as nylon, PS, PE, and PP, are more susceptible to developing respiratory diseases and lung cancer. The risk of cancer is related to chronic pulmonary inflammation and oxidative stress [42]. Through inhalation, MNPs may end up embedded deep into the lungs and stay on the alveolar resulting in lung damage. The alveolar surface area of the lungs measures approximately 150 m^2 and has a thin tissue barrier that allows NPs to permeate through it, proving that they can translocate across different body parts. However, the absorption of plastic particles in the lungs depends on several factors such as hydrophobicity, surface charge and functionalization, surrounding protein coronas, and particle size.

Dermal exposure is likely to be considered the least significant route of exposure. The potentially harmful effects of MNPs are related to the constant dermal exposure to plastic particles, such as dust, synthetic fibers, and microbeads in cosmetics. The stratum corneum is the outermost layer of the epidermis that protects the skin forming a barrier against injuries, chemicals, and microbial agents. Considering MNPs are hydrophobic, the absorption of contaminated water through the stratum corneum is not expected. However, MNPs could enter the body through hair follicles, skin wounds, or sweat glands [48]. If the skin is damaged by UV rays or small tears, MNPs may be able to penetrate the skin barrier. Studies have also shown that medical devices implanted in the human body, including PE articulating spacers, cosmetic and dental implants, etc., also allow MNPs particle production and their posterior translocation to other parts of the body [42]. In addition, research has reported that human epithelial cells can also suffer oxidative stress from exposure to MNPs. It is worth noting that there is still a lack of data on the direct human health implications and more research should be done in the future to fully understand the impact of MNPs on the human body [16].

4. Enzymes in microplastic degradation

The enzymatic degradation consists of the use of enzymes as natural biocatalysts to break down complex organic compounds such as plastic polymers into smaller units. The resulted products are considered more benign for the environment, such as water, carbon dioxide, and biomass [23]. The enzymatic degradation can be experimentally detected through different strategies such as visual observation, plastic properties modifications, weight reduction, carbon dioxide evolution, and chromatography, among others [52].

Plastic-degrading enzymes have been discovered in microorganisms; more than 90 microorganisms, including fungi and bacteria, have demonstrated abilities to degrade plastic wastes in vitro environments [53]. Considering the huge abundance of MPs and NPs in the environment and the prodigious metabolic and genetic diversity of microbial communities, different microorganisms have developed capacities in plastic utilization. It is assumed that the plastic-degrading enzymes identified to date are only a fraction of the enzymes involved in the degradation of plastics. Thus, the research community has shown increasing interest in the discovery of new plastic-degrading enzymes, using metagenomics as a tool with great potential for this purpose [54]. The typical procedure to identify plastic-degrading enzymes follows a culture-based approach, where target microorganisms are grown from environmental samples and then screened for a specific activity.

Two main categories of plastic-degrading enzymes are actively implicated in the biodegradation of polymer structures: extracellular and intracellular enzymes [23,55]. Different activities have been ascribed to each type of enzyme. The extracellular enzymes have been more widely studied for plastic biodegradation, showing a wide variety of functions like oxidative and hydrolytic activities. Their main role in plastic degradation is during the depolymerization process, which consists of breaking down the long carbon chains presented in complex polymers into short polymer intermediates. The resultant smaller molecules (oligomers, dimers, or monomers) can access the semi-permeable outer membranes and be used as carbon sources by microbial cells to release carbon dioxide [23,53]. The decrease in the molecular weight of the polymeric structure is a critical process during the degradation; smaller molecules are more easily transported through the cell membrane, and they are suitable substrates for some enzymes than can only act on smaller molecules.

Lipases, proteases, and cellulases are some examples of extracellular hydrolase enzymes involved in breaking down long-chain polymers into smaller molecules. In general, these enzymes cause hydrolytic cleavage of the long chains forming smaller units that are easier to transport and assimilate into the cell for subsequent enzymatic degradation and ultimately the release of environmentally harmless products [56]. For instance, three hydrolases presented in *Flavobacterium* strains were found responsible for the degradation of nylon [57]. Similarly, Shah et al. [58] reported *Bacillus subtilis* MZA-75 as a polyurethane degrading bacteri isolated from soil. Extracellular and cell-associated esterases were employed to utilize polyurethane as a carbon source. MPs degradation was demonstrated through different techniques including FTIR, SEM, and GC-MS. Although evidence of mineralization of ester hydrolysis products into carbon dioxide and water was presented, further studies were suggested to exactly define the biodegradation mechanism for its effective employment in waste management [58]. Esterases have been widely explored in plastic degradation since they can hydrolyze esters presented in the polymeric structure or produced during previous oxidation reactions [59].

Glycoside hydrolases have also been associated with MPs degradation; Yoshida et al. [60] isolated *Ideonella sakaiensis* 201-F6, a novel bacterium able to use poly(ethylene terephthalate) as carbon and energy source. Two enzymes were responsible for hydrolyzing poly(ethylene terephthalate) and producing ethylene glycol and terephthalic acid, monomers that are safer for the environment [60]. More recently, Elsayed and Kim [61] performed lab-scale experiments to measure the kinetic constants for the degradation of high-density polyethylene using lipase, cellulase, and protease. Different experimental conditions were evaluated such as temperature and enzyme concentration. The authors concluded that degradation was mainly caused by the surface's rapid destruction and the polymer's shape by its collision with enzymes. Among the enzymes tested, protease was the most efficient, whereas lipase showed the lowest efficiency. However, regardless of the hydrolase used, increasing the enzyme concentration and higher temperatures led to enhanced degradation performances. The enhanced degradation of polyethylene under thermophilic temperatures and higher doses of enzymes are associated with an increase in collisions between the polymer and the enzymes [61].

Overall, hydrolases have demonstrated an active role in the degradation of MPs presented in wastewater through their effective catalytic reactions. Current microbial degradation processes are slow or ineffective for complete plastic degradation. Moreover, petroleum-based plastic usually possesses chemical and physical properties that provide higher resistance to enzymatic degradation, hindering the action of naturally occurring plastic-degrading enzymes. However, the extraction and manipulation of microbial enzymes are considered a valuable approach for improving the degradation performance, being currently an important research area [56,62]. Typically, microorganisms with plastic-degrading capacities are grown in a plastic-rich media and isolated for taxonomic identification. Enzymes are then extracted from the cultured microorganisms and subjected to plastic degradation experiments. Finally, techniques like mass-spectrometry can be useful to determine the sequence of the plastic-degrading enzyme and biochemical assays to determine the optimal conditions and specificity [52]. In this manner, the identification of plastic-degrading enzymes requires molecular biology and biochemistry.

The catalytic efficiency of plastic-degrading enzymes can be enhanced through protein engineering, which is a recently emerging research area. Different strategies to maximize depolymerization efficiency have been explored such as: improving the enzyme thermostability, strengthening the binding of the substrate to the active site of the enzyme, enhancing the interaction substrate-enzyme, reducing the effect of inhibitory products/intermediates, and combining different enzymes to form bifunctional catalysts, among others. In this respect, Zhu et al. [54] have successfully summarized the most recent advances in protein engineering applied to plastic-degrading enzymes. The evolution of this research topic might lead to great improvements in the utilization of microorganisms as a sustainable waste-management solution.

Another innovative method to remove MPs and NPs consists of the immobilization of enzymes on functional supports including different nano-scaled materials. This might result in greater efficiencies and advantageous features associated with recyclability. Different nanoparticle-enzyme complexes can be formed with variations in their properties and performance. In this context, inorganic nanoparticles have demonstrated great potential as enzyme support due to their high surface area and well-defined pore distribution and geometry, which in turn allow higher enzyme loadings [23]. Recently, Schaminger et al. [63] immobilized a PET-degrading enzyme (PETase) on superparamagnetic iron oxide nanoparticles. The immobilization was performed via His-tag increasing enzyme stability and allowing high loads of PETase. Immobilization on magnetic support enabled a simple magnetically recovery. Moreover, reusability tests suggested that the catalytic system maintained approximately 50% of the initial catalytic activity after 10 cycles [63]. Similarly, Jia et al. [64] immobilized PETase enzyme derived from *Ideonella sakaiensis* onto cobaltous phosphate nanoparticles. Their results demonstrated that using nanostructures as supports favored the stability of the enzyme; the immobilized enzyme exhibited 75% of the initial efficiency after 12 days, which was much higher than the one presented by the free enzyme. The remarkable better stability and performance towards the degradation of PET by the immobilized enzyme system was attributed to the unique nanostructure (nanoflowers) of the support [64].

Different enzymes have been also immobilized on inorganic nanostructures. For instance, Krakor et al. [65] immobilized lipase and cutinase on SiO_2 nanoparticles and Fe_3O_4@SiO_2 nanostructures via covalent bonding. The prepared catalytic systems showed high stability and efficiency to degrade polycaprolactone. On the other hand, carbon-based materials have also presented potential as support for plastic-degrading enzymes. Hegde and Veeranki [66] immobilized two recombinant cutinases on chitosan beads due to the abundant and biocompatible nature of chitosan. Immobilization was performed through covalently coupling with glutaraldehyde, showing more than 70% of immobilization under optimal conditions. Moreover, reusability tests after 10 cycles showed 80% of efficiency, demonstrating chitosan as a candidate to assist in enzymatic catalysis [66].

Carbon-based nanomaterials are receiving increased research interest because of their additional benefits including higher surface area, easy surface modification, and stability. In this respect, carbon nanotubes have been explored to attach different enzymes aimed to degrade different pollutants such as dyes [67,68]. Fewer studies related to immobilized enzymes on carbon-based nanomaterials were found. As a representative example, Costa et al. [69] evaluated the degradation of 4-methoxyphenol used as a plastic additive by immobilizing laccase on functionalized multi-walled carbon nanotubes. Carbon nanotubes were modified using different strategies to increase the immobilization efficiency; the best results were obtained from carbon nanotubes oxidized with nitric acid due to the higher content of surface groups containing oxygen. Under optimal conditions, the laccase-carbon nanotubes complexes showed excellent immobilization efficiency (100%) and stability at high temperatures.

5. Analytical methods to analyze MNPs

For proper mitigation of MNPs from different environmental matrices, highly effective and robust analytical-based detection methods are of supreme interest. Classically, the firsthand identification and quantification of plastic-contents persistence in water bodies is done by visual inspection for MPs [70], which sometimes fails to detect MNPs. Thus, it is important to establish and follow biotechnological advances to identify and characterize plastic-contents persistence at nanoscale to monitor MNPs at large and NPs, in particular. There are several steps involved prior to reach the detection of MNPs, for instance, (a) sampling, (b) extraction and/or cleanup, and (c) determination [71, 72]. Owing to the diverse variations, such as sampling matrices, MNPs occurrence level, sample preconditioning and/or pretreatment, detective tools, several in-practice analytical methods are not coherent in their handling and detection mechanisms. However, all chemical and physical detection methods share the basic handling measures and characteristic procedures with the same central skeleton. Considering the above-mentioned variations, results also vary in each adopted method. Fig. 3 shows a fundamental overview of different sampling routes, treatment, and detection procedures [71]. Various techniques, including visual detection though microscopy (light), SEM, FTIR, Raman spectroscopy, atomic force microscopy based infrared spectroscopy, flow cytometry, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, GC-MS, and others have been thoroughly reviewed elsewhere [71–76].

6. Current challenges and recommendations

Biodegradation occurs through complex pathways in which a large number of factors are involved including the availability of substrates and some characteristics of the polymer structures such as their physicochemical properties, morphology, types of bonds, and molecular weight, among others [62]. The variables increase when immobilized enzymes perform biodegradation due to the interaction with inorganic or carbon-based nanoparticles. In this context, there is a limited understanding of the degradation mechanisms involved, which represents a current barrier that hinders the full potential.

Immobilized enzymes on different materials represent great opportunities to enhance stability and reusability without compromising efficiency. Thus, the immobilization concept has attracted huge research interest for decades, which has recently been extended to nanomaterials [65]. The advantages of nanomaterials over their bulk counterparts include higher surface areas, unique properties related to their shape/size, and ease of surface modification. However, the immobilized enzymes require complex and careful synthesis procedures to achieve high immobilization efficiencies. In this context, research focused on a technical, energy, and environmental assessment of the degradation of MP and NP by this type of system should be performed to prove its feasibility.

As biological catalysts, enzymes have exhibited good performances in the degradation of various types of pollutants; however, their full potential still has significant limitations including structural instability, chemical sensitivity, and high-cost manufacturing and storage. In this context, engineered nanomaterials termed “nanozymes” have been developed aimed to act as artificial enzymes with improved catalytic stability, ease of modification, and cost-effective processes [77]. Different nanozyme-based systems have been developed and employed for the degradation of various pollutants, including dyes, endocrine-disrupting chemicals, pesticides, and phenolic pollutants [78–81]. In contrast to emerging pollutants, there is much less information about nanozymes for the degradation of MP or NP. In this manner, a natural progression of this research field is to explore the applicability of artificial enzymes to overcome the limitations of natural enzymes.

Furthermore, optimization processes should be considered to ensure wider experimental conditions in terms of efficiency, robustness, and recyclability. The chemical composition of plastics should also be considered; commercial plastics usually contain small molecules used as

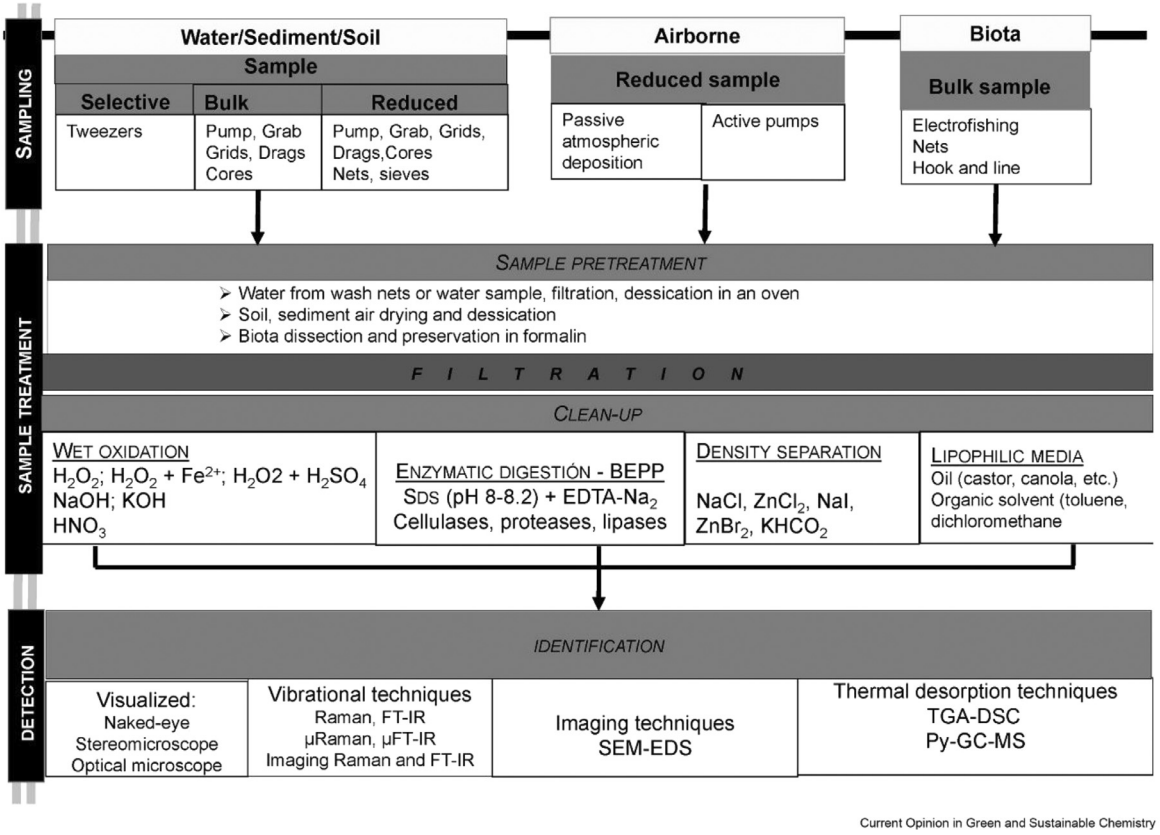

Fig. 3. Summary of the analytical procedures to determine MPs and NPs. BEPP, basic enzymatic purification protocol; EDS, energy-dispersive X-ray spectroscopy; EDTA, ethylenediaminetetraacetic acid; FT-IR, Fourier-transform infrared; MP, microplastic; NP, nanoplastic; SDS, sodium dodecyl sulfate; SEM, scanning electron microscopy; TGA–DSC, thermogravimetric analysis coupled to differential scanning calorimetry. Reprinted from Ref. [71] with permission from Elsevier under the terms of the Creative Commons CC-BY license.

additives that might obstruct the in-depth understanding of the plastic degradation mechanisms [23]. Similarly, the complex nature of wastewater samples should be considered since other co-existing contaminants are typically presented in addition to MP and NP.

The identification of plastic-degrading enzymes has been dominated by culture-based approaches. It possesses advantageous features such as the possibility to identify several enzymes with a key role in the plastic degradation activity from a selected microorganism. However, those approaches follow tedious procedures and a great fraction of bacteria do not have cultured representatives [52]. Currently, large datasets can be efficiently analyzed due to the development of computational tools and technological advances. Powerful techniques are emerging to facilitate the identification of new enzymes for biotechnological applications. For example, stable-isotope probing, metatranscriptomics, and metaproteomics might have great potential; however, their exploration for the discovery of plastic-degrading enzymes is still rare. In addition, challenges related to high costs must also be considered. Some technical challenges could also occur, which should be addressed with an interdisciplinary approach involving experts in different areas like microbiology, computational biology, and polymer degradation.

Genetic engineering approaches to create genetically engineered microorganisms and enzymes are considered is one of the preferred strategies to enhance the biodegradation of petroleum-based plastic wastes. However, it is important to perform an ecological risk assessment for their real-world applications since the mechanisms considering toxic chemicals, interactions, pH variations, and polymer composition are rarely described.

7. Conclusion

Plastic has positively impacted our lives due to its advantageous features like versatility, affordability, and resistivity, which are highly desired for various products and packaging. The important role that plastic has played has led to an almost continuous increase in its production –and subsequent disposal– for several decades. This increase was further intensified during the COVID-19 pandemic caused by the usage of plastic-based medical products and packaging. However, plastic can cause serious problems to the ecosystem if its disposal is improperly managed. Moreover, plastics can break down into MPs and NPs during their degradation process; thus, environmental accumulation of those emerging pollutants might occur in oceans, rivers, lakes, and other matrices leading to new interactions with the environment and living organisms. In conclusion, we have described their main sources, characteristics, occurrence, and harmful effects on both the environment and the human population. Furthermore, we have discussed different enzyme-based methods as green analytical tools for their sustainable mitigation, including innovative approaches like immobilized enzymes onto inorganic and carbon-based nanostructures. Finally, several current challenges were identified to propose recommendations for further research. In this manner, genetic engineering and the development of novel nanozymes might represent great opportunities and future potential for the effective degradation of microplastics and nanoplastics.

Declaration of Competing Interest

The authors declare no conflict of interest.

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