

Review

# Enzymatic Degradation and Advanced Methods for Microplastic Removal

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## Abstract

Microplastic (MP) pollution has become a global environmental crisis, adversely affecting ecosystems, aquatic life, and human health. Addressing this issue requires a multifaceted approach that combines physical, chemical, and biological strategies. Physical methods, such as filtration and sedimentation, offer straightforward solutions but are often inefficient at removing small-sized MPs. Chemical approaches, including advanced oxidation processes (AOPs) and photodegradation, enable the breakdown of MPs into smaller, less toxic fragments; however, the associated high energy requirements and potential for secondary pollution remain significant limitations. Biological methods, particularly enzymatic degradation, offer an eco-friendly solution by converting MPs into biodegradable monomers, although further optimization is needed for large-scale implementation. This review focuses on advanced technologies for MP mitigation, particularly the synergistic integration of physical, chemical, and biological strategies. Among these, metal–organic frameworks (MOFs) have emerged as a groundbreaking solution due to the associated high surface area, tunable porosity, and chemical functionality, which together enable selective adsorption and capture of MPs from complex water matrices. By addressing the limitations of existing methods, this integrated approach improves the efficiency and sustainability of MP removal, thereby contributing to global environmental restoration and advancing remediation technologies.

**Keywords:** chemical techniques; enzymatic degradation; MP adsorption; metal–organic frameworks; physical techniques

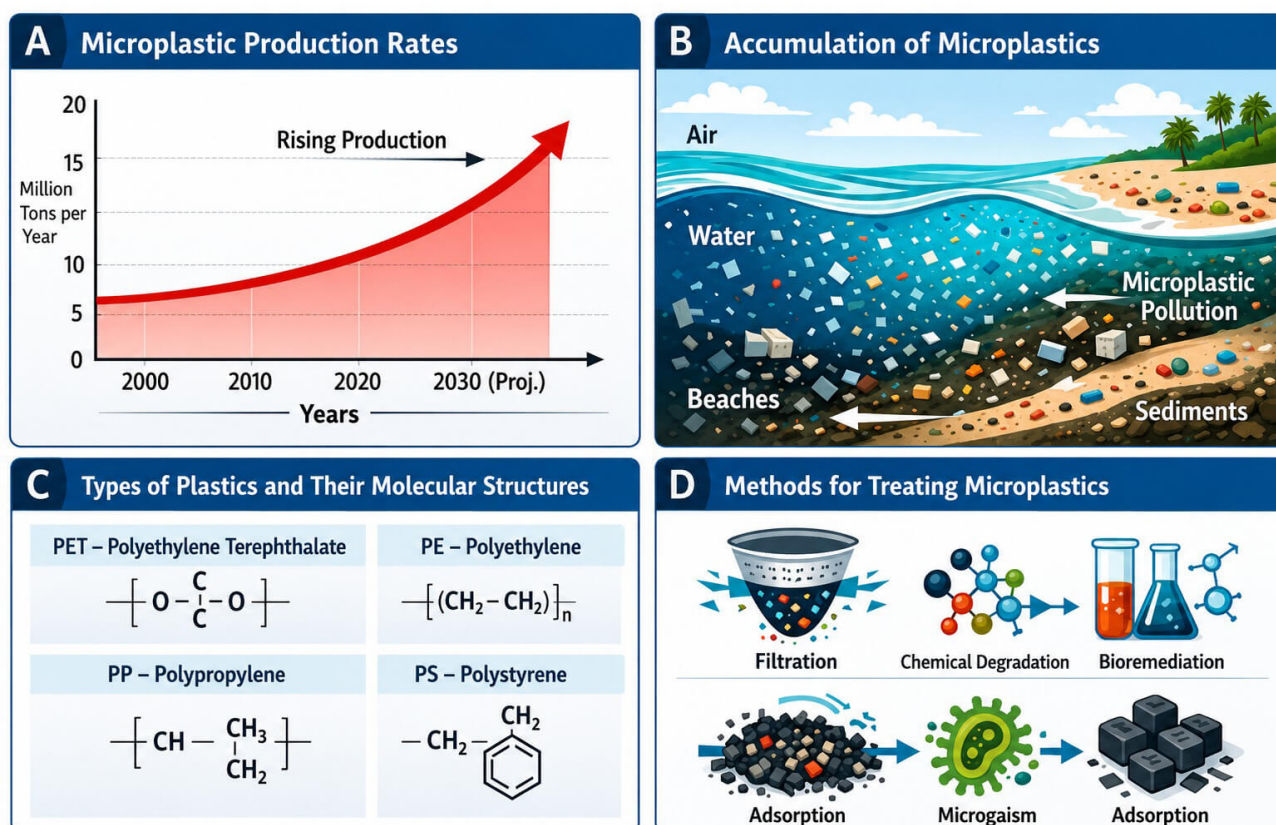
## 1. Introduction

Plastics are synthetic organic polymers produced by polymerizing fossil fuel-derived monomers. The superior physical and chemical properties, durability, cost-effectiveness, and manufacturing versatility of plastics have made these polymers widely used in numerous industries [1]. Fig. 1 presents a line graph illustrating the production and accumulation rates of microplastics (MPs) in the environment. However, the specific levels of plastics in various environmental compartments (terrestrial, marine, freshwater, and air) and the associated biological consequences remain poorly understood. This knowledge gap reflects the recent focus on the topic, limitations in sampling and analytical methods, and the vastness and complexity of the oceans. Van Seville et al. [2] and Jambeck et al. [3] highlighted that approximately 236,000 metric tons of plastic are floating in the ocean. Additionally, 4.8 to 12.7 million tons of plastic waste enter the ocean each year, with the total input projected to have become tenfold higher in 2025. Plastics are typically tailored for specific applications and consist of long-chain organic polymers. These materials can be homogeneous, made from a single type of polymer, or a blend of polymers that have been combined or cross-reacted to achieve the desired properties. Polymer chains are created by combining chemical monomers into repeat-

ing unit strands, with monomers often derived from fossil fuels. Polymers are also found naturally in molecules such as starch, as well as in more durable compounds such as cellulose and chitin. In modern culture, synthetic polymers have largely supplanted many traditional natural materials [4]. Presently, these materials are used in various applications, including food containers, thermal insulation, home furnishings, electrical devices, vehicle interiors, toys, fabrics, surface coatings, and medical devices.

MPs are classified as synthetic polymers with particle sizes smaller than 5 mm [5,6]. MPs are categorized into two types: primary and secondary [7]. Primary MPs are intentionally manufactured as small particles designed for specific applications [8]. In contrast, secondary MPs result from the degradation of larger plastic polymers, such as water bottles, ropes, and other materials, through environmental processes including seawater aging, exposure to light and heat, microbial activity, and mechanical stress. The discharge of textile effluents into aquatic environments is also increasing at an alarming rate [8]. Additional sources of MPs include air contamination, packaging and distribution processes for bottled water, effluents from laundry operations, fertilizers, and domestic and industrial wastewater streams. Moreover, the review underscores the significance of MP particles as carriers that facilitate the transport of





**Fig. 1. Overview of microplastic production, accumulation, composition, and treatment strategies.** (A) Global microplastic production rates. (B) Environmental accumulation trends of microplastics. (C) Types of plastics and their associated molecular structures. (D) Overview of microplastic treatment and removal methods. (Created with [BioRender.com](https://www.biorender.com)).

heavy metals, persistent organic pollutants, and emerging contaminants in drinking water [9]. Airborne MPs are dispersed by wind currents, while the characteristics, anthropogenic activities, and climatic conditions of the MPs influence the subsequent transport. In terrestrial ecosystems, MPs are transported by water and biota, with environmental factors, MP properties, and soil characteristics exerting significant control. Aquatic systems receive MP inputs from runoff and atmospheric deposition, while organisms, salinity levels, waves, and currents act as key determinants. Thus, optimal remediation approaches have been identified for different settings based on these distinct transport mechanisms [10].

As reported by Obbard [11] and Peng et al. [12], MPs have been detected in diverse ecosystems worldwide, including seas, rivers, sea ice, sediments, polar regions, air, soil, animals, and even the deepest parts of the ocean. MP pollutants occur in airborne, marine, and terrestrial environments. Meanwhile, polyethylene (PE), polyester, and polyethylene terephthalate are the most common airborne MPs pollutants, transported by wind as particulate dust. In marine pollution, PE tends to float on the water surface and interact with aquatic species, whereas denser polymers sink and affect the seafloor and biota at the bottom of the

ocean. Terrestrial pollutants, such as microfiber polyesters, can alter the physicochemical properties of soil and disrupt microorganism activity [13]. When MPs enter the human body, these materials can be absorbed via ingestion, including contaminated seafood and drinking water, as well as inhalation of airborne particles [14]. Since MPs impact ecosystems and human health, studies should explore the value of using soft computational methods, such as inferential and predictive modeling, to identify emerging themes and examine the challenges of applying soft computing to MP modeling. Indeed, recent work has highlighted advanced developments in the field, particularly the use of machine learning and artificial intelligence [15]. Despite the limited discussion on MPs, research has shown that plastic fibers are present in dust and can be transported by wind [16,17,18]. However, the specific mass concentrations and types of MPs that are hazardous to human health remain unknown. Recent studies by Napper et al. [19] found that stream water and snow samples from Mount Everest contained 56% polyester, 31% acrylic, 9% nylon, and 5% polypropylene. Notably, regulations on targeting primary MPs, which are predominantly found in pharmaceutical and cosmetic products, remain limited, particularly in developing countries [20]. When plastics are disposed of

in landfills alongside other debris due to inadequate plastic waste management, secondary MPs are eventually produced. MPs are difficult to remove because of the associated widespread distribution and small size, which allows these particles to pass through screening and filtration processes. Consequently, conventional wastewater treatment plants are largely ineffective at removing MPs, leading to the presence of these particles in the final effluents. Perren et al. [20] reported that when such effluents are discharged into surface water bodies or enter via surface runoff, MPs can contaminate drinking water sources. Similarly, Yuan et al. [21] noted that untreated MPs in sludge, which is often disposed of on land, may percolate into soil and groundwater, posing additional contamination risks [22]. Groundwater is often considered safe for drinking and is bypassed by treatment processes, allowing MPs to remain unfiltered and increasing human exposure. In low- and middle-income countries, inadequate waste and wastewater management further complicate MP removal, and the adoption of new treatment technologies may cause additional strain on existing infrastructure. Therefore, cost-effective and easily implementable solutions for MP mitigation are essential.

#### *Sources and Toxicity of MPs*

MPs have recently gained significant attention. While research has mainly focused on the presence of MPs in marine environments, these particles are now recognized as ubiquitous pollutants found in both densely populated urban areas and remote regions. MPs originate from both primary and secondary sources. Primary MPs include industrial materials such as plastic manufacturing feedstocks and plastic resin powders or pellets used in air-blasting processes [23,24]. In contrast, secondary MPs result from the breakdown of larger plastic debris due to environmental factors, such as ultraviolet (UV) light exposure. According to Erikson et al. [25], these degradation processes are among the primary contributors to the substantial presence of MPs in the atmosphere. A major source of secondary MPs is the washing of synthetic textiles, which releases fibers primarily composed of polyester, acrylic, and polyamide; wastewater from laundering has been reported to contain up to 100 MP fibers per liter [26]. The growing concern over MPs stems from both the persistence of these particles in the environment and the subsequent biological effects. Thus, research interest has steadily increased over recent decades, largely due to the improper disposal of plastic waste and the subsequent ecological impacts [27]. The ingestion of MPs by marine organisms has been well documented [8]. Meanwhile, recent studies have identified MPs in various marine biota, including fish, mussels, and shrimp. The distribution of MPs is influenced by factors such as population density, urbanization, and industrialization [28,29,30,31]. The behavior of MPs in aquatic environments varies with density: some MPs float at the water surface, whereas others sink to the seabed [32]. A significant concern associated with MPs

is the toxicity to both humans and animals. Luo et al. [33] highlighted that additives in these polymers, which have molecular sizes comparable to MPs and are not chemically bonded to the polymer matrix, are prone to leaching into the environment and contaminating food chains. Furthermore, Forte et al. [34] found that MPs 44 nm in size were more efficiently absorbed by cell lines and caused greater cellular damage than polystyrene MPs 100 nm in size, raising concerns about potential health risks.

## **2. Methods for the Removal of MPs**

The degradation of plastics into MP is primarily influenced by environmental factors such as UV radiation, mechanical wear, and chemical breakdown. Larger plastic materials, including polystyrene (PS), polyethylene (PE), Polyethylene terephthalate (PET), Polyvinyl chloride (PVC), and polyurethane (PUR), gradually fragment into smaller particles, leading to the formation of MPs that persist in ecosystems and pose substantial environmental concerns. Addressing MP pollution involves two primary approaches: preventing additional MP accumulation in water bodies and eliminating existing MPs from polluted environments. Researchers have explored various removal techniques, including advanced filtration, adsorption processes, and chemical treatments. Moreover, biological strategies, such as bioremediation, employ microorganisms and other biological agents to capture and degrade MPs [35,36]. These methods can be categorized into physical, chemical, and biological treatments, as well as emerging advanced technologies aimed at improving MP removal efficiency. Collectively, these measures aim to mitigate MP pollution and the associated long-term impacts on ecosystems and human health.

### *2.1 Physical Methods*

Common physical methods for removing MPs include adsorption, filtration, and sedimentation; most have been tested in laboratory settings. Thus, effective techniques for MP removal include filtration, a commonly employed method for extracting MPs from wastewater and water. A study by Simon et al. [37] discusses advances in innovative materials and techniques, such as biochar, magnetic nanotubes, electrocoagulation, and chitin oxide sponges, for effective adsorption and filtration. Simon et al. [37] and Talvitie et al. [38] also found that a disc filter comprising 13 polyester mesh discs with 18  $\mu\text{m}$  pores removed 89.7% of MPs larger than 10  $\mu\text{m}$ . The filter trapped particles from wastewater, creating a sludge cake on the water surface. However, the accumulation of larger plastics on the filter can block the pores, diminishing the efficiency of the filter. Overall, the reported removal efficiency of the filter ranged from 40% to 98.5%.

Rapid sand filtration is another effective filtration technology that utilizes sand grains to remove MPs. These filters typically consist of layers of 1 mm gravel (3–5 mm

grain size) and 0.5 m quartz (0.1–0.5 mm grain size). This cost-effective approach is suitable for removing MPs larger than 20  $\mu\text{m}$ . Dissolved air flotation is another method used to remove MPs from water. Indeed, this process involves dissolving air under high pressure to form bubbles that attach to solid particles, such as MPs, which are then removed by skimmers. Bui et al. [39] reported that, when enhanced with polyaluminum chloride to improve flocculation, this method achieved 95% effectiveness, making the process highly effective for removing low-density particles. In the rapid sand filtration process, particle removal is primarily achieved through physical mechanisms, although physicochemical interactions, such as van der Waals forces, can also contribute [40]. The use of chemical filter aids, including coagulants and flocculants, can further enhance adhesion forces [6]. In one study, four different filtration rates were tested over a 10-hour period [37,38]. Recently, ion-based methods for coagulating MPs were devised, in addition to adsorption. Wastewater treatment facilities employ electrocoagulation as the electrochemical treatment technique [20]. This technique aggregates and destabilizes waterborne suspended particles, such as colloids, MPs, and heavy metals, using electricity in an electrochemical cell with an anode and a cathode powered by a direct power source. The resulting flocs are then removed by settling, enabling more than 90% removal of microbeads. Electrocoagulation relies on metal electrodes to promote coagulation and is effective across a wide pH range (pH 3–10), despite potential interference from wastewater characteristics. The electrocoagulation approach proved effective owing to the associated wide pH tolerance. This technology offers numerous benefits, including low capital costs, low energy consumption, minimal sludge production, and high efficiency. Misra et al. [41] found that elevated chloride ions ( $\text{Cl}^-$ ) in wastewater have minimal impact on the removal efficiency of MPs; efficient adsorption requires careful consideration of MP size and the selection of appropriate adsorbents. Thus, Misra et al. [41] developed a physical separation technique that successfully eliminates MPs through adsorption using magnetic polyoxometalate-supported ionic liquid phases. This system removes MPs and filters out inorganic, organic, and microbiological contaminants while handling large volumes of water. Notably, this technique achieved 90% removal efficiency for PS microparticles (1–10  $\mu\text{m}$ ). An advanced approach involves using magnetic carbon nanotubes (M-CNTs) as adsorbents; when combined with permanent magnets, M-CNTs effectively remove MPs from water, achieving 100% absorption efficiency for PET, PE, and polyamide MPs.

A unique method for extracting MPs from saline water involves anodization and liquid-phase deposition of lauric acid to create superhydrophobic surfaces. These surfaces were designed to resist corrosion and abrasion, enabling effective removal of MPs. Rius-Ayra and Llorca-Isern [42] demonstrated that this approach effectively re-

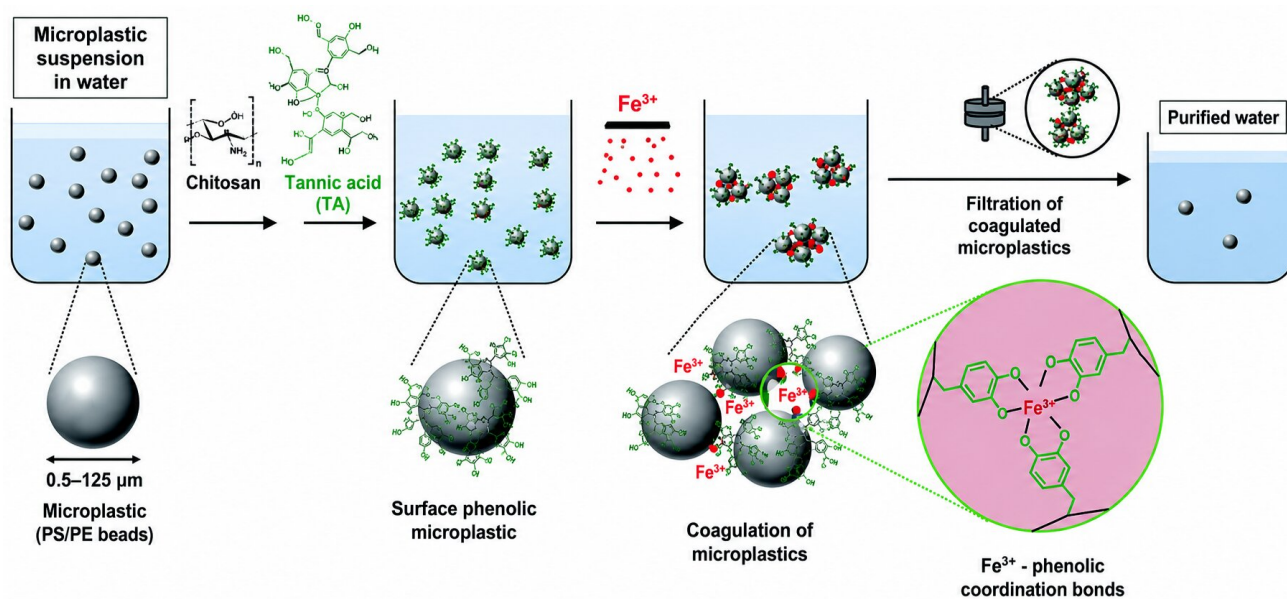
moves MPs from aqueous NaCl solutions with 99% efficiency. Coagulative colloidal gas aphrons represent another unique technology that removes MP particles approximately 5  $\mu\text{m}$  in diameter, achieving over 94% effectiveness [42]. Zhang et al. [43] proposed a prospective approach for eliminating micron-sized MPs from natural environments. The two main physical methods for removing MPs include soil washing and the use of magnetic nanoparticles, which can effectively remove emerging pollutants, including heavy metals and MPs.

### 2.1.1 Soil Washing

MPs can be separated from soil by washing, using differences in density, particle size, or hydrophobicity [44]. MPs are commonly removed from soil through water-based washing procedures that involve agitation or shaking [45]. Kida et al. [46] explained that ultrasonication, which applies high-frequency sound waves to agitate soil–water mixtures, can help remove MPs originating from soil particles. Cyclone separators employ centrifugal force to separate MPs based on size and density, directing particles to specific collection sites [47,48]. The success of soil washing varies depending on soil type, MP characteristics, and operational conditions. Gu et al. [45] emphasized that optimizing washing parameters, including the water-to-soil ratio, agitation duration, and settling time, is essential for enhancing removal effectiveness while minimizing the loss of MPs and soil particles. The authors also noted that the efficiency of MP recovery is affected by factors such as organic matter, moisture content, and soil texture [45].

### 2.1.2 Magnetic Separation

Magnetic separation uses the magnetic properties of MPs to remove the particles from complex soil environments. The main approach involves attracting and capturing MPs using magnetic fields or nanoparticles, thereby enabling their removal [49]. This procedure entails injecting ferromagnetic nanoparticles or chemicals into soil samples, where MPs physically or chemically interact with the magnetic particles. An external magnetic field is then applied to extract and separate the magnetic MP complexes from the soil. These complexes can then be collected and processed to obtain MPs. The efficiency of this method varies with MP properties, magnetic field strength and configuration, and particle concentration [50]. Functionalized magnetic nanoparticles can enhance MP removal by targeting specific MP types via surface coatings, thereby increasing overall affinity [51]. Although alternative methods for MP removal have been developed, these approaches have proven less effective than magnetic separation. Techniques such as ultrafiltration (42% efficiency) and magnetic microsubmarines (70%) exhibit lower success rates. Despite the advantages of these technologies, further research is necessary to improve the associated effectiveness and adaptability under diverse environmental conditions. Fil-



**Fig. 2.** Coagulated microplastics are filtered to remove microplastics, resulting in purified water [52]. (Under a Creative Commons license).

tration techniques struggle to capture smaller MPs, particularly those below 10 μm, allowing nanoplastics to persist in the environment. Additionally, filter clogging due to accumulated debris reduces efficiency and requires frequent maintenance, thereby increasing operational costs. High energy consumption, especially for electrocoagulation and rapid sand filtration, further constrains large-scale implementation. Meanwhile, chemical treatment methods offer high removal efficiency, versatility, and the potential to enhance other treatment processes. Coagulation and flocculation can achieve up to 99.4% MP removal by aggregating particles into larger flocs that can be more easily filtered or settled. These methods are effective for a wide range of MPs, with metal–organic frameworks (MOFs) demonstrating strong adsorption capabilities across different environmental conditions. Additionally, chemical treatments can be applied in various settings, from wastewater treatment plants to industrial applications, conferring high adaptability. Some advanced materials, such as MOFs, also offer reusability, thereby reducing long-term costs and improving sustainability.

## 2.2 Chemical Method

Chemical approaches involve using chemicals to degrade MPs into simpler compounds, facilitate floc formation, and aid the removal of these particles from water through filtration or other treatment processes. These added chemicals induce aggregation and agglomeration of MPs, forming flocs that can be removed by sedimentation or filtration. Fig. 2 (Ref. [52]) illustrates coagulation and flocculation, which are typical processes for removing MPs. Coagulation/flocculation creates flocs by neutralizing the

charge of colloidal particles in a solution. Researchers have employed a wide range of substances and combinations to increase the effectiveness of these processes. Razaviarani et al. [52] discussed the use of iron, aluminum, and polyamine to remove MPs, achieving 99.4% removal efficiency, with ferric chloride and chloride outperforming the polyamine. Zhou et al. [53] used ferric chloride and polyaluminum chloride as coagulants to remove MPs from wastewater. In this method, negatively charged wastewater particles are attracted to positively charged coagulants, promoting gravitational settling [53]. The supernatant was then collected, filtered, dried, and weighed for coagulation and sedimentation analysis, while characterization experiments were performed on the precipitated MP flocs. Rapid stirring speeds and alkaline conditions are important for maximizing the effectiveness of MP removal. Other chemical strategies, including inorganic–organic hybrid silica gels, photocatalysis, and alkoxy-silyl-induced agglomeration, have also been studied; however, the efficiencies of these processes were low (less than 30%). Hence, to improve performance, these approaches should be further evaluated under a broader range of conditions.

Compared with other methods, MOFs are considered the most effective for adsorbing MPs. Table 1 (Ref. [53,54,55,56,57,58,59,60,61]) shows the efficiency of MP removal using chemical methods. The versatility of MOFs stems from the ability of these materials to integrate organic, inorganic, and biological components, enabling the development of novel and efficient platforms for pollutant removal. Moreover, the high hydrophobicity associated with MOFs enhances pollutant adsorption while also ensuring stability and reusability, making these materials eco-

**Table 1. Microplastic removal techniques, target polymer types, size ranges, and removal efficiencies.**

| S. No. | Technique                                                            | Types of microplastics     | Size                                   | Removal efficiency                                          | Reference |
|--------|----------------------------------------------------------------------|----------------------------|----------------------------------------|-------------------------------------------------------------|-----------|
| 1      | Granular activated carbon                                            | Various microplastic types | 1–5 $\mu\text{m}$                      | 70.7–92.7%                                                  | [54]      |
| 2      | Inorganic–organic hybrid silica gels                                 | PE, PP, PET                | Not specified                          | Not specified                                               | [55]      |
| 3      | Aluminum coagulant with cationic polyamine-coated sand               | PE                         | 10–100 $\mu\text{m}$                   | 70.7–92.7%                                                  | [54]      |
| 4      | Coagulation/flocculation (iron, aluminum, polyamine-based chemicals) | PS spheres                 | 1 and 6.3 $\mu\text{m}$                | 95% (1 $\mu\text{m}$ ); >76% (6.3 $\mu\text{m}$ )           | [56]      |
| 5      | Photocatalysis                                                       | HDPE                       | 700 and 1000 $\mu\text{m}$             | Not specified                                               | [57]      |
| 6      | Coagulation combined with sedimentation                              | Various microplastic types | >10 $\mu\text{m}$ ; 5–10 $\mu\text{m}$ | >99% (>10 $\mu\text{m}$ ); 40.5–54.5% (5–10 $\mu\text{m}$ ) | [58]      |
| 7      | Alkoxy-silyl-induced agglomeration                                   | PE, PP                     | Independent of size and type           | Not specified                                               | [59]      |
| 8      | Alkyltrichlorosilanes (linear and branched)                          | LDPE, HDPE, PP             | 1 $\mu\text{m}$ –1 mm                  | 98.3 $\pm$ 1.0%                                             | [60]      |
| 9      | Coagulation using polyaluminum chloride and ferric chloride          | PS, PE                     | Not specified                          | Not specified                                               | [53]      |
| 10     | Ozonation                                                            | Various microplastic types | Not specified                          | 89.9%                                                       | [61]      |

Notes: PE, polyethylene; PP, polypropylene; PET, polyethylene terephthalate; PS, polystyrene; HDPE, high-density polyethylene; LDPE, low-density polyethylene. ‘Not specified’ indicates data not reported in the cited reference.

nomically viable for long-term applications [62,63]. The adsorption efficiency of MPs using MOF is presented in Table 2 (Ref. [41,64,65,66,67,68,69]). Additionally, the electronic properties of MOFs, particularly under sunlight, allow these materials to function as self-powered systems for pollutant degradation. This is particularly beneficial for MPs, which are often charged and vary in size. The combination of multifunctional sites and tunable electronic properties makes MOFs ideal candidates for MP removal [70,71]. MOFs have demonstrated high performance efficiency in diverse aquatic environments, including both freshwater and seawater, effectively capturing pollutants at varying concentrations [72,73]. Moreover, the thermal stability of MOFs enables these materials to operate over a wide temperature range, while the associated ability to harness solar energy further enhances their sustainability. With multifunctional sites, high porosity, and diverse morphologies, MOFs provide excellent platforms for designing new adsorbents. Nonetheless, despite the significant advantages of using MOFs in laboratory-scale applications, developing MOFs for large-scale filtration systems remains a critical challenge for practical environmental applications. Structurally, MOFs consist of metal nodes connected by organic ligands, forming robust frameworks capable of removing various toxic contaminants. The permanent porosity of these materials further enhances the ability of MOFs to cap-

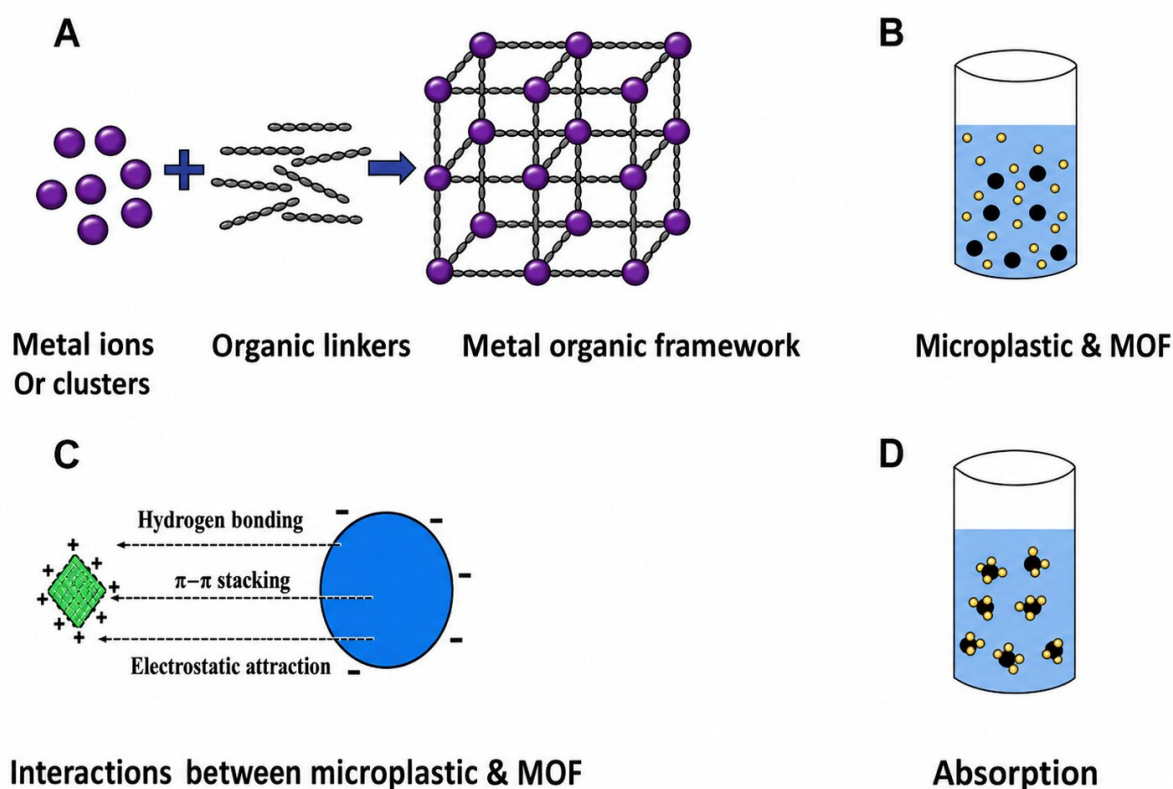
ture and retain pollutants [74]. The potential for creating an extensive range of MOFs arises from the numerous possible metal–ligand combinations, each offering distinct properties suited to specific environmental applications [75]. Various synthetic approaches, including solvothermal, hydrothermal, and layering methods, have been employed to design MOFs with enhanced porosity and active surface area [76,77,78]. Meanwhile, the integration of metal ions and multifunctional sites within the MOF architecture increases porosity and improves pollutant removal capabilities [79]. Furthermore, precise control over pore sizes through the use of short or long ligands adds to the versatility of MOFs [80]. Compared with traditional materials such as zeolites and activated carbon, MOFs offer far greater structural and chemical tunability, with some exhibiting surface areas exceeding 7000 m<sup>2</sup>/g [81].

According to Haris et al. [82], the incorporation of C@FeO nanopillars renders the magnetic properties to the material, enabling easy separation from water. This method can remove a large quantity of MPs within approximately one hour. The two-dimensional (2D) MOF@C@FeO combination can simultaneously remove both microplastics and methylene blue from mixed solutions. For single-component systems, removing MPs takes about 1 hour, whereas methylene blue can be removed in roughly half an hour. The nanopillars increase the surface area and fa-

**Table 2. Adsorption efficiency of microplastics using metal–organic frameworks (MOFs) and MOF-based composites.**

| S. No. | MOF or MOF-based composite                                                | MPs/NPs                          | Application | Process efficiency                  | Reference |
|--------|---------------------------------------------------------------------------|----------------------------------|-------------|-------------------------------------|-----------|
| 1      | Nano-Fe@ZIF-8                                                             | PS                               | Adsorbent   | 98%                                 | [64]      |
| 2      | MIL-101(Cr)                                                               | PS (65 nm)                       | Adsorbent   | Up to 96% removal at 5–70 ppm, pH 5 | [65]      |
| 3      | Polydopamine-enhanced magnetic chitosan (PDAMCS) aerogels (physisorption) | PET; PE/PS                       | Adsorbent   | 97.3%, 94.6%/92.3%                  | [66]      |
| 4      | MOF                                                                       | NPs                              | Adsorbent   | High removal efficiency             | [64]      |
| 5      | ZIF-67                                                                    | PS (1–3 $\mu$ m)                 | Adsorbent   | Up to 92.1% removal at 298 K        | [66]      |
| 6      | FeMAC                                                                     | PE                               | Adsorbent   | 60 to 90%                           | [67]      |
| 7      | ZIF-8 in a wood aerogel                                                   | PVDF (60–110 nm); PS (90–140 nm) | Adsorbent   | Up to 91.4% removal                 | [68]      |
| 8      | MagPOM-SILPs                                                              | PS                               | Adsorbent   | 100%                                | [41]      |
| 9      | Zn-MBCs                                                                   | PS                               | Adsorbent   | 95.8%                               | [69]      |

Notes: MOFs, metal–organic frameworks; MPs, microplastics; NPs, nanoplastics; PS, polystyrene; PE, polyethylene; PET, polyethylene terephthalate; PVDF, poly(vinylidene fluoride); ZIF, zeolitic imidazolate framework; MIL, Materials of Institute Lavoisier; PDAMCS, polydopamine-enhanced magnetic chitosan; FeMAC, iron-based magnetic activated carbon; MagPOM-SILPs, magnetic polyoxometalate-supported ionic liquid phases; Zn-MBCs, zinc-modified biochar composites. All efficiencies are reported as removal percentages under specified conditions.



**Fig. 3. Mechanism of microplastic removal using metal–organic frameworks (MOFs).** (A) Synthesis of MOFs. (B) Microplastic and MOFs. (C) Interactions between microplastics and MOFs. (D) Absorption process. (Created with [Biorender.com](https://www.biorender.com)). MOF, metal–organic framework.

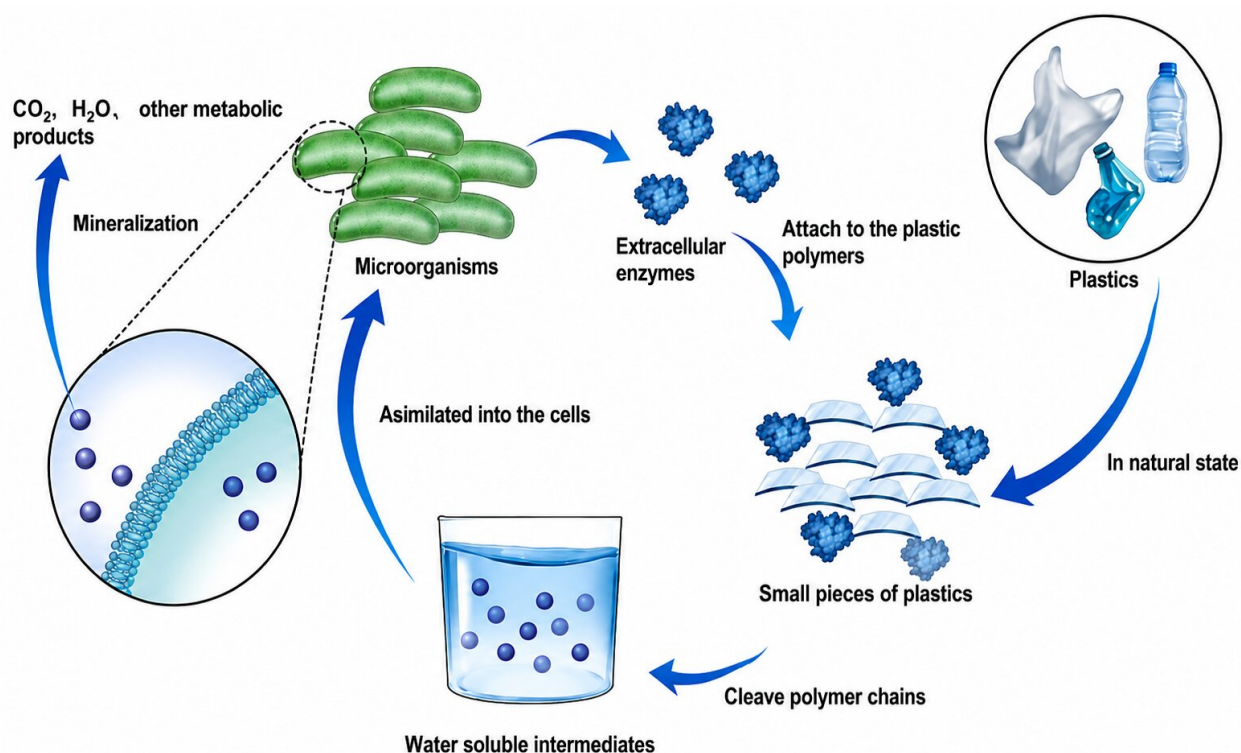
cilitate magnetic separation, enhancing the practicality and cost-effectiveness of the system. This new 2D structure, formed by growing MOF sheets on magnetic particles, represents a promising strategy for removing MPs from water [82]. The synthesis of MOFs is influenced by several factors, including reaction time, particle size, yield, and morphology, which together produce a wide variety of MOF structures. Over the past two decades, various synthesis techniques, including mechanochemistry, ultrasonic heating, room temperature synthesis, microwave synthesis, and electrochemistry, have been used to create MOF-based materials, including membranes and thin films. Structurally, MOFs consist of metal nodes connected by organic ligands, forming robust frameworks capable of removing MPs (Fig. 3).

However, given the vast range of MOFs reported in the literature, only unconventional synthesis approaches are discussed [83]. MPs release several hazardous chemical byproducts, including vinyl chloride, 1,3-butadiene, and ethylene oxide, as well as toxic additives such as tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), and phthalate esters. These toxic chemicals cause noxious and endocrine disruptions in living organisms [84]. Other volatile compounds, including methylene chloride, ethylbenzene, benzene, and toluene, also adversely affect aquatic life and human health [85]. Additionally, these methods require substantial chemical input, making these treatments expensive and resource-intensive, particularly for large-scale applications. Moreover, the efficiency of these methods varies with MP size, with coagulation and flocculation proving less effective for nanoscale MPs, which can remain suspended in water. In addition, these processes demand precise optimization, as factors such as pH, temperature, mixing speed, and chemical dosage significantly influence performance. Furthermore, the process generates sludge containing MPs and chemical residues, which must be properly treated and disposed of to prevent recontamination. Certain coagulants, such as aluminum-based compounds, also pose potential health risks if not carefully managed [53]. A disadvantage of the chemical method is that high consumption of coagulants, catalysts, and adsorbents increases operational costs, and certain materials, such as MOFs, require complex and expensive synthesis processes. Additionally, coagulation and flocculation are less effective for nanosized MPs, as smaller particles may remain suspended in water, requiring precise optimization of factors such as pH, temperature, and chemical dosage. Another major concern is the generation of toxic byproducts and sludge, which must be properly managed to prevent secondary contamination. Some coagulants, particularly aluminum-based compounds, pose potential health risks if not carefully regulated. Environmental concerns also arise from the excessive use of chemical additives, as they can introduce harmful substances into water systems, affecting aquatic life and human health [54].

Therefore, moving to biofilms, composed of microbial communities, enhances MP degradation by providing a stable environment for bacteria and fungi that secrete plastic-degrading enzymes. These biofilms facilitate continuous enzyme production, enhance microbial attachment to MP surfaces, and prolong interactions between microbes and plastics, leading to more efficient degradation. Similarly, enzymatic degradation plays a crucial role in breaking down MPs into biodegradable monomers without generating harmful byproducts. Enzymes such as PETase, laccase, and cutinase selectively cleave polymer bonds, ensuring precise degradation while minimizing unintended effects on surrounding materials.

### 2.3 Biofilm Formation and Microplastic Degradation

The molecular weight, hydrophobicity, and surface roughness of MPs influence both microbial degradation and biofilm formation. Nag et al. [86] suggested that when more easily accessible carbon sources are present in the environment, microbes may neither adhere to MP surfaces nor utilize MPs as carbon sources. Compared with other methods, biodegradation is more environmentally friendly, as this approach converts organic molecules into smaller fragments and ultimately into carbon dioxide (CO<sub>2</sub>). Biodegradation primarily involves two stages: depolymerization and mineralization [86]. Depolymerization breaks down polymers into monomers, dimers, and short oligomers, whereas mineralization converts these products into CO<sub>2</sub>, water, and methane (Fig. 4; Ref. [87]). Ahmed et al. [87] highlighted that microbial disintegration, driven by exoenzyme activity, promotes both depolymerization and mineralization of MPs; this process plays a crucial role in converting MPs into environmentally benign products [87]. Both fungi and bacteria participate in MP degradation, with fungi typically achieving this more rapidly. Fungi produce hydrophobic proteins that enable structures such as fruiting bodies and mycelia to adhere to the hydrophobic surfaces of MPs. Microbial adhesion to plastic surfaces is a significant environmental concern, and the interactions between bacteria and biofilm formation on these surfaces are critical for understanding plastic behavior [88]. Therefore, the properties of flexible surfaces, such as hydrophobicity, roughness, crystallinity, and structure, influence microbial biofilm formation [89]. Microorganisms flourish on highly hydrophilic MP surfaces, and increasing the hydrophilicity of plastic surfaces has been shown to enhance microbial film formation. Guo et al. [90] investigated biofilm formation on three types of plastic (PE, PP, and PET) collected from the Huangpu River. The authors observed that the biofilms formed on PE and PET exhibited higher biomass than those formed on PP. However, PP showed a notably higher abundance of *Pseudomonadota* (81.9%) compared with PE (53.06%) and PET (37.06%) (Table 3; Ref. [86,91,92,93,94,95,96,97,98,99,100,101,102,103,104,105]).



**Fig. 4. Enzymatic degradation process of plastic polymers.** Illustration of enzyme-mediated breakdown of plastic into smaller molecules [87].

Cyanobacteria were more abundant on the PE and PET surfaces than on the PP surface. Environmental conditions play a significant role in shaping microbial population composition on MP surfaces [105]. De Tender et al. [106] stated that factors such as light intensity, pH, water temperature, dissolved oxygen levels, and changes in microbial community characteristics in aquatic environments can affect the composition of bacterial colonies attached to MPs, especially as penetration depth increases. Therefore, these environmental conditions are expected to influence the structure and diversity of biofilm communities on MP surfaces [86]. However, the overall process of microbial degradation can take years or even decades, making this approach an inefficient strategy for large-scale MP removal. Additionally, selective microbial activity limits degradation, as not all microbes can effectively break down MPs, and many preferentially utilize alternative carbon sources that are easier to metabolize. Another challenge is that biofilm formation can promote MP persistence by creating a protective layer around the plastic, thereby limiting further environmental degradation.

Moreover, MPs with biofilms can act as carriers of pollutants, accumulating toxic substances such as heavy metals and persistent organic pollutants (POPs), thereby increasing the risk of contamination in aquatic ecosystems. Finally, enzymatic degradation of MPs is mainly mediated by hydrolases and oxidoreductases, enzymes involved

in plastic biodegradation that have received substantial research attention due to the associated participation in both natural and industrial processes [99].

### 2.3.1 Bacterial Hydrolases and Oxidoreductases

Bacterial hydrolases are essential for the breakdown of plastics, as these enzymes disassemble polymers into smaller fragments. Enzymes produced by specific bacteria catalyze hydrolytic reactions that cleave the chemical bonds in plastics. Subsequently, microorganisms can use plastic as a carbon source by converting these polymers into smaller molecules or biomass via bacterial hydrolases. Thus, using this natural enzymatic process enables the development of eco-friendly methods to mitigate plastic pollution.

PETase is a remarkable enzyme in plastic degradation, which can break down PET into mono(2-hydroxyethyl) terephthalic acid (MHET) [107]. Classified as an esterase enzyme, PETase belongs to the broader  $\alpha/\beta$ -hydrolase family. Moreover, the tertiary structure of PETase comprises a core containing eight strands and six helices, which contribute to the associated functional properties. A conserved catalytic triad shared with cutinases and lipases underlies the role of PETase in hydrolyzing ester linkages in PET [108]. The discovery of *Ideonella sakaiensis* 201-F6, a novel bacterium, has significantly advanced our understanding of plastic degradation. This bacterium demon-

**Table 3. Enzymatic degradation of MPs.**

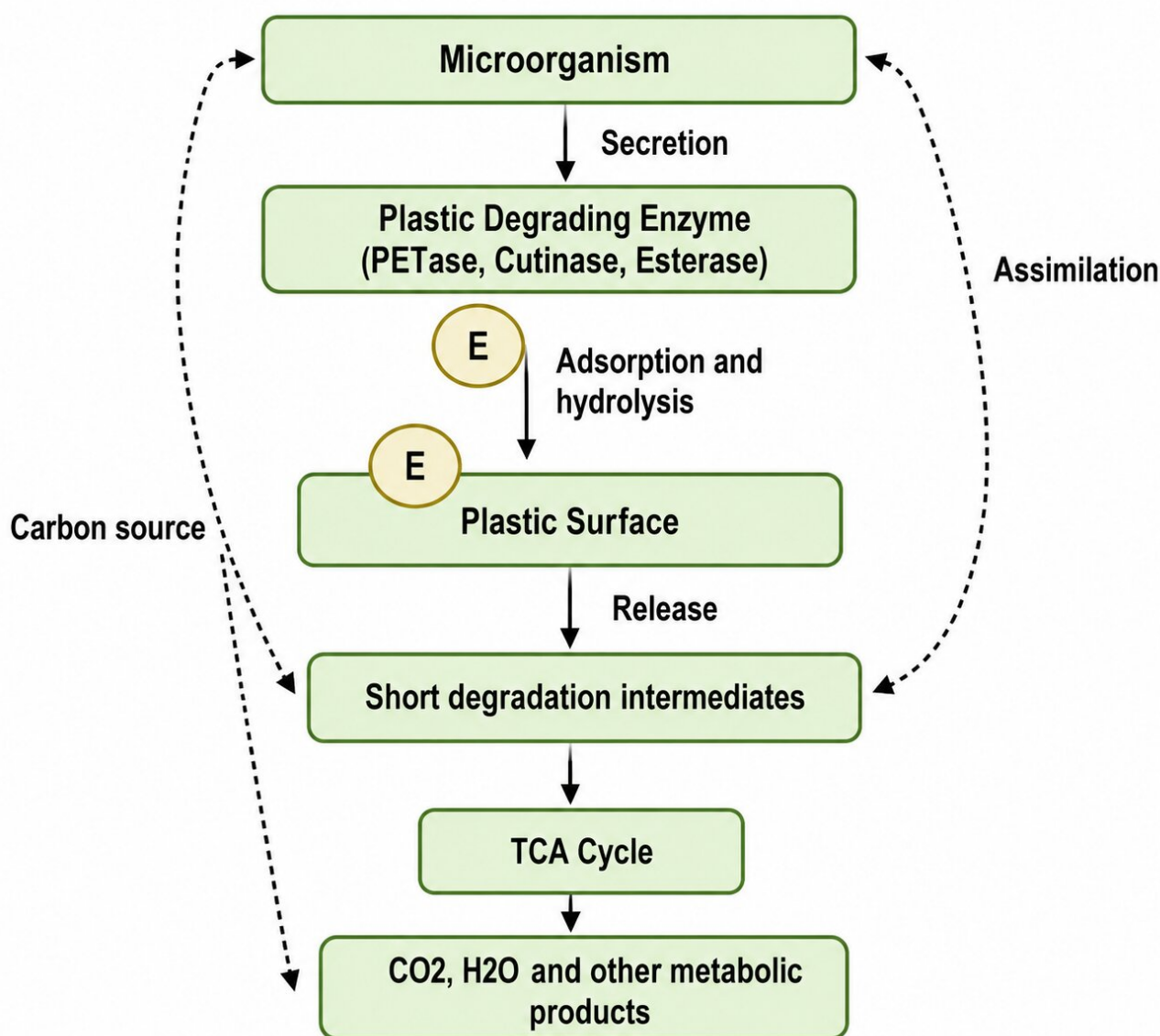
| S. No | Type of MPs | Strain                                           | Species type | Enzyme                                         | Period of time | Efficiency                               | References |
|-------|-------------|--------------------------------------------------|--------------|------------------------------------------------|----------------|------------------------------------------|------------|
| 1     | PE          | <i>Alcanivorax borkumensis</i>                   | Bacterial    | Alkane hydroxylase (alkB1, alkB2)              | 80 days        | Weight loss with 3.5% $\pm$ 0.34%        | [91]       |
| 2     | PP          | <i>Rhodococcus</i>                               | Bacterial    | Excrete-specific enzymes                       | 40 days        | Weight loss with 6.4%                    | [92]       |
| 3     | TPU         | <i>Penicillium</i> sp. MH410559                  | Fungal       | Membrane enzymes                               | 2 months       | Weight loss with 8.9%                    | [93]       |
| 4     | PS          | <i>Pseudomonas, Bacillus</i>                     | Bacterial    | Lipase                                         | 30 days        | Weight loss with 12.4%                   | [94]       |
| 5     | PLA         | <i>Bacillus pumilus</i>                          | Bacterial    | Lipase                                         | 150 days       | Weight loss with 32%                     | [95]       |
| 6     | PVC         | <i>Phanerochaete chrysosporium</i>               | Fungal       | Esterases                                      | 28 days        | Weight loss with 11%                     | [96]       |
| 7     | PE          | <i>Aspergillus oryzae</i> strain A5,1 (MG779508) | Fungal       | PHB depolymerases                              | 16 weeks       | Weight loss with 36.4% $\pm$ 5.53%       | [97]       |
| 8     | PS          | <i>Pseudomonas aeruginosa</i> DSM 50071          | Bacterial    | Hydrolases and esterase                        | 15 days        | Weight loss with 2.6% (serine hydrolase) | [98]       |
| 9     | PP          | <i>Bacillus</i> sp. and <i>Paenibacillus</i> sp. | Bacterial    | Oxidoreductase                                 | 60 days        | Weight loss with 14.7%                   | [99]       |
| 10    | PU          | <i>Aspergillus tubingensis</i>                   | Fungal       | Esterase and lipase                            | 2 months       | Weight loss with 90%                     | [100]      |
| 11    | PE          | <i>Serratia</i> sp.                              | Bacterial    | Lipase                                         | 150 days       | Weight loss with 40%                     | [101]      |
| 12    | HDPE        | <i>Aspergillus flavus</i> PEDX3                  | Fungal       | Laccase-like multicopper oxidases              | 28 days        | Weight loss with 3.90% $\pm$ 1.18%       | [102]      |
| 13    | PE          | <i>Pseudomonas knackmussii</i> N1–2              | Bacterial    | Dioxygenases, hydroxylases, and monooxygenases | 8 weeks        | Weight loss with 5.95 $\pm$ 0.03%        | [103]      |
| 14    | PU          | <i>Pseudomonas</i> sp. AKS31                     | Bacterial    | Hydroxylase                                    | 10 days        | Weight loss with 70%                     | [104]      |
| 15    | PET         | <i>Penicillium simplicissimum</i>                | Fungal       | Lipase                                         | 28 days        | Weight loss with 3.09%                   | [86]       |
| 16    | PE          | <i>Alcaligenes faecalis</i> LNDR-1               | Bacterial    | Lipase, CMCase, xylanase, and protease         | 10 weeks       | Weight loss with 21.72 $\pm$ 2.1%        | [105]      |

PU, Polyurethane; PP, Polypropylene; TPU, Thermoplastic Polyurethane; PVC, Polyvinyl Chloride; PLA, Polylactic Acid; HDPE, High-Density Polyethylene.

strates the special ability to use PET as a source of carbon and energy [109]. In particular, *I. sakaiensis* adheres to the PET surface and secretes PETase, which promotes PET degradation [110]. The resulting products include MHET, terephthalic acid (TPA), and bis(2-hydroxyethyl) terephthalate (BHET). Owing to the strong affinity for PET, PETase is a powerful catalyst for the breakdown of plastics and has great potential for future applications. Miri et al. [111] discovered that MHETase further degrades MHET into TPA and ethylene glycol (EG). The authors also suggested that a TPA transporter protein imports TPA into the cytoplasm, where the compound is converted to protocatechuic acid (PCA) and subsequently funneled into the tricarboxylic acid (TCA) cycle [111]. Han et al. [112] elucidated the structure of PETase from *I. sakaiensis*, revealing that this enzyme is a serine hydrolase with an  $\alpha/\beta$ -fold structure. The catalytic activity of PETase is mediated by serine, histidine, and arginine residues, and is significantly influenced by two unique

structural features: disulfide bonds within the enzyme and the amino acid residue W156 near the catalytic core. Fig. 5 illustrates the proposed PET biodegradation mechanism.

Han et al. [112] further proposed a catalytic mechanism for PETase, in which the W156 side chain forms a groove that facilitates nucleophile binding on the enzyme surface (Fig. 6; Ref. [100,113]). In addition to hydrolases, oxidoreductases contribute to plastic degradation by catalyzing oxidation–reduction reactions that transfer electrons from one molecule (electron donor) to another (electron acceptor). Cytochrome P450 is a highly efficient enzyme for plastic degradation owing to the associated broad substrate specificity [100]. Notably, cytochrome P450 has been recognized as a major contributor to the formation of reactive oxygen species (ROS) during plastic degradation [113]. Moreover, cytochrome P450 enzymes have been reported in bacterial species such as *Bacillus subtilis* and *Sphingomonas paucimobilis*, where specific isoforms (e.g.,



**Fig. 5. Potential biodegradation pathway of PET.** TCA, tricarboxylic acid.

CPY152A1 and CPY152B1) catalyze key reactions, including hydroxylation and epoxidation, thereby contributing significantly to PS breakdown [114].

### 2.3.2 Fungal Hydrolases and Oxidoreductases

Fungal hydrolases are enzymes produced by fungi that are crucial for the biodegradation of synthetic polymers such as PET and PUR. Srikanth et al. [115] explained that fungal hydrolases can alter the plastic surface, increasing the associated hydrophilicity, which enhances the ability of the enzyme to degrade the plastic. This change in surface characteristics enables the enzyme to interact more effectively with the polymer, facilitating depolymerization into smaller, more manageable molecules [115]. Cutinases are a subfamily of eukaryotic and prokaryotic hydrolases with distinct structures, including alpha/beta folds, core beta-

sheets, exposed active sites, and catalytic triads. The most extensively studied cutinases include those from *Humicola insolens* (HiC), *Fusarium solani pisi* (FsC), and *Fusarium oxysporum* (FoCut5a). Among these, HiC exhibits superior thermostability and a higher hydrolysis rate constant than FsC.

According to Temporiti et al. [116], genetic engineering has been applied to enhance the active site of *Fusarium solani* cutinase, thereby improving the effectiveness of the enzyme against PET fibers. Laccases are blue copper oxidases that catalyze the oxidation of phenolic and non-phenolic compounds using oxygen as an electron acceptor. These enzymes have been identified in fungal species such as *Trichoderma harzianum*, *Aspergillus flavus* PEDX3, and *Phanerochaete chrysosporium*, which have shown promise for degrading PE and PVC. According to Gollan et al.

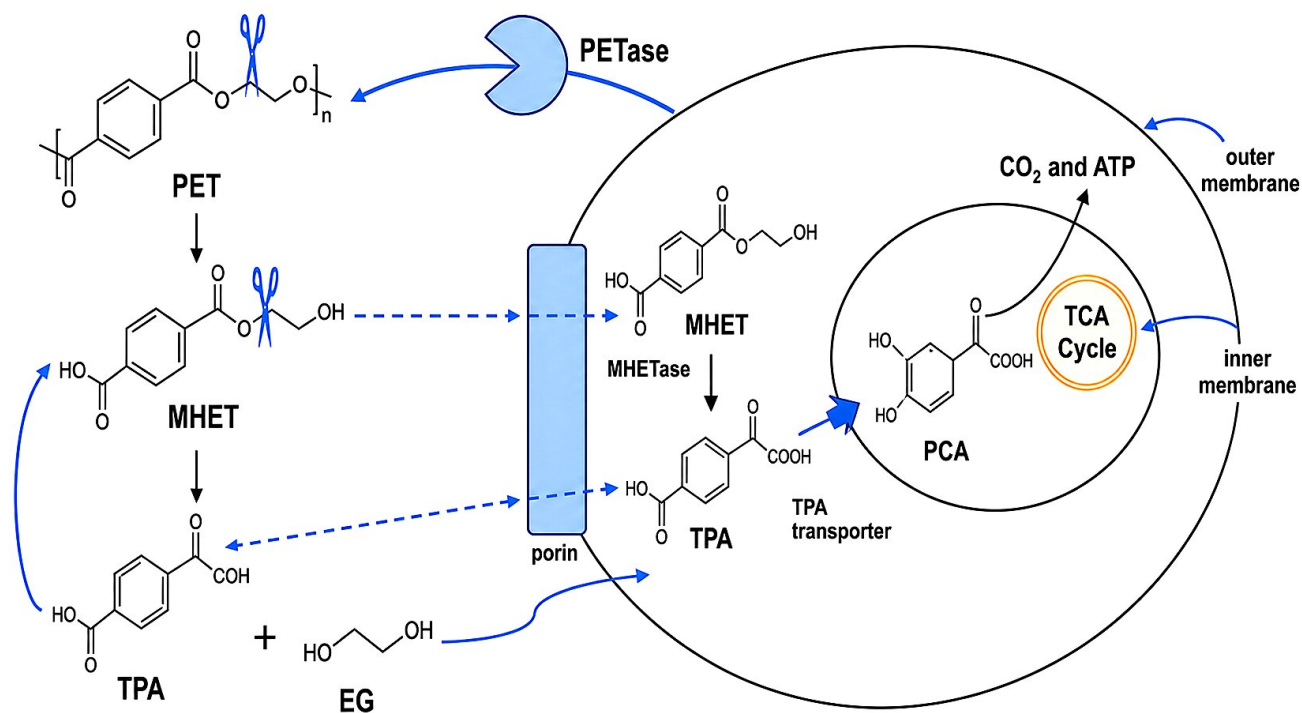


Fig. 6. Enzymatic hydrolysis mechanism of PET [100,113].

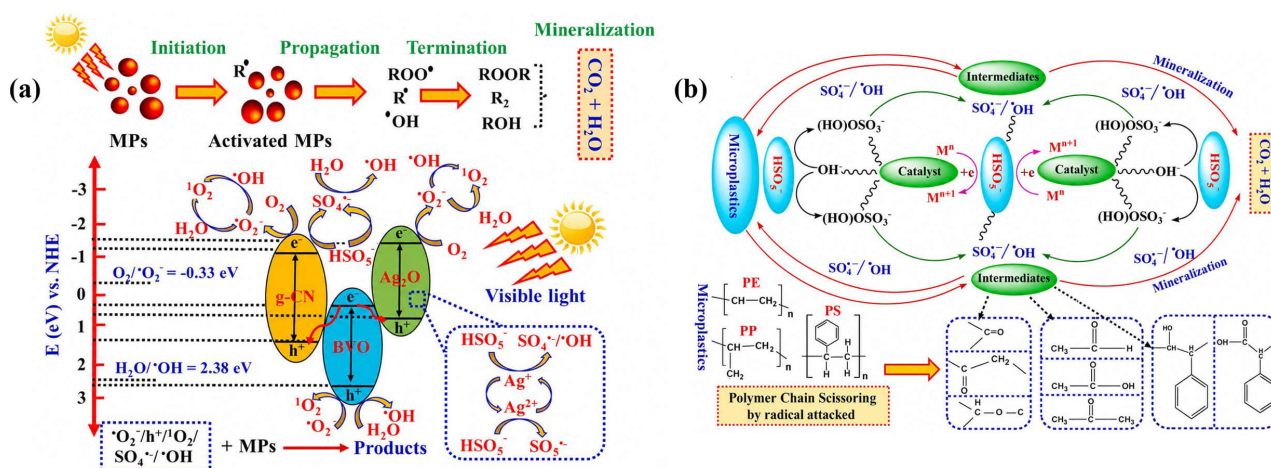
[117], *Trichoderma harzianum* produces laccase that, after 10 days of incubation, results in a 0.5% reduction in PE mass. *Aspergillus flavus* PEDX3 degrades high-density polyethylene (HDPE) MPs, a process attributed to the production of laccases and laccase-like multicopper oxidases (LMCOs). Basidiomycetes such as *Phanerochaete chrysosporium* and *Pleurotus ostreatus* also contribute to PE biodegradation through laccase activity [114]. A recent study used computational molecular simulations to investigate the interaction between PE and laccase, reporting a binding affinity of 40.11  $\mu\text{M}$  and a binding energy score of  $-6.00$ . These values indicated that lower binding energy requirements facilitate bond formation, suggesting that laccase plays a significant role in PE biodegradation [114,115].

Despite these promising findings, microbial degradation efficiency varies widely due to environmental factors such as temperature, salinity, oxygen levels, and pH, leading to inconsistent degradation rates across different ecosystems. Additionally, microplastics provide surfaces for the attachment and transport of pathogenic bacteria, potentially facilitating the spread of harmful microbes in marine and freshwater environments. The overall degradation rate is often slow, as natural enzymes and microbial biofilms may require weeks or even months to break down MPs, limiting the effectiveness of the process for rapid remediation. Meanwhile, limited enzyme specificity poses an additional challenge, as different plastics require different enzymes, and many high-crystallinity polymers, such as PP and PS, are resistant to enzymatic breakdown. The

stability and activity of enzymes are also highly dependent on environmental conditions, such as pH, temperature, and salinity, which can reduce the efficiency of enzymes in diverse ecosystems. Biofilm-based degradation presents further challenges, including biofilm detachment and maintenance, since environmental fluctuations can disrupt microbial communities and lead to inconsistent MP degradation. Moreover, competition with other microbes in natural environments can limit the dominance of plastic-degrading species, reducing overall degradation efficiency.

#### 2.4 Advanced Techniques for Degradation of MPs

Traditional removal methods, such as filtration and sedimentation, often fail to eliminate small and nano-sized MPs, necessitating more effective chemical and photochemical approaches. Advanced oxidation processes (AOPs) and photocatalytic degradation have emerged as promising solutions that utilize highly reactive species to break down MPs into smaller, less harmful molecules. AOPs, including the Fenton reaction, ozonation, and hydroxyl radical-based oxidation, leverage powerful oxidants to degrade MPs by cleaving polymer chains and reducing MP persistence. These methods are widely applied in wastewater treatment and offer high degradation efficiency, although challenges such as pH sensitivity and byproduct formation must still be addressed. Du et al. [118] highlighted that AOPs are among the most effective methods for degrading persistent organic pollutants. Shen et al. [119] identified an environmentally favorable elimination strat-



**Fig. 7. Illustrates the mechanisms involved in microplastic degradation via advanced oxidation processes.** (a) Mechanism of photocatalytic degradation of MPs and ROS generation using a Z-Scheme BiVO<sub>4</sub>-Ag<sub>2</sub>O@g-C<sub>3</sub>N<sub>4</sub> heterojunction photocatalyst [128]. (b) Generation of ROS in sulfate radical-based advanced oxidation processes (SR-AOPs) for the scission of polymer chains [129]. ROS, reactive oxygen species. (Under a Creative Commons License).

egy, emphasizing the safety, efficiency, and strong degradation capability of this method. These approaches offer high oxidation efficiency and do not generate secondary pollutants. AOPs generate ROS, also known as radicals. ROS generation can be triggered by light, heat, catalysts, or plasma, either individually or in combination [120,121]. The main AOP methods for MP degradation are photocatalysis and Fenton/Fenton-based strategies, which are discussed below.

#### 2.4.1 Photocatalytic Degradation

Photocatalytic degradation uses solar energy to break down MPs in the presence of semiconductor photocatalysts [118,122,123]. When photons with sufficient energy (UV or visible light) strike the photocatalyst, the electrons become excited [124]. This excitation promotes an electron from the valence band (VB) to the conduction band (CB), leaving behind a positively charged hole (h<sup>+</sup>) in the VB [124]. The holes in the VB can oxidize organic substances, producing extremely reactive hydroxyl radicals that can then oxidize electron-rich chemicals. Concurrently, the electrons in the CB interact with oxygen to form superoxide radicals that combine with water to produce HO<sub>2</sub>•. Subsequently, HO<sub>2</sub>• is converted to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which in turn generates hydroxyl radicals (OH•) [124]. These radicals target MPs, inducing chain breakage, scission, crosslinking, and polymer mineralization [125]. Common photocatalysts for MP degradation include ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), zinc oxide (ZnO), zinc sulfide, cadmium sulfide (CdS), bismuth oxychloride (BiOCl), and titanium dioxide (TiO<sub>2</sub>) [125].

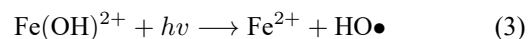
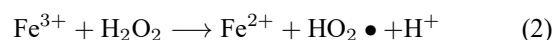
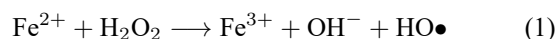
Photochemical degradation produces ROS when photoexcited MPs interact with oxygen and then react with other MP molecules. Thus, photodegradation depends

strongly on direct interactions between MP molecules. In contrast, photocatalysis does not require the presence of MPs. In addition to the ROS generated by the interaction between MPs and oxygen, photocatalyst-generated holes and electrons interact with oxygenated species [126]. These ROS penetrate the polymer matrix and form carbon-centered radicals via oxygen insertion, leading to polymer chain cleavage. Photooxidation yields intermediates containing carbonyl and carboxyl groups, which eventually mineralize into CO<sub>2</sub> and H<sub>2</sub>O. MP degradation is primarily accomplished using TiO- and TiO<sub>2</sub>-based photocatalysts, which are highly efficient, less toxic, cost-effective, resistant to acids and alkalis, readily available, and stable. Titanium dioxide (TiO<sub>2</sub>) is an excellent photocatalyst owing to the associated relatively small energy bandgap between the valence and conduction bands [124]. Natural photolysis serves as a crucial precursor to photocatalytic processes: photo-initiated degradation of the plastic carbon-carbon (C-C) backbone proceeds through three main stages: initiation, propagation, and termination. During initiation, C-H bonds are cleaved, generating free radicals that react with oxygen in the propagation stage to form reactive species such as R• and ROO• [127]. This process leads to autooxidation, which can result in either chain scission or crosslinking. The chain reaction concludes in the termination stage, in which two radicals combine to form inert products [125]. Li et al. [128] further investigated the photocatalytic mechanism of MP removal using an innovative Z-scheme-structured photocatalyst, BiVO<sub>4</sub>-Ag<sub>2</sub>O@g-C<sub>3</sub>N<sub>4</sub>, activated with peroxymonosulfate (PMS). The BiVO<sub>4</sub>-Ag<sub>2</sub>O@g-C<sub>3</sub>N<sub>4</sub>/PMS/visible light system generates ROS, as illustrated schematically in Fig. 7 (Ref. [128,129]). To enhance active sites (BiVO<sub>4</sub>/Ag<sub>2</sub>O), surface modification is essential for effi-

cient PMS activation. The combination of photocatalysis ( $\text{BiVO}_4\text{-Ag}_2\text{O@g-C}_3\text{N}_4/\text{PMS/visible light}$ ) with PMS activation thus represents a promising strategy for the effective elimination of MPs [128]. In another study, Easton et al. [130] treated polyester fiber debris (16.7 mg/L) derived from laundry wastewater, achieving a maximum MP weight loss of 52.7% and a carbon index (C.I.) of 6.75 under operating conditions of 0.8 g/L  $\text{H}_2\text{O}_2$  dose, a UV intensity of 129 J/cm<sup>2</sup>, and a reaction time of 5 hours. Additionally, Uheida et al. [131] proposed a sustainable green photocatalysis strategy for removing PP MPs ( $\leq 5 \mu\text{m}$  in size and  $\sim 10^4$  particles/L) from wastewater using ZnO nanorods. After two weeks of irradiation, the average volume of PP MPs decreased significantly by 65%, with a carbon index of 40, under specific operating conditions including a flow rate of 300 mL/min, a UV power of 120 W, a wavelength of 354 nm, and a UV intensity of 60 mW/cm<sup>2</sup> [131].

#### 2.4.2 Advanced Oxidation Processes

AOPs refer to a set of chemical treatment methods designed to degrade organic pollutants, including MPs, by generating highly reactive species, primarily hydroxyl radicals ( $\bullet\text{OH}$ ), which break down contaminants into harmless end products such as water and carbon dioxide. The Fenton process is a key AOP frequently used to degrade MPs in wastewater treatment plants [120]. This process involves the catalytic decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of ferrous ( $\text{Fe}^{2+}$ ) ions. The optimal pH range for the Fenton process is between 2.5 and 3; above pH 3, iron precipitates as iron hydroxides, thereby reducing process efficiency. This reaction produces hydroxyl radicals ( $\text{HO}\bullet$  and  $\text{HO}_2\bullet$ ) (Eqns. 1,2), with  $\text{H}_2\text{O}_2$  serving as the oxidizing agent and iron as the catalyst [130]. The photo-Fenton process refers to the Fenton reaction that occurs under UV-visible light [123]. According to Ahmed et al. [87], at acidic or near-neutral pH levels, several light-absorbing iron-hydroxyl complexes ( $[\text{Fe}(\text{OH})]^{2+}$ ,  $[\text{Fe}(\text{O}_2\text{H})]^{2+}$ ) develop. Upon exposure to light, an electron from the ligand excites the metal, reducing  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  and creating  $\text{HO}\bullet$  radicals (Eqn. 3) [125]. The photo-Fenton technique is more efficient and faster than the standard Fenton procedure because this approach combines light irradiation with  $\text{HO}\bullet$  radicals. The electro-Fenton procedure was developed to address the limitations of the conventional Fenton method. This technique involves the continuous electrochemical synthesis of  $\text{H}_2\text{O}_2$  under mild conditions [87], achieved by reducing oxygen at the cathode while continuously regenerating  $\text{Fe}^{2+}$  ions and generating OH radicals [125]. However, photocatalytic degradation may lead to secondary pollution due to residual catalysts in the effluent [118]. Although other AOPs, such as the Fenton process and ozone-based degradation, are extremely efficient, the wide-scale applicability of these processes is currently being investigated.



#### 2.4.3 Sulfate Radical Oxidation for MPs

Sulfate radical-based advanced oxidation processes (SR-AOPs) have gained recognition as effective methods for degrading MPs due to the associated high efficiency and ability of these processes to mineralize MPs into harmless byproducts. These processes generate ROS, including sulfate radicals ( $\text{SO}_4\bullet^-$ ), superoxide radicals ( $\text{O}_2\bullet^-$ ), singlet oxygen ( $^1\text{O}_2$ ), and hydroxyl radicals ( $\bullet\text{OH}$ ), primarily through the activation of persulfate or peroxymonosulfate. The generated ROS interact with MPs, leading to polymer chain cleavage and subsequent degradation. The degradation mechanism, illustrated in Fig. 7 (Ref. [128,129]), involves multiple pathways, including oxidative scission of polymer backbones, hydroxylation of polymer chains, and the formation of reactive intermediates such as carbonyl groups [132]. Additionally, co-reactants and reaction conditions play a significant role in enhancing the efficiency of SR-AOPs by influencing reaction kinetics and overall process effectiveness. Despite the potential of these approaches, research on SR-AOPs for MP degradation remains limited. Therefore, a more comprehensive understanding of these intricate mechanisms is essential for optimizing SR-AOPs and developing effective strategies to mitigate MP pollution in aquatic environments. A recent study by Dai et al. [132] investigated the degradation efficiency and mechanism of PE using a novel catalyst, S-nZVI@ATP (sulfidized nanoscale zero-valent iron supported on attapulgite), activated by persulfate oxidants. Over 24 hours, the average size of PE particles decreased significantly from 64.2  $\mu\text{m}$  to 28.1  $\mu\text{m}$  as a result of persulfate oxidation. This process transformed PE into smaller molecular components, including alcohols, ketones, alkanes, alkenes, and carboxylic acids. The continuous supply of  $\text{Fe}^{2+}$  by S-nZVI@ATP facilitated persulfate activation, generating potent oxidants such as  $\text{SO}_4\bullet^-$ ,  $\text{O}_2\bullet^-$ ,  $^1\text{O}_2$ , and  $\bullet\text{OH}$ , with  $\text{SO}_4\bullet^-$  playing a dominant role in the oxidation process [132]. Similarly, Liu et al. [129] examined the degradation of nylon-6 and PS MPs using PMS and  $\text{Fe}^{2+}$ -based Fenton AOPs. Significant mass losses were observed after four treatment cycles, with nylon-6 and PS showing reductions of 25.6% and 22.1%, respectively [129]. While these advanced techniques demonstrate significant potential for MP remediation, large-scale application is constrained by chal-

allenges related to energy consumption, catalyst stability, and cost-effectiveness. Future research should prioritize optimizing these methods and integrating these processes with complementary remediation strategies, such as biodegradation and adsorption, to develop sustainable and efficient solutions for mitigating MP pollution.

### 3. Conclusion

Managing MP contamination is important for protecting ecosystems and human health. Although several removal procedures show potential, each presents distinct advantages and limitations. Physical, chemical, biological, and advanced techniques all contribute to reducing MP contamination. Physical methods such as filtration and sedimentation are straightforward and efficient, but struggle to remove fine particles completely, especially those embedded in sediments. Chemical treatments, including advanced oxidation processes and enzymatic degradation, hold promise for transforming MPs into less harmful byproducts; however, the large-scale application of these strategies requires further optimization and careful consideration of associated environmental impacts. Biological approaches, such as biodegradation by microorganisms, offer sustainable removal options but depend heavily on factors including microbial diversity and environmental conditions. Enzymes from the hydrolase family, such as lipases, depolymerases, esterases, and PETases, degrade plastic polymers into smaller units that can be more readily mineralized in the environment and assimilated by microbes as carbon sources, before being further converted into CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and N<sub>2</sub>. This review examines these enzymes and further elucidates the applications and efficiency of each. Based on comparative analysis, we conclude that hydrolases are efficient enzymes capable of degrading most plastics via a direct bond-cleavage mechanism. MOFs are unique among emerging technologies owing to the associated large surface area and tunable porosity, which enable excellent adsorption of MPs from aqueous environments. MOFs align with circular economy principles by enabling the recovery and recycling of adsorbed MPs. Nevertheless, the energy-intensive production and environmental implications of MOFs must be evaluated meticulously. Overall, the critical role of MOFs represents a promising avenue for addressing the escalating issue of MP contamination in aquatic environments.

### 4. Future Aspects

The development of advanced filtration technologies increasingly leverages nanotechnology to enhance filtration systems, making these methods more efficient at capturing even the smallest MP particles. Hybrid filtration systems that combine physical filtration with biological and chemical processes can create multifunctional systems capable of removing a broad range of MPs from different environments. Biotechnological advancements in enzymatic

degradation include genetic engineering to create genetically modified microorganisms or enzymes with enhanced capabilities to efficiently break down various types of plastics. Additionally, enzyme discovery and optimization involve exploring diverse environments, such as the deep sea and extreme habitats, to identify new enzymes with unique plastic-degrading properties and optimize existing enzymes for higher efficacy. Furthermore, real-time monitoring and adaptive systems are being developed to create smart systems that adjust the associated operations based on continuous monitoring of MP concentration and composition across different environments.

### Author Contributions

NM: literature review, data curation, SEJ: Literature review, data acquisition, data interpretation, writing – original draft; SS: Literature review, data analysis, data interpretation, writing – original draft; JS: Methodology, literature review, critical revision of the manuscript, writing – original draft; SG: Conceptualization, supervision, Fund acquisition, review & editing. All authors read and approved the final manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

### Ethics Approval and Consent to Participate

Not applicable.

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### Conflicts of Interest

The authors declare no conflicts of interest.

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