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Catalytic approaches for the removal of microplastics from water: Recent advances and future opportunities

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ABSTRACT

Microplastics, which are small plastic particles, have become a growing environmental concern due to their prevalence in aquatic and terrestrial environments. They persist for decades and potentially centuries due to their resistance to degradation and can harm organisms and release toxic chemicals. There has been increasing interest in developing methods for their removal from the environment, particularly from water. Catalytic processes have shown promise as a potential method for microplastic elimination, including biological methods, advanced oxidation processes, and hydrolysis. This review article focuses on recent advances in catalytic processes for the removal of microplastics from water, including various types of catalysts and their applications. It also discusses the potential for catalytic processes to be integrated into real-world water treatment systems for the removal of microplastics. The review highlights the challenges and opportunities associated with the removal of microplastics from the environment and aims to contribute to the development of more effective and sustainable methods for addressing this growing environmental issue. Future research should focus on developing hybrid catalyst systems that combine the strengths of multiple processes for improved efficiency and effectiveness. Additionally, research should explore the use of natural materials and biological processes for microplastic elimination, which may offer more sustainable and environmentally friendly options. Collaboration between scientists, engineers, policymakers, and the public will be critical for the development and implementation of these systems. The elimination of microplastics from the environment requires a multifaceted approach, and continued research and collaboration are necessary to develop effective and sustainable methods for their removal and to protect the health of our environment and communities.

1. Introduction

In the last few decades, global plastic production has increased substantially, reaching 322 million tons in 2015. The leading sectors of application are packaging (40%), construction and building (20%), and automotive (10%). The majority of plastics, such as PE (polyethylene), PP (polypropylene), PS (polystyrene), PVC (polyvinyl chloride), PET (polyethylene terephthalate), and PUR (polyurethane), account for 80% of the total demand in Europe and are made from fossil feedstocks [1–3]. Due to the high consumption and widespread use of plastics, more than 26 million tons of post-consumer plastic waste are generated annually in Europe alone. This makes plastic a major source of environmental pollution. Only 69% of post-consumer plastic waste is recycled in Europe (either through recycling or energy production), while 31% still ends up in landfills. Additionally, careless disposal of plastic waste in developing countries aggravates the environmental problem. As plastics undergo meteorization in the environment, their particle size decreases, leading to the emergence of microplastics as a kind of persistent contamination.

Microplastics (MPs) are small plastic particles, ranging in size from 0.1 to 5 mm [4,5], that have become a growing environmental concern due to their prevalence in aquatic and terrestrial environments [6] since, once released into the environment, microplastics can persist for decades, and potentially centuries, due to their resistance to degradation.

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The occurrence of microplastics in the environment has been documented in various habitats, including oceans, rivers, lakes, soils, and even the air [4–11]. They are ingested by a wide range of organisms, from plankton to fish to birds, and have been found in human tissues as well.

The potential dangers associated with microplastics in the environment include physical harm to organisms, as well as the potential for the release of toxic chemicals contained within the plastics [7,12]. Microplastics can block digestive tracts, inhibit feeding, and impair reproduction in organisms, which can have cascading effects throughout ecosystems.

As a result of these concerns, there has been increasing interest in the development of methods for the removal of microplastics from the environment, particularly from water. The use of catalytic processes is one such approach that has shown promise for the degradation of microplastics [13].

This review article will focus on recent advances in catalytic processes for the removal of microplastics from water, including various types of catalysts and their applications. The article will also discuss the potential for catalytic processes to be integrated into real-world water treatment systems for the removal of microplastics. By highlighting the challenges and opportunities associated with the removal of microplastics from the environment, this review aims to contribute to the development of more effective and sustainable methods for addressing this growing environmental issue.

2. The ubiquity and diversity of microplastics in the environment

Microplastics are ubiquitous in the environment and can come in many different forms. Some of the most commonly found microplastics include microbeads, fibers, fragments, foam particles, film particles, micro pellets, industrial beads, and paint chips. These microplastics have been found in a wide range of environments, including oceans, rivers, lakes, and even in drinking water. Microplastics are a significant concern in the current environmental scenario due to their long-lasting and indestructible nature [14]. They are tiny, lightweight particles that can be easily ingested by aquatic organisms, animals, and birds, leading to their accumulation in the food chain [15] and eventual ingestion by humans. These particles have a high surface area-to-volume ratio and an extraordinary vector capacity that enables them to adsorb various toxic contaminants.

Studies have shown that microplastics can be present in large quantities in the environment [9], with concentrations as high as 150, 000 particles per square kilometer in some areas [16]. For example, microbeads, which are commonly used in personal care products and cleaning products, have been found in concentrations of up to 4.1% of the total weight of plastics in the Great Lakes region of North America [17]. Fibers, which are shed from textiles and clothing during washing, have been found in concentrations ranging from 1700 to 7000 fibers per cubic meter in wastewater treatment plants [18,19].

Fragments, which are small pieces of plastic that result from the degradation of larger plastic items, such as bags and bottles, have been found in concentrations ranging from 0.1 to 23.6 particles per cubic meter in rivers and lakes. Foam particles, which are commonly used in packaging materials and insulation, have been found in concentrations ranging from 0.4 to 8.4 particles per cubic meter in rivers and estuaries. Film particles, which are commonly used in packaging materials, have been found in concentrations ranging from 0.2 to 9.2 particles per cubic meter in rivers and lakes [10,20,21].

Micro pellets, which are raw materials used in plastics manufacturing, have been found in concentrations ranging from 0.5 to 14.6 particles per cubic meter in rivers and estuaries. Industrial beads, which are used as abrasives and blasting materials, have been found in concentrations ranging from 3.3 to 16.3 particles per cubic meter in rivers and lakes. Paint chips, which are produced by the degradation of coatings and paints, have been found in concentrations ranging from 0.01 to 4.9 particles per cubic meter in rivers and lakes.

For instance, MPs can absorb chemicals such as polychlorinated biphenyls (PCBs) [22,23], which are commonly used in electrical equipment and have been linked to several health hazards. Similarly, polycyclic aromatic hydrocarbons (PAHs) are byproducts of incomplete combustion, commonly found in car exhausts, and are known to cause cancer and other diseases [24,25]. Polybrominated diphenyl ethers (PBDEs), which are flame retardants used in several household products, are also known to be harmful to human health [26–28]. Additionally, heavy metals such as lead, cadmium, and mercury can accumulate in microplastics, posing a significant risk to human health [14].

Table 1 provides a breakdown of different types of microplastics based on their size range and environmental occurrence [8,20,21, 28–37]. These microplastics are commonly found in personal care products, packaging materials, textiles, and other consumer products, and they pose significant environmental risks.

3. Microplastics identification and quantification

Visual observation is a suitable method for identifying large plastic particles (>1 mm). Manual sorting based on physical characteristics such as color, shape, and hardness is used, aided by optical microscopes, electron microscopes, and scanning probe microscopes. Scanning electron microscopy (SEM) provides high magnification and clear images, enabling the distinction between microplastics and organic particles. Various shapes and sizes of microplastics can be accurately determined using SEM [38,39]. This assessment requires a significant amount of time, trained personnel, and is a difficult process to automate, with the disadvantage of not being able to detect all present particles. Therefore, a preselection of samples needs to be performed prior to measurements, which poses a limitation on the species that can be identified [40].

In addition to imaging, AFM has also been utilized for the quantification of microplastics [39]. By analyzing the force interactions between the probe and the microplastic particles, it is possible to estimate their mechanical properties, such as stiffness and elasticity. This information is valuable for understanding the behavior and degradation mechanisms of microplastics in different environments.

Other techniques, such as Fourier transform infrared (FTIR) spectroscopy, are used to identify the composition of microplastics by analyzing their chemical bonds . FTIR is advantageous due to its simple operation and accurate identification, although it can be time-consuming and limited in detecting smaller particles. Raman spectroscopy is another technique that provides molecular structure information [39] and can be used to observe microscopic features of microplastics. It has higher spatial resolution and is not sensitive to interference signals from water and atmospheric carbon dioxide but may be affected by fluorescence.

In the context of microplastic degradation, H NMR [41,42] analysis allows for the identification and quantification of the resulting products from plastic decomposition. This technique provides detailed information about the molecular structure of the degradation products, aiding in

Table 1
Classification of microplastics by size and environmental occurrence.

Microplastic Type	Size Range (mm)	Environmental Occurrence
Microbeads	0.1–1	Personal care products, cleaning products
Fibers	<5	Textiles, clothing, fishing nets, ropes
Fragments	<5	Degradation of larger plastic items, such as bags and bottles
Foam particles	<5	Packaging materials, insulation
Film particles	<5	Packaging materials
Micro pellets	<5	Raw material in plastics manufacturing
Industrial beads	<5	Abrasives, blasting materials
Paint chips	<5	Coatings, paints

the understanding of the decomposition processes and their final products. H NMR analysis can reveal changes in functional groups and chemical bonds present in the degradation products of microplastics. This is particularly useful for determining the chemical composition of the degradation products and comparing them to the original plastic monomers.

Pyrolysis gas chromatography/mass spectrometry (Pyr-GC/MS) is commonly used for polymer characterization [43], offering qualitative and quantitative analyses of microplastics. Quality assurance and quantity control are crucial during sampling, including wearing appropriate clothing, sealing samples to avoid environmental interference, conducting blank tests, and comparing collected samples with standards. Non-plastic materials and careful cleaning procedures are employed to minimize contamination during analysis.

A variant of this method, as developed by Dumichen et al. [40], involved the quantification of polyethylene microplastic polymers in solid environmental samples using a technique that involves thermal decomposition. This is based on thermogravimetric analysis followed by solid-phase extraction (TGA-SPE), to which the obtained absorbents are then analyzed by thermal desorption gas chromatography-mass spectrometry (TDS-GC-MS), resulting in higher sensitivity than pyrolysis gas chromatography-mass spectrometry (Py-GC-MS). With this technique, polymer particles present in environmental samples can be studied without any preselection or visual analysis. In this way, thermogravimetric Analysis (TGA) is a technique commonly used for the identification of microplastics [41]. TGA can provide valuable information on their thermal stability and decomposition temperature, aiding in their identification and differentiation from other organic or inorganic particles, contributing to a better understanding of their environmental presence and impact.

In conclusion, a combination of visual observation, microscopy techniques, spectroscopy, and chromatography/mass spectrometry, and resonance methods provides valuable tools for the identification and characterization of microplastics in various environmental samples. Each technique has its advantages and limitations, and their appropriate selection depends on the specific research objectives and sample characteristics.

4. Methods to degrade microplastics

As concerns about the presence of MPs in the aqueous environment grow daily, research into methods of removing these emerging plastic pollutants is being rigorously studied. Thus, in recent years, removal strategies, including physical, chemical, and biological treatments, have been reported [15]. As for the biodegradation method, in which micro-organisms that adhere to the surface of the plastic, deteriorate it and cause its disintegration into oligomers, dimers, and monomers [44], the main limitation is determined by the unduly long degradation period (up to months) [45].

On the other hand, the incineration method proved to be much faster and more efficient for the degradation of MPs [44]. However, the incineration produces the emission of more toxic by-products, including toxins, such as toxicants and polycyclic aromatic hydrocarbons. In general, conventional techniques are not effective for the removal of MP. Furthermore, additional treatment is still necessary for the complete decomposition of MP, as most of the disposal of MPs by conventional processes consists only of physical separation from the environment.

The subsequent paragraphs provide an in-depth exploration of the primary techniques used to degrade microplastics, with a particular focus on catalyst-driven processes. These methods encompass Biological Methods, Advanced Oxidation processes, and Hydrolysis processes.

4.1. Biological methods

Nowadays, there is a strong trend towards biodegradation, including the degradation of microplastics to obtain environmentally friendly compounds. This process is mediated by different microorganisms and biological catalysts (enzymes). In the case of cell cultures, microplastics are used as a carbon source in the growth medium of the microorganism, resulting in increased biomass levels and the decomposition of plastic metabolic intermediates into monomeric units, followed by the mineralization of these monomeric intermediates [39,41,42]. In enzymatic degradation, plastic polymers are broken down into carbon dioxide, water, and bioproducts [46,47,45].

For example, the work of Paço et al. [42]demonstrated that strains of the fungus *Zalerion maritimum*, a native fungus from the coast of Portugal, were able to degrade polyethylene when subjected to different exposure times in batch cultures with a diluted growth medium. The best result was found after 14 days of incubation, where the removal of the polymeric materials exceeded 43%.

Another example mentioned in the literature is the degradation of high-impact brominated polystyrene (HIPS) by *Pseudomonas spp* and *Bacillus spp*, as described by Mohan et al. [41]. In this work, HIPS was used as the sole carbon source in the culture medium for these bacterial strains, and results showed a reduction in turbidity after 4 days of culture, with values of 94% for *Bacillus spp* and 97% for *Pseudomonas spp*.

Peixoto et al. isolated nine types of bacteria from the Brazilian Cerrado soil with potential abilities to degrade polyethylene (PE). Among them, they mentioned that genera such as *Comamonas, Delftia*, and *Stenotrophomonas* have shown metabolic and cellular activity after 90 days of incubation when subjected to a culture medium with polyethylene as the sole carbon source, effectively degrading the plastic waste. Peixoto et al. (2016) [39] found that the studied microorganisms are capable of degrading polyethylene without pre-treatment of very high molecular weight, and they can survive for long periods under the tested conditions.

Regarding enzymatic degradation, [47] present advancements in the degradation of polyethylene terephthalate (PET) using biocatalysts such as hydrolases, elucidating their mechanism of action and improving factors such as catalytic efficiency, solubility, and productivity. They also discuss the immobilization of biocatalysts on supports for reuse, aiming to reduce the production cost on a large scale, making this "green" degradation process attractive for industrial applications.

Amobonye et al. [46] conducted a study on the enzymatic degradation of organic polymers, classifying biological catalysts into two categories: extracellular and intracellular enzymes. They emphasize that most of the literature focuses on extracellular enzymes such as hydroxylases, laccases, peroxidases, and reductases, as they have a wide range of degradation actions on microplastics. These mentioned enzymes are found in microorganisms such as algae, bacteria, and fungi.

Fig. 1 illustrates the various biological processes involved in microplastic degradation and highlights the factors that influence this degradation process. The figure showcases the key steps involved in the biodegradation of microplastics. The first step in the process is the utilization of microplastics as a carbon source by microorganisms. These microorganisms metabolize the plastic polymers, leading to the production of monomeric units and eventually the mineralization of these units into harmless byproducts. Enzymatic degradation plays a crucial role in this process, with extracellular enzymes like hydroxylases, laccases, peroxidases, and reductases [45] being particularly effective in breaking down microplastics. The figure also highlights the factors that can significantly impact the efficiency and effectiveness of the degradation process, underscoring the need for careful optimization and control in biodegradation studies.

In conclusion, the growing interest in biodegradation, including the degradation of microplastics, is fueled by the promising results obtained through the utilization of microorganisms and biological catalysts. The studies mentioned above demonstrate the potential of cell cultures and enzymatic degradation in breaking down plastic polymers into environmentally friendly compounds. As research continues to advance, the application of these "green" degradation processes holds great promise for mitigating the environmental impact of plastic waste.

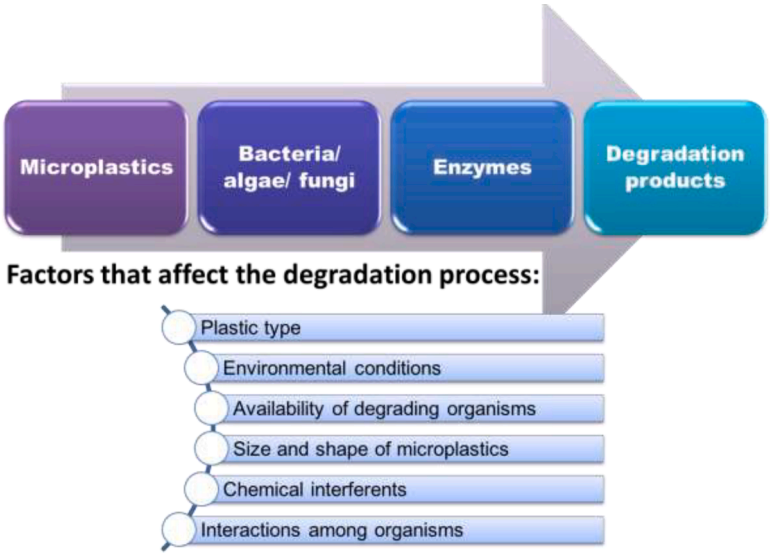

Fig. 1. Biological Processes and Factors Affecting Microplastic Degradation.

4.2. Advanced oxidation processes

An alternative chemical method of lower energy are the advanced oxidation processes (AOPs) that produce highly reactive radicals that can oxidize and decompose organic contaminants [48]. One of these AOPs are the Fenton (and Fenton-like) processes, which use peroxides to generate reactive oxygen species. AOPs utilize highly reactive radical species such as HO•, $O•^{-2}$, $HO•^{2}$, RO•, $SO•^{-4}$, and Cl• to facilitate the process [49]. Hydrogen peroxide and ozone are both strong oxidants that can effectively break down microplastics in the environment. Hydrogen peroxide (H_2O_2) is a readily available and relatively inexpensive oxidant that can be used in a variety of applications.

Due to the slow pace of natural degradation and the possibility of leaving fragments, additional methods are necessary to ensure complete degradation. Consequently, chemical-based techniques have been developed, as mentioned by Cholewinski et al. [50]. However, certain methods require high temperatures, which is a drawback, as noted by Wang et al. [51]. To address this energy issue, advanced oxidation processes (AOP) have become the most widely used method of chemical degradation.

Through photocatalysis, photons activate the catalyst, producing electron-hole pairs that initiate a redox reaction with the adsorbed pollutants. In Fenton/Fenton-like processes, the reaction of hydrogen peroxide with metallic active phase (ex: Fe^{+2}) produces hydroxyl radicals that can oxidize and degrade the pollutants [13,52,53].

TiO_2 nanoparticles have also been shown to be effective in breaking down microplastics through photocatalytic reactions when exposed to UV light. Modifying TiO_2 with Ag metals or graphene proves to be effective in increases the photocatalyst performance of TiO_2, Fadli et al. [54] studied the photocatalytic activity of TiO_2 in the degradation of microplastics under UV radiation.

Similarly, Co_3O_4 nanoparticles have been shown to enhance the oxidative degradation of microplastics under visible light irradiation [55,56]. As an example, Din et al. [56] synthesized Co_3O_4/BOC heterostructures using a solvothermal method to enhance their photocatalytic performance for the degradation of Rhodamine-B (RhB) and Bisphenol-A (BPA). The results showed that the 20-Co_3O_4/BOC heterostructure had a significantly higher degradation efficiency compared to pure $Bi_{12}O_{17}Cl_2$ (BOC), with RhB degraded by 97.4% and BPA by 88.4%. The hierarchical Co_3O_4/BOC heterostructure was found to have a higher specific surface area and to extend light absorption to the visible light region, which, along with the suppression of photoexcited electron-hole recombination, led to the improved photocatalytic performance. The developed nanocomposites are promising for use in high-performance photocatalytic applications for microplastic degradation. This study highlights the potential of Co_3O_4 as an efficient catalyst for degrading MPs and provides insights into the development of effective photocatalytic methods for environmental remediation.

Table 2 presents a compilation of materials utilized in combination with diverse light sources for the purpose of microplastic degradation. These materials have demonstrated their efficacy in effectively breaking down microplastics across different environmental scenarios.

Maulana et al. [58] synthesized Ag/TiO_2 nano-composites and evaluated their efficacy in degrading microplastics in water, specifically varying sizes of polyethylene microplastic particles as pollutants in drinking water. The Photo Assisted Deposition (PAD) method was utilized for synthesizing Ag/TiO_2, and characterizations were performed using SEM-EDX and UV–Vis Diffuse Reflectance Spectroscopy to compare TiO_2 and Ag/TiO_2. The microplastics had varying sizes of 100–125, 125–150, and 150–250 micrometers with an initial concentration of 100 ppm. Magnetic stirrers were used at 2000 rpm during the degradation process, which was aided by UV lamp irradiation. The addition of Ag dopant demonstrated a significant improvement in microplastic degradation, reaching 100% degradation within 120 min of irradiation at an initial concentration of 100 ppm. The best percent degradation was achieved at a particle size of 125–150 micrometers, with 100% degradation achieved after 90 min of irradiation at an initial concentration of 100 ppm.

Zinc oxide (ZnO) has been extensively used as a photocatalyst in water and wastewater treatments due to its high redox potential, superior catalytic performance, and enhanced electron mobility. Hexagonal ZnO nanorods offer higher surface area and stability, leading to an efficient photo-oxidation process. To improve photocatalysis, ZnO can

Table 2
Examples of materials and light sources commonly employed for Microplastic Removal.

Light source	Example Material	Refs.
Visible light irradiation	ZnO	[57]
UV	TiO_2	[58]
Visible light irradiation	Co_3O_4	[56]
UV	TiO_2	[59]
UV	TiO_2/$Fe(St)_3$	[60]
UV	Ag/ TiO_2	[58]
UV-C	ZnO	[61]
UV-C	ZnO-Pt	[61]

be modified with metals, nonmetals, and carbon materials to enhance electron-hole pair separation and optical characteristics [61]. In the study of Tofa et al. [61], Platinum, a plasmonic metal, has been shown to improve photocatalytic efficiency by reducing electron-hole pair recombination and enhancing visible light absorption when deposited on ZnO. In this study, platinum nanoparticles were deposited on ZnO nanorods, resulting in over 15% improvement in photocatalytic performance under visible light. ZnO-Pt showed effective degradation of microplastic pollutants like residual low density polyethylene (LDPE) films in water, with ca. 13% higher potential for oxidation than as-grown ZnO nanorods. Modifying ZnO with plasmonic metals could be a promising approach to accelerate the oxidation of microplastic pollutants in water using sunlight.

4.2.1. Mechanisms of microplastic degradation in advanced oxidation processes

The degradation of microplastics by advanced oxidation processes involves complex reaction mechanisms that can vary depending on the specific AOP employed. It is important to note that the specific mechanisms and reaction pathways can vary depending on the AOP used, the properties of the microplastics, and the environmental conditions. Furthermore, the presence of other chemicals, such as catalysts or additives, can also influence the degradation process.

A common mechanism in AOPs is the generation of highly reactive hydroxyl radicals (•OH) that react with microplastics (See Fig. 2). This process typically involves the following steps:

a. Generation of •OH: AOPs, such as photocatalysis using semiconductors like titanium dioxide (TiO_2) or Fenton-like reactions using iron (Fe) catalysts, produce •OH radicals through reactions with oxidizing agents or light energy. **b**. Adsorption of •OH: The •OH radicals adsorb onto the surface of microplastics. **c**. Initiation of degradation: The adsorbed •OH radicals react with the polymer chains, leading to the cleavage of chemical bonds and the formation of reactive intermediates. **d**. Further oxidation: The reactive intermediates undergo subsequent oxidation reactions with •OH radicals, resulting in the formation of smaller fragments or degradation products.

During the *photocatalytic degradation* of microplastics using TiO_2, the highly reactive hydroxyl radical (•OH) attacks the C–H bond present in the polymer molecules. The hydrogen atom from the C–H bond combines with the •OH radical, forming water as a byproduct. This process results in the formation of a carbon-centered radical in the remaining polymer molecule, with an unpaired electron on the carbon atom. The introduction of carbon-centered radicals into the polymer chain allows them to undergo continuous reactions with various reactive oxygen species (ROS), see Eqs. (1)–(7). These reactions lead to the breaking of polymer chains and the formation of hydroxyl derivatives, carboxyl groups, and carbonyl intermediates [62]. Additionally, intermediates such as CO_2 and H_2O are also produced during the degradation process [63].

$$PH\ (polymer) + \ \bullet OH \rightarrow \bullet P + H_2O \quad (1)$$

$$\bullet P + O_2 \rightarrow \bullet POO \quad (2)$$

$$PH + HO_2^{\bullet} \rightarrow \bullet P + H_2O_2 \quad (3)$$

$$\bullet POO + PH \rightarrow POOH + \ \bullet P \quad (4)$$

$$\bullet POO + PH \xrightarrow{hv} \bullet PO + \ \bullet OH \quad (5)$$

$$\bullet PO + PH \xrightarrow{hv} POH + \ \bullet P \quad (6)$$

$$\bullet PO \xrightarrow{chain\ \ cleavage} Intermediates + CO_2 + H_2O \quad (7)$$

Yang et al. [64] aimed to analyze the degradation pathway of polystyrene microplastics (PS-MPs) by detecting the water-soluble low-molecular-weight products using GC-MS. After 14 days, a benzene ring derivative, and nonahexacontanoic acid were detected. These compounds likely originated from the low-molecular-weight products generated during the chain depolymerization of long-chain molecules of PS-MP. Then, the process of chain breaking occurred in both normal and weak chains, resulting in the formation of terminal radicals. These radicals had the capability to react with molecular oxygen, leading to

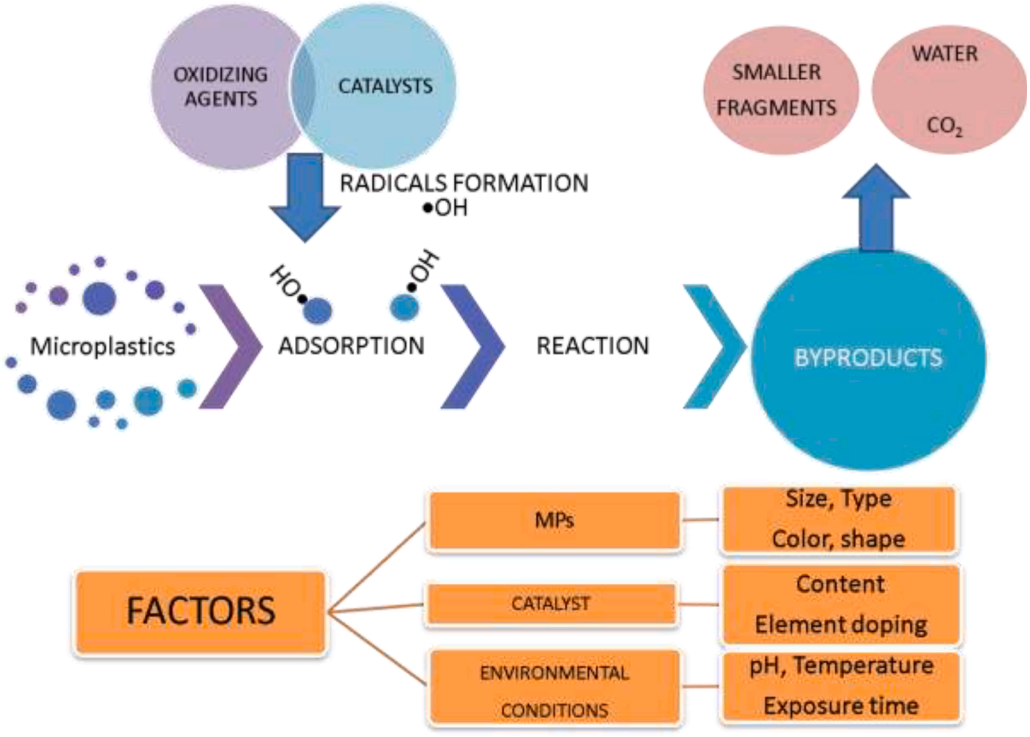

Fig. 2. Mechanisms of microplastic degradation in advanced oxidation processes.

the generation of peroxy radicals. The peroxy radicals then formed stable groups on the polymer chain through hydrogen abstraction, such as -OH. Through recombination and other reactions, such as radical addition, the -OH groups transformed into -COOH, -C = O, and other functional groups. As the reaction time extended and the intensity deepened, a succession of low-molecular-weight products emerged. Examples of such products include 2-isopropyl-5-methyl-1-heptanol and nonahexacontanoic acid.

In conclusion, advanced oxidation processes (AOPs) offer a chemical approach to the degradation of microplastics by utilizing highly reactive radicals to oxidize and decompose organic contaminants. AOPs such as Fenton and Fenton-like processes, as well as photocatalysis, have shown promising results in breaking down microplastics into smaller fragments and degradation products. The generation of highly reactive hydroxyl radicals (•OH) plays a crucial role in the degradation process, where these radicals react with the surface of microplastics, initiating the cleavage of chemical bonds and forming reactive intermediates. Further oxidation reactions with •OH radicals lead to the formation of smaller fragments and degradation products. The specific mechanisms and reaction pathways can vary depending on the AOP used, the properties of the microplastics, and the environmental conditions. The addition of dopants and modifications to photocatalysts such as TiO_2 and ZnO have been explored to enhance the photocatalytic performance and extend light absorption to visible light regions. Overall, AOPs present a promising approach for the complete degradation of microplastics and offer potential solutions for mitigating the environmental impact of plastic waste.

4.3. Hydrolysis

Hydrolysis is a method used for the degradation of microplastics in which the polymer chains are broken down by the reaction with water. The hydrolysis process can be carried out in either acidic or basic conditions, depending on the nature of the polymer. Fig. 3 describes the materials that can be degraded using hydrolysis with either acidic or basic solutions.

In acidic hydrolysis, strong acids such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) are used to break down the polymer chains . Polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polymethyl methacrylate (PMMA), polylactic acid (PLA), Nylon, polybutylene terephthalate (PBT), and polyoxymethylene (POM) are some of the common materials that can be degraded using acidic hydrolysis [65–68].

In basic hydrolysis, strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are used to break down the polymer chains. PET, PVC, PS, PLA, Nylon, PBT, and POM are some of the common materials that can be degraded using basic hydrolysis [67,69,70].

For example, the study of Sarno et al. [71] focused on developing an accelerated hydrolytic degradation method using alkaline hydrolysis, which is commonly used in the softening process of PET fabrics and chemical recycling of PET. The researchers tested PET degradation at different pH values and temperatures to optimize the process. Results showed that an aqueous solution with pH 14.4 (10% NaOH) was the most effective in hydrolyzing PET microplastic fiberss, with lower pH values resulting in insignificant hydrolysis. A temperature of 90 °C was also found to significantly reduce the hydrolysis time compared to 60 and 70 °C, with over 90% degradation achieved after 3 h and complete degradation after 24 h.

The authors also conducted PET degradation using UV rays, simulating solar exposure in a marine environment. Physical changes such as small holes in the fibers were observed after ~33 days, but significant morphological changes were evident at 5 months, which further pronounced after 10 months of exposure, corresponding to approximately 7.5 years under natural environmental conditions.

As a result, both UV exposure and accelerated hydrolysis tests generated partially degraded PET fibers exhibiting many physical similarities between the two methods, such as a change from a smooth surface to an irregular one and the formation of cracks and holes along the length of the fiber.

This method provides an efficient way to degrade PET materials, which can be useful in various applications such as the production of partially degraded PET microplastic fibers reference materials for fate and effect studies.

Regarding acid hydrolysis, the study conducted by Yoshioka et al. in 1994 [65] demonstrated the hydrolysis of PET powder using relatively

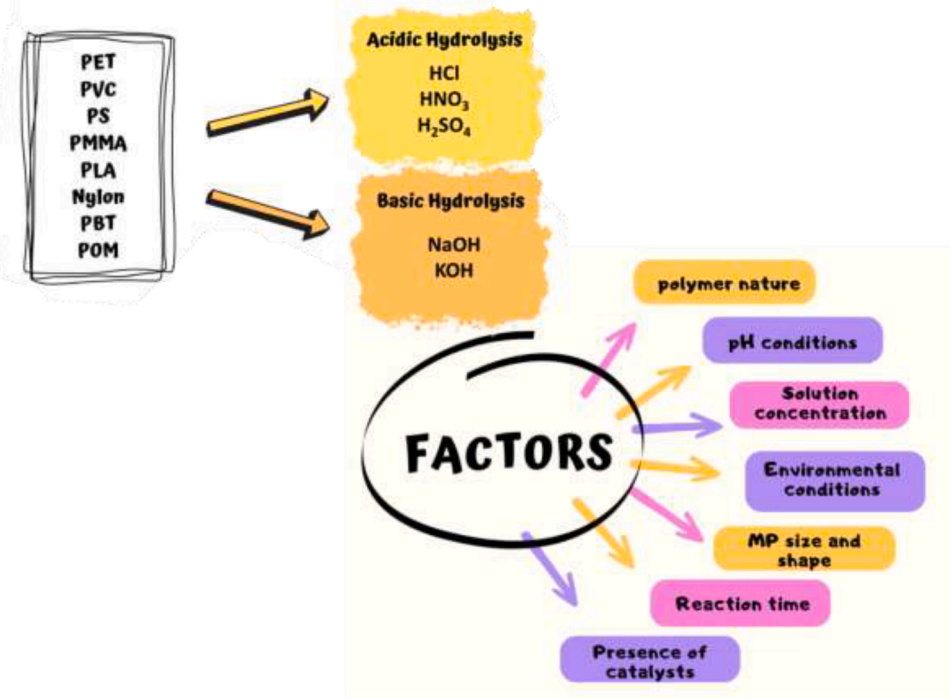

Fig. 3. Acidic and basic hydrolysis conditions for degradation of common microplastics.

diluted sulfuric acid (H_2SO_4). The percentage of PET degradation was evaluated at various concentrations of H_2SO_4 (ranging from 1 to 10 M), revealing a progressive increase in degradation at a concentration of 5 M. At 6 M, degradation rapidly increased to 48.7% by weight. At 7 M, the degraded amount reached 95.5% by weight, and complete degradation was achieved at a concentration of 10 M. The authors suggest that H_2SO_4 can be reused through recovery methods like dialysis.

Yang et al. (2021) [66] studied PET hydrolysis using terephthalic acid (TA), one of the PET units, as an acid catalyst. The hydrolysis was conducted within a temperature range of 180 °C to 220 °C, with a reaction time ranging from 60 to 240 min. The best performance was observed at 220 °C and 180 min, resulting in up to 100% PET conversion and a 95.5% TA yield. Since the recovered TA exhibited high purity (99%), it could be reused for eight consecutive reaction cycles while maintaining hydrolysis efficiency. This presents an environmentally friendly, feasible, and cost-effective technology for recovering TA and utilizing it in new PET waste hydrolysis processes.

Deshoulles et al. [72] investigated the chemical degradation of 6-polyamide by combining oxidation and hydrolysis techniques. Their objective was to achieve the removal of secondary microplastics, which originate from larger plastics, in the marine environment. For the study, polymer films were aged for different periods (up to 2 years) and subsequently characterized using differential scanning.

It was found that the degradation rate is 80 times faster in oxygenated water than in oxygen-free water. Once the degradation techniques were optimized, the two sequential stages were performed: first, thermal oxidation in dry air, followed by hydrolysis in oxygen-free water to simulate an aging state and further study the nature of coupling.

During thermal oxidation, the formed chemical products are carboxylic acids and imides, and the latter undergo the hydrolysis process, resulting in a rapid decrease in their concentration during immersion. This indicates that the hydrolysis of this chemical group seems to be involved in the degradation process of the polyamide. The results obtained revealed a synergy between oxidation and hydrolysis in 6-polyamide, establishing a chemical interaction, as they clearly show that the polymer degradation level is much faster when the samples are placed in a humid environment compared to dry air. Furthermore, the higher the humidity level, the higher the degradation rate. However, the degradation rate is not of the same magnitude as the results in oxygenated water. This means that, at least for 6-polyamide, the synergy between various aging sources needs to be carefully considered, and further study is necessary, especially when considering accelerated aging to understand the formation of microplastics in the oceans, as they are subjected to different aging sources such as UV rays, water, oxygen, and the living environment. These factors were not taken into account in this study, so the authors propose further experiments in the future.

Overall, the removal of microplastics from the environment is a complex issue that requires a multifaceted approach. While there is still much to be learned about the long-term impacts of microplastics on the environment and human health, it is clear that action is needed to prevent further accumulation and to develop effective methods for their removal.

5. Advances and limitations

The field of microplastic degradation has seen significant advancements in recent years, particularly in the development of removal strategies using physical, chemical, and biological treatments. Among these methods, biological degradation shows promise, utilizing microorganisms and biological catalysts to break down plastic polymers into environmentally friendly compounds. The use of cell cultures and enzymatic degradation has demonstrated successful results in the decomposition of various types of microplastics. For example, studies have shown the ability of certain microorganisms to degrade polyethylene and high-impact brominated polystyrene, leading to significant reductions in plastic waste.

Enzymatic degradation, in particular, has shown advancements in the degradation of specific types of plastics, such as polyethylene terephthalate (PET). Researchers have focused on improving factors such as catalytic efficiency, solubility, and productivity of enzymes to enhance the degradation process. The immobilization of biocatalysts on supports for reuse has also been explored, aiming to reduce production costs and make the degradation process more attractive for industrial applications.

On the chemical front, advanced oxidation processes (AOPs) have emerged as effective methods for microplastic degradation. These processes generate highly reactive radicals that can oxidize and decompose microplastics. For example, photocatalysis using semiconductors like titanium dioxide (TiO_2) and Fenton-like reactions using iron (Fe) catalysts have been studied extensively. These AOPs produce hydroxyl radicals (•OH) that react with microplastics, leading to the cleavage of chemical bonds and the formation of smaller fragments or degradation products.

However, despite these advancements, there are still limitations to consider. In the case of biodegradation, the main limitation is the unduly long degradation period, which can take up to months. This slow pace of degradation necessitates additional methods to ensure complete degradation. Chemical-based techniques, such as AOPs, have been developed to address this issue, but some of these methods require high temperatures, which can be a drawback. The emission of toxic by-products, including toxins and polycyclic aromatic hydrocarbons, is another concern associated with certain degradation methods, such as incineration.

Advances in the hydrolysis process for microplastic degradation have shown promising results. Acidic and basic hydrolysis methods have been developed to break down various types of polymers, including PET, PVC, PS, PLA, Nylon, PBT, and POM. Researchers have optimized the hydrolysis conditions by testing different pH values and temperatures, leading to efficient degradation of microplastics. Additionally, studies have explored alternative catalysts like terephthalic acid (TA) and combined oxidation and hydrolysis techniques for enhanced degradation. These advancements offer environmentally friendly and cost-effective approaches, such as recovering TA for reuse and removing secondary microplastics in the marine environment.

However, there are limitations to consider. Hydrolysis processes may require strong acids or bases, which can be corrosive and challenging to handle safely. Furthermore, hydrolysis methods may not achieve complete degradation, leaving behind partially degraded microplastics with potential environmental impacts. Long-term effects of microplastics and their degraded byproducts on ecosystems and human health are still being studied. Moreover, the optimization of hydrolysis techniques should account for factors like UV exposure and various aging sources in real-world environmental conditions. Continued research and experimentation are necessary to address these limitations and develop comprehensive strategies for microplastic removal.

In conclusion, while significant advances have been made in the field of microplastic degradation, there are still challenges and limitations that need to be addressed. Further research and development are needed to optimize and refine the existing methods, ensuring complete degradation of microplastics without generating harmful by-products. It is crucial to continue exploring innovative approaches, such as biological degradation, advanced oxidation processes, and hydrolysis, while also considering the long-term environmental and health impacts of these degradation techniques. By taking a multifaceted and comprehensive approach, we can work towards effective and sustainable solutions for the removal and mitigation of microplastics from our environment.

6. Hybrid catalysts systems

Hybrid catalyst systems have shown great potential in the elimination of microplastics. These systems combine two or more types of catalysts to enhance the degradation efficiency of microplastics. For

example, a hybrid catalyst system may combine the use of a photocatalyst and an enzymatic catalyst to achieve faster and more efficient degradation of microplastics.

The use of hybrid catalyst systems offers several advantages over traditional single catalyst systems. One major advantage is the increased effectiveness of the degradation process. The combination of multiple catalysts can lead to faster degradation of microplastics and higher rates of conversion of the plastics into harmless byproducts.

In the study of Miao et al. [73], the authors propose an electro-Fenton-like technology using a TiO_2/graphite (TiO_2/C) cathode for the efficient degradation of polyvinyl chloride (PVC) microplastics in water. The technology demonstrates a remarkable performance in degrading PVC through cathodic reduction dechlorination and hydroxyl radical (•OH) oxidation simultaneously. The effects of reaction temperature and initial PVC concentration were investigated, and optimal conditions achieved a 75% dechlorination efficiency after 6 h of potentiostatic electrolysis. The study also explores the intermediate products and proposes a possible degradation process for PVC. Overall, the TiO2/C cathode-based electro-Fenton-like technology offers an eco-friendly method for microplastic wastewater treatment. The findings show a significant removal of PVC microplastics and suggest the potential application of this technology for other chlorinated species or plastics.

In the Celik et al. (2019) work [74], the authors present a catalytic process for the transformation of polyethylene (PE) into valuable liquid products, such as lubricants and waxes, using Pt nanoparticles supported on $SrTiO_3$ perovskite nanocuboids. The catalytic system efficiently converts PE samples of various molecular weights into high-quality products under solvent-free conditions at 300 °C and 170 psi H_2. The binding of PE onto the catalyst surface contributes to the narrow distribution and high molecular weight of the resulting liquid products. The $Pt/SrTiO_3$ catalyst demonstrates superior performance compared to Pt/Al_2O_3, showing selective hydrogenolysis of longer PE chains while minimizing the production of light hydrocarbons. The study highlights the importance of catalyst design and the role of Pt nanoparticle size, distribution, and nanoparticle-support interactions in achieving efficient and selective PE hydrogenolysis. The findings suggest the potential for developing catalytic materials with ordered and organized structures for further advancements in upcycling catalysis. This research contributes to mitigating plastic pollution and promoting the circular economy by converting waste PE into value-added products.

In other study [75], the authors demonstrate the effective conversion of polypropylene (PP) plastic waste into valuable lubricant-range hydrocarbons using ruthenium deposited on titania (Ru/TiO_2) catalysts. The catalytic process operates at low temperatures (250 °C) and modest reaction times, with high oil yields (66–80%) and low gasification. The catalyst shows versatility in processing different types of polypropylene, including isotactic, amorphous, and varying molecular weights, producing similar products. The resulting lubricant-range hydrocarbons possess promising properties for use as base oils, offering potential applications in the circular economy. The study reveals the complex reaction network and evolution, involving sequential polymer conversion, gradual molecular weight reduction, and gradual liquid gasification. The catalytic mechanism involves dynamic adsorption/desorption and internal C-C bond breaking, facilitated by the loss of polymer stereoregularity and demethylation of the polymer backbone. The resulting oil exhibits reduced tertiary carbon content and enhanced cracking reactivity, minimizing gas production. The findings highlight the potential for engineering plastic recycling and upcycling processes, with the Ru/TiO_2 catalyst offering an exciting approach to address the environmental challenges associated with plastic waste.

On the other hand, Jie Ye et al. [76] address the issue of low selectivity in conventional processes and propose a biotic-abiotic photocatalytic system by combining Methanosarcina barkeri (M. b) and carbon dot-functionalized polymeric carbon nitrides (CDPCN). This system effectively converts microplastics into methane, providing a new method for the reuse of non-biodegradable plastic. The study demonstrates the applicability of M. b-CDPCN for this conversion process.

In the research of Paula Mayorga-Burrezo et al. [77], the authors investigated Fe_3O_4@$BiVO_4$ microrobots to study the effects of independent photocatalytic propulsion and simultaneous application of an external rotating magnetic field on their motion. They discovered that the magnetic motion of the microrobots could be disrupted by the generation of photoinduced species on their surface. This finding highlights the limitations of external magnetic field propulsion. The authors also utilized the photocatalytic magnetic microrobots to successfully remove cellulose acetate microfilaments, which are major contributors to microplastic pollution, from cigarette filters. Furthermore, they tested the microrobots' dynamics in a photodegradation context and found improved performance when light and the external rotating magnetic field were combined. These results have significant implications for the development of advanced functional microrobots with optimized photocatalytic capabilities and precise magnetic control, with potential applications in various fields.

Another advantage is the increased stability of the catalysts. In some cases, combining different types of catalysts can result in a more stable system that is less likely to degrade or lose effectiveness over time. This can be particularly important for large-scale applications where stability over long periods of time is critical.

The scalability of hybrid catalyst systems is also an advantage. By combining different types of catalysts, the systems can be tailored to specific applications and easily scaled up or down depending on the size of the system needed. This makes hybrid catalyst systems more adaptable to a wide range of scenarios, from small-scale laboratory tests to large-scale industrial applications.

However, hybrid catalyst systems also have some limitations that must be considered. One major limitation is the potential for increased cost. Using multiple types of catalysts can increase the overall cost of the system, especially if the catalysts are expensive or difficult to produce.

In addition, the use of hybrid catalyst systems requires careful design and optimization. The different catalysts must work together effectively to achieve the desired result, and the system must be carefully balanced to prevent one catalyst from overpowering or inhibiting the other.

Overall, the potential of hybrid catalyst systems in microplastics elimination is promising. With careful design and optimization, these systems could offer significant advantages in terms of effectiveness, stability, scalability, and adaptability. However, the potential for increased cost and the need for careful optimization must also be considered.

7. Future perspectives

The research on the degradation of microplastics and the development of removal strategies is an evolving field that holds great potential for addressing the issue of plastic pollution. As concerns about the presence of microplastics in the environment continue to grow, future perspectives in this area can be focused on the following aspects

Developing more efficient and cost-effective methods for removing microplastics from the environment, such as the use of hybrid catalyst systems and the optimization of existing biological methods, advanced oxidation processes and hydrolysis.

Minimizing the generation of toxic substances during the degradation process by improving the selectivity of chemical reactions or exploring new catalysts that promote cleaner degradation pathways.

Investigating the potential long-term impacts of microplastic contamination on ecosystems and human health, as well as evaluating the effectiveness of various mitigation strategies.

Increasing public awareness of the issue of microplastic pollution and promoting individual actions to reduce plastic waste, such as using reusable containers and supporting policies to reduce plastic production and consumption.

Developing new technologies for the detection and characterization

of microplastics, which can help to better understand their distribution and impact on the environment.

Scaling up and implementing degradation methods on a larger scale for effective mitigation of microplastic pollution. This involves developing cost-effective and scalable technologies that can be applied in real-world scenarios, such as wastewater treatment plants or plastic waste management facilities.

Considering the complex nature of microplastic pollution, future research should explore the integration of multiple strategies for microplastic removal. This can involve combining physical, chemical, and biological treatments to achieve comprehensive and efficient degradation of microplastics. Integrated approaches that leverage the strengths of different methods can lead to more effective removal and environmental remediation.

Overall, the future research in microplastics elimination should focus on the development and optimization of water treatment systems that integrate multiple physical, chemical, and biological processes. The scalability, cost-effectiveness, and environmental impact of these systems should also be evaluated to ensure their practical implementation in real-world settings.

8. Conclusion

In conclusion, microplastics have emerged as a significant environmental and human health concern, demanding the development of effective methods for their elimination. The pervasive use of plastics in daily life has resulted in the accumulation of microplastics, particularly in aquatic systems. Therefore, it is imperative to explore scalable and efficient approaches to address this issue.

Catalytic processes, including biological treatment, Advanced Oxidation Processes (AOPs), and hydrolysis, have demonstrated promise as potential methods for microplastics elimination. These techniques have shown effectiveness in laboratory studies, and some have been tested in real-world water treatment systems with encouraging results. However, it is crucial to overcome certain limitations associated with these processes, such as scalability, cost-effectiveness, and potential environmental impacts.

Future research should focus on the development of hybrid catalyst systems that harness the strengths of multiple processes to enhance efficiency and effectiveness. Furthermore, investigating the utilization of natural materials and biological processes for microplastics elimination could provide more sustainable and environmentally friendly options.

Real-world water treatment systems must also be developed and implemented to address the issue of microplastics in our water supply. These systems must be scalable, cost-effective, and efficient, while also considering potential environmental impacts. Collaboration between scientists, engineers, policymakers, and the public will be critical for the development and implementation of these systems.

In conclusion, the elimination of microplastics from the environment is a complex issue that requires a multifaceted approach. While there is no one-size-fits-all solution, advances in catalytic processes and water treatment systems offer promising avenues for progress. However, continued research and collaboration are necessary to develop effective and sustainable methods for microplastics elimination and to protect the health of our environment and communities.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

[1] R. Wei, W. Zimmermann, Microbial enzymes for the recycling of recalcitrant petroleum-based plastics: how far are we? Microb. Biotechnol. 10 (2017) 1308–1322, https://doi.org/10.1111/1751-7915.12710.
[2] L. Maiuolo, F. Olivito, V. Algieri, P. Costanzo, A. Jiritano, M.A. Tallarida, A. Tursi, C. Sposato, A. Feo, A. De Nino, Synthesis, characterization and mechanical properties of novel bio-based polyurethane foams using cellulose-derived polyol for chain extension and cellulose citrate as a thickener additive, Polymers 13 (2021), https://doi.org/10.3390/polym13162802 (Basel).
[3] Y. Gao, P. romero, H. Zhang, M. Huang, F. Lai, Unsaturated polyester resin concrete: a review, Constr. Build. Mater. 228 (2019), https://doi.org/10.1016/j.conbuildmat.2019.116709.
[4] M. Padervand, E. Lichtfouse, D. Robert, C. Wang, Removal of microplastics from the environment. A review, Environ. Chem. Lett. 18 (2020) 807–828, https://doi.org/10.1007/s10311-020-00983-1.
[5] A.A. Horton, A. Walton, D.J. Spurgeon, E. Lahive, C. Svendsen, Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities, Sci. Total Environ. 586 (2017) 127–141, https://doi.org/10.1016/j.scitotenv.2017.01.190.
[6] N.P. Ivleva, Chemical analysis of microplastics and nanoplastics: challenges, advanced methods, and perspectives, Chem. Rev. 121 (2021) 11886–11936, https://doi.org/10.1021/acs.chemrev.1c00178.
[7] P.K. Rose, M. Jain, N. Kataria, P.K. Sahoo, V.K. Garg, A. Yadav, Microplastics in multimedia environment: a systematic review on its fate, transport, quantification, health risk, and remedial measures, Groundw. Sustain. Dev. 20 (2023), 100889, https://doi.org/10.1016/j.gsd.2022.100889.
[8] A.L. Andrady, Microplastics in the marine environment, Mar. Pollut. Bull. 62 (2011) 1596–1605, https://doi.org/10.1016/j.marpolbul.2011.05.030.
[9] X. Shi, Z. Chen, L. Wu, W. Wei, B.J. Ni, Microplastics in municipal solid waste landfills: detection, formation and potential environmental risks, Curr. Opin. Environ. Sci. Health 31 (2023), 100433, https://doi.org/10.1016/j.coesh.2022.100433.
[10] R. Trevisan, S.M. Brander, S. Coffin, Microplastics in water and potential impacts on human health, Front. Water 4 (2022), https://doi.org/10.3389/frwa.2022.1101313.
[11] D. Gola, P. Kumar Tyagi, A. Arya, N. Chauhan, M. Agarwal, S.K. Singh, S. Gola, The impact of microplastics on marine environment: a review, Environ. Nanotechnol. Monit. Manag. 16 (2021), 100552, https://doi.org/10.1016/j.enmm.2021.100552.
[12] P.U. Iyare, S.K. Ouki, T. Bond, Microplastics removal in wastewater treatment plants: a critical review, Environ. Sci. 6 (2020) 2664–2675, https://doi.org/10.1039/d0ew00397b (Camb).
[13] Y. Jeong, G. Gong, H.J. Lee, J. Seong, S.W. Hong, C. Lee, Transformation of microplastics by oxidative water and wastewater treatment processes: a critical review, J. Hazard. Mater. 443 (2023), 130313, https://doi.org/10.1016/j.jhazmat.2022.130313.
[14] S. Sharma, S. Basu, N.P. Shetti, M.N. Nadagouda, T.M. Aminabhavi, Microplastics in the environment: occurrence, perils, and eradication, Chem. Eng. J. 408 (2021), 127317, https://doi.org/10.1016/j.cej.2020.127317.
[15] N. Badola, A. Bahuguna, Y. Sasson, J.S. Chauhan, Microplastics removal strategies: a step toward finding the solution, Front. Environ. Sci. Eng. 16 (2022) 1–18, https://doi.org/10.1007/s11783-021-1441-3.
[16] A. Cózar, F. Echevarría, J.I. González-Gordillo, X. Irigoien, B. Úbeda, S. Hernández-León, Á.T. Palma, S. Navarro, J. García-de-Lomas, A. Ruiz, M.L. Fernández-de-Puelles, C.M. Duarte, Plastic debris in the open ocean, Proc. Natl. Acad. Sci. U. S. A. 111 (2014) 10239–10244, https://doi.org/10.1073/pnas.1314705111.
[17] M. Eriksen, S. Mason, S. Wilson, C. Box, A. Zellers, W. Edwards, H. Farley, S. Amato, Microplastic pollution in the surface waters of the Laurentian Great Lakes, Mar. Pollut. Bull. 77 (2013) 177–182, https://doi.org/10.1016/j.marpolbul.2013.10.007.
[18] Y.L. Cheng, J.G. Kim, H. Bin Kim, J.H. Choi, Y. Fai Tsang, K. Baek, Occurrence and removal of microplastics in wastewater treatment plants and drinking water purification facilities: a review, Chem. Eng. J. 410 (2021), 128381, https://doi.org/10.1016/j.cej.2020.128381.
[19] E. Hernandez, B. Nowack, D.M. Mitrano, Polyester textiles as a source of microplastics from households: a mechanistic study to understand microfiber

release during washing, Environ. Sci. Technol. 51 (2017) 7036–7046, https://doi.org/10.1021/acs.est.7b01750.
[20] A.K. Baldwin, S.R. Corsi, S.A. Mason, Plastic Debris in 29 great lakes tributaries: relations to watershed attributes and hydrology, Environ. Sci. Technol. 50 (2016) 10377–10385, https://doi.org/10.1021/acs.est.6b02917.
[21] M. Eriksen, L.C.M. Lebreton, H.S. Carson, M. Thiel, C.J. Moore, J.C. Borerro, F. Galgani, P.G. Ryan, J. Reisser, Plastic pollution in the World's Oceans: more than 5 trillion plastic pieces weighing over 250,000 Tons afloat at sea, PLoS ONE 9 (2014) 1–15, https://doi.org/10.1371/journal.pone.0111913.
[22] B. Rios-Fuster, C. Alomar, L. Viñas, J.A. Campillo, B. Pérez-Fernández, E. Álvarez, M. Compa, S. Deudero, Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) occurrence in Sparus aurata exposed to microplastic enriched diets in aquaculture facilities, Mar. Pollut. Bull. 173 (2021), 113030, https://doi.org/10.1016/j.marpolbul.2021.113030.
[23] X. Li, Q. Xu, Y. Cheng, C. Chen, C. Shen, C. Zhang, D. Zheng, D. Zhang, Effect of microplastics on microbial dechlorination of a polychlorinated biphenyl mixture (Aroclor 1260), Sci. Total Environ. 831 (2022), 154904, https://doi.org/10.1016/j.scitotenv.2022.154904.
[24] X. Kong, J. Zhang, Q. Ji, C. Li, X. Chen, X. Cao, F. Zhu, S. Yang, S. Li, H. He, Insights into adsorption mechanisms of nitro polycyclic aromatic hydrocarbons on common microplastic particles: experimental studies and modeling, Chemosphere 320 (2023), 138050, https://doi.org/10.1016/j.chemosphere.2023.138050.
[25] Y. Lin, Z. Cen, J. Peng, H. Yu, P. Huang, Q. Huang, Z. Lu, M. Liu, H. Ke, M. Cai, Occurrence and sources of microplastics and polycyclic aromatic hydrocarbons in surface sediments of Svalbard, Arctic, Mar. Pollut. Bull. 184 (2022), 114116, https://doi.org/10.1016/j.marpolbul.2022.114116.
[26] B. Sun, J. Liu, Y.Q. Zhang, K.M.Y. Leungb, E.Y. Zeng, Leaching of polybrominated diphenyl ethers from microplastics in fish oil: kinetics and bioaccumulation, J. Hazard. Mater. 406 (2021), 124726, https://doi.org/10.1016/j.jhazmat.2020.124726.
[27] H. Li, Y. Li, B. Maryam, Z. Ji, J. Sun, X. Liu, Polybrominated diphenyl ethers as hitchhikers on microplastics: sorption behaviors and combined toxicities to Epinephelus moara, Aquat. Toxicol. 252 (2022), 106317, https://doi.org/10.1016/j.aquatox.2022.106317.
[28] P. Xu, W. Ge, C. Chai, Y. Zhang, T. Jiang, B. Xia, Sorption of polybrominated diphenyl ethers by microplastics, Mar. Pollut. Bull. 145 (2019) 260–269, https://doi.org/10.1016/j.marpolbul.2019.05.050.
[29] J. Wilkinson, P.S. Hooda, J. Barker, S. Barton, J. Swinden, Occurrence, fate and transformation of emerging contaminants in water: an overarching review of the field, Environ. Pollut. 231 (2017) 954–970, https://doi.org/10.1016/j.envpol.2017.08.032.
[30] T. Hüffer, T. Hofmann, Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution, Environ. Pollut. 214 (2016) 194–201, https://doi.org/10.1016/j.envpol.2016.04.018.
[31] O.H. Fred-Ahmadu, G. Bhagwat, I. Oluyoye, N.U. Benson, O.O. Ayejuyo, T. Palanisami, Interaction of chemical contaminants with microplastics: principles and perspectives, Sci. Total Environ. 706 (2020), 135978, https://doi.org/10.1016/j.scitotenv.2019.135978.
[32] J. Wu, Y. Zhang, Y. Tang, Fragmentation of microplastics in the drinking water treatment process - A case study in Yangtze River region, China, Sci. Total Environ. 806 (2022), 150545, https://doi.org/10.1016/j.scitotenv.2021.150545.
[33] W. Dellisanti, M.M.L. Leung, K.W.K. Lam, Y. Wang, M. Hu, H.S. Lo, J.K.H. Fang, A short review on the recent method development for extraction and identification of microplastics in mussels and fish, two major groups of seafood, Mar. Pollut. Bull. 186 (2023), 114221, https://doi.org/10.1016/j.marpolbul.2022.114221.
[34] R.M. Baena-Nogueras, E. González-Mazo, P.A. Lara-Martín, Degradation kinetics of pharmaceuticals and personal care products in surface waters: photolysis vs biodegradation, Sci. Total Environ. 590–591 (2017) 643–654, https://doi.org/10.1016/j.scitotenv.2017.03.015.
[35] Y. Pan, S.H. Gao, C. Ge, Q. Gao, S. Huang, Y. Kang, G. Luo, Z. Zhang, L. Fan, Y. Zhu, A.J. Wang, Removing microplastics from aquatic environments: a critical review, Environ. Sci. Ecotechnol. 13 (2023), 100222, https://doi.org/10.1016/j.ese.2022.100222.
[36] Z. Zhan, J. Wang, J. Peng, Q. Xie, Y. Huang, Y. Gao, Sorption of 3,3′,4,4′-tetrachlorobiphenyl by microplastics: a case study of polypropylene, Mar. Pollut. Bull. 110 (2016) 559–563, https://doi.org/10.1016/j.marpolbul.2016.05.036.
[37] A. Müller, R. Becker, U. Dorgerloh, F.G. Simon, U. Braun, The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics, Environ. Pollut. 240 (2018) 639–646, https://doi.org/10.1016/j.envpol.2018.04.127.
[38] S. Xiang, Y. Xie, X. Sun, H. Du, J. Wang, Identification and quantification of microplastics in aquaculture environment, Front. Mar. Sci. 8 (2022), https://doi.org/10.3389/fmars.2021.804208.
[39] J. Peixoto, L.P. Silva, R.H. Krüger, Brazilian Cerrado soil reveals an untapped microbial potential for unpretreated polyethylene biodegradation, J. Hazard. Mater. 324 (2017) 634–644, https://doi.org/10.1016/j.jhazmat.2016.11.037.
[40] E. Dümichen, A.K. Barthel, U. Braun, C.G. Bannick, K. Brand, M. Jekel, R. Senz, Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method, Water Res. 85 (2015) 451–457, https://doi.org/10.1016/j.watres.2015.09.002.
[41] A.J. Mohan, V.C. Sekhar, T. Bhaskar, K.M. Nampoothiri, Microbial assisted high impact polystyrene (HIPS) degradation, Bioresour. Technol. 213 (2016) 204–207, https://doi.org/10.1016/j.biortech.2016.03.021.
[42] A. Paço, K. Duarte, J.P. da Costa, P.S.M. Santos, R. Pereira, M.E. Pereira, A. C. Freitas, A.C. Duarte, T.A.P. Rocha-Santos, Biodegradation of polyethylene microplastics by the marine fungus Zalerion maritimum, Sci. Total Environ. 586 (2017) 10–15, https://doi.org/10.1016/j.scitotenv.2017.02.017.
[43] M. Fischer, B.M. Scholz-Böttcher, Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chromatography-mass spectrometry, Environ. Sci. Technol. 51 (2017) 5052–5060, https://doi.org/10.1021/acs.est.6b06362.
[44] S. Shabbir, M. Faheem, N. Ali, P.G. Kerr, L.F. Wang, S. Kuppusamy, Y. Li, Periphytic biofilm: an innovative approach for biodegradation of microplastics, Sci. Total Environ. 717 (2020), https://doi.org/10.1016/j.scitotenv.2020.137064.
[45] A.U.R. Bacha, I. Nabi, L. Zhang, Mechanisms and the engineering approaches for the degradation of microplastics, ACS ES&T Eng. 1 (2021) 1481–1501, https://doi.org/10.1021/acsestengg.1c00216.
[46] A. Amobonye, P. Bhagwat, S. Raveendran, S. Singh, S. Pillai, Environmental impacts of microplastics and nanoplastics: a current overview, Front. Microbiol. 12 (2021), https://doi.org/10.3389/fmicb.2021.768297.
[47] N.A. Samak, Y. Jia, M.M. Sharshar, T. Mu, M. Yang, S. Peh, J. Xing, Recent advances in biocatalysts engineering for polyethylene terephthalate plastic waste green recycling, Environ. Int. 145 (2020), 106144, https://doi.org/10.1016/j.envint.2020.106144.
[48] P. Liu, L. Qian, H. Wang, X. Zhan, K. Lu, C. Gu, S. Gao, New insights into the aging behavior of microplastics accelerated by advanced oxidation processes, Environ. Sci. Technol. 53 (2019) 3579–3588, https://doi.org/10.1021/acs.est.9b00493.
[49] W. Hamd, E.A. Daher, T.S. Tofa, J. Dutta, Recent advances in photocatalytic removal of microplastics: mechanisms, kinetic degradation, and reactor design, Front. Mar. Sci. 9 (2022) 1–28, https://doi.org/10.3389/fmars.2022.885614.
[50] A. Cholewinski, E. Dadzie, C. Sherlock, W.A. Anderson, T.C. Charles, K. Habib, S. B. Young, B. Zhao, A critical review of microplastic degradation and material flow analysis towards a circular economy, Environ. Pollut. 315 (2022), 120334, https://doi.org/10.1016/j.envpol.2022.120334.
[51] J. Wang, C. Sun, Q.X. Huang, Y. Chi, J.H. Yan, Adsorption and thermal degradation of microplastics from aqueous solutions by Mg/Zn modified magnetic biochars, J. Hazard. Mater. 419 (2021), 126486, https://doi.org/10.1016/j.jhazmat.2021.126486.
[52] K. Li, J. Liu, J. Li, Z. Wan, Effects of N mono- and N/P dual-doping on H2O2, [rad] OH generation, and MB electrochemical degradation efficiency of activated carbon fiber electrodes, Chemosphere 193 (2018) 800–810, https://doi.org/10.1016/j.chemosphere.2017.11.111.
[53] J. Wang, R. Zhuan, Degradation of antibiotics by advanced oxidation processes: an overview, Sci. Total Environ. 701 (2020), 135023, https://doi.org/10.1016/j.scitotenv.2019.135023.
[54] M.H. Fadli, M. Ibadurrohman, S. Slamet, Microplastic pollutant degradation in water using modified TiO photocatalyst under UV-irradiation, IOP Conf. Ser. Mater. Sci. Eng. 1011 (2021), https://doi.org/10.1088/1757-899X/1011/1/012055.
[55] T..M. Tien, E.L. Chen, A novel ZnO/Co3O4 nanoparticle for enhanced photocatalytic hydrogen evolution under visible light irradiation, Catalysts 13 (2023) 852, https://doi.org/10.3390/catal13050852.
[56] S.T.U. Din, W.F. Xie, W. Yang, Synthesis of Co3O4 nanoparticles-Decorated Bi12O17Cl2 hierarchical microspheres for enhanced photocatalytic degradation of RhB and BPA, Int. J. Mol. Sci. 23 (2022), https://doi.org/10.3390/ijms232315028.
[57] A. Uheida, H.G. Mejía, M. Abdel-Rehim, W. Hamd, J. Dutta, Visible light photocatalytic degradation of polypropylene microplastics in a continuous water flow system, J. Hazard. Mater. 406 (2021), 124299, https://doi.org/10.1016/j.jhazmat.2020.124299.
[58] D.A. Maulana, M. Ibadurrohman, Slamet, Synthesis of nano-composite Ag/TiO for polyethylene microplastic degradation applications, IOP Conf. Ser. Mater. Sci. Eng. 1011 (2021), https://doi.org/10.1088/1757-899X/1011/1/012054.
[59] J. Shang, M. Chai, Y. Zhu, Solid-phase photocatalytic degradation of polystyrene plastic with TiO2 as photocatalyst, J. Solid State Chem. 174 (2003) 104–110, https://doi.org/10.1016/S0022-4596(03)00183-X.
[60] W. Fa, L. Guo, J. Wang, R. Guo, Z. Zheng, F. Yang, Solid-phase photocatalytic degradation of polystyrene with TiO2/Fe(St)3 as catalyst, J. Appl. Polym. Sci. 128 (2013) 2618–2622, https://doi.org/10.1002/app.37751.
[61] T.S. Tofa, F. Ye, K.L. Kunjali, J. Dutta, Enhanced visible light photodegradation of microplastic fragments with plasmonic platinum/zinc oxide nanorod photocatalysts, Catalysts 9 (2019), https://doi.org/10.3390/catal9100819.
[62] S. Cho, W. Choi, Solid-phase photocatalytic degradation of PVC-TiO 2 polymer composites, 2001.
[63] I. Nabi, A.U.R. Bacha, K. Li, H. Cheng, T. Wang, Y. Liu, S. Ajmal, Y. Yang, Y. Feng, L. Zhang, Complete photocatalytic mineralization of microplastic on TiO2 nanoparticle film, iScience 23 (2020), https://doi.org/10.1016/j.isci.2020.101326.
[64] Y. Yang, J. Chen, Z. Chen, Z. Yu, J. Xue, T. Luan, S. Chen, S. Zhou, Mechanisms of polystyrene microplastic degradation by the microbially driven Fenton reaction, Water Res. 223 (2022), https://doi.org/10.1016/j.watres.2022.118979.
[65] T. Yoshioka, T. Sato, A. Okuwaki, Hydrolysis of waste PET by sulfuric acid at 150°C for a chemical recycling, J. Appl. Polym. Sci. 52 (1994) 1353–1355, https://doi.org/10.1002/app.1994.070520919.
[66] W. Yang, R. Liu, C. Li, Y. Song, C. Hu, Hydrolysis of waste polyethylene terephthalate catalyzed by easily recyclable terephthalic acid, Waste Manag. 135 (2021) 267–274, https://doi.org/10.1016/j.wasman.2021.09.009.
[67] H.B. Lee, K.S. Lee, S.J. Kim, B. Il Choi, B.R. Go, C.J. Rhu, T.H. Han, Effect of chemical agents on the morphology and chemical structures of microplastics, Polymers 14 (2022) 1–15, https://doi.org/10.3390/polym14204353 (Basel).
[68] M.E. Miller, C.A. Motti, P. Menendez, F.J. Kroon, Efficacy of microplastic separation techniques on seawater samples: testing accuracy using high-density polyethylene, Biol. Bull. 240 (2021) 52–66, https://doi.org/10.1086/710755.

[69] G.P. Karayannidis, A.P. Chatziavgoustis, D.S. Achilias, Poly(ethylene terephthalate) recycling and recovery of pure terephthalic acid by alkaline hydrolysis, Adv. Polym. Technol. 21 (2002) 250–259, https://doi.org/10.1002/adv.10029.

[70] G.M. de Carvalho, E.C. Muniz, A.F. Rubira, Hydrolysis of post-consume poly (ethylene terephthalate) with sulfuric acid and product characterization by WAXD, 13C NMR and DSC, Polym. Degrad. Stab. 91 (2006) 1326–1332, https://doi.org/10.1016/j.polymdegradstab.2005.08.005.

[71] A. Sarno, K. Olafsen, S. Kubowicz, F. Karimov, S.T.L. Sait, L. Sørensen, A.M. Booth, Accelerated hydrolysis method for producing partially degraded polyester microplastic fiber reference materials, Environ. Sci. Technol. Lett. 8 (2021) 250–255, https://doi.org/10.1021/acs.estlett.0c01002.

[72] Q. Deshoulles, M.Le Gall, C. Dreanno, M. Arhant, D. Priour, P.Y. Le Gac, Chemical coupling between oxidation and hydrolysis in polyamide 6 - A key aspect in the understanding of microplastic formation, Polym. Degrad. Stab. 197 (2022), https://doi.org/10.1016/j.polymdegradstab.2022.109851.

[73] F. Miao, Y. Liu, M. Gao, X. Yu, P. Xiao, M. Wang, S. Wang, X. Wang, Degradation of polyvinyl chloride microplastics via an electro-Fenton-like system with a TiO2/graphite cathode, J. Hazard. Mater. 399 (2020), 123023, https://doi.org/10.1016/j.jhazmat.2020.123023.

[74] G. Celik, R.M. Kennedy, R.A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A. M. Lapointe, S.C. Ammal, A. Heyden, F.A. Perras, M. Pruski, S.L. Scott, K. R. Poeppelmeier, A.D. Sadow, M. Delferro, Upcycling single-use polyethylene into high-quality liquid products, ACS Cent. Sci 5 (2019) 1795–1803, https://doi.org/10.1021/acscentsci.9b00722.

[75] P.A. Kots, S. Liu, B.C. Vance, C. Wang, J.D. Sheehan, D.G. Vlachos, Polypropylene plastic waste conversion to lubricants over Ru/tio2catalysts, ACS Catal. 11 (2021) 8104–8115, https://doi.org/10.1021/acscatal.1c00874.

[76] J. Ye, Y. Chen, C. Gao, C. Wang, A. Hu, G. Dong, Z. Chen, S. Zhou, Y. Xiong, Sustainable conversion of microplastics to methane with ultrahigh selectivity by a biotic–abiotic hybrid photocatalytic system, Angew. Chem. Int. Ed. 61 (2022), https://doi.org/10.1002/anie.202213244.

[77] P. Mayorga-Burrezo, C.C. Mayorga-Martinez, M. Pumera, Photocatalysis dramatically influences motion of magnetic microrobots: application to removal of microplastics and dyes, J. Colloid Interface Sci. 643 (2023) 447–454, https://doi.org/10.1016/j.jcis.2023.04.019.