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Chemical Degradation of Microplastics: Current Technologies, Mechanisms, Challenges, and Future Perspectives

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Abstract. Plastic pollution and pervasive microplastic contamination across terrestrial-aquatic ecosystems have raised widespread environmental concerns. Nevertheless, conventional water treatment only physically separates microplastics instead of destroying polymer structures, merely transferring pollutants rather than eliminating them completely. Against this backdrop, advanced oxidation processes (AOPs)- based chemical degradation stands out as a promising strategy, for highly reactive radicals can directly cleave polymer backbones. This review first outlines chemical properties and degradation patterns of typical microplastics including PE, PP, PET, PS and PVC. Subsequently, it systematically compares core mechanisms, merits and drawbacks of representative AOP technologies: photocatalysis, Fenton-like oxidation, ozonation, electrochemical oxidation and persulfate-activated hybrid systems. Notably, particle fragmentation should not be confused with genuine mineralization, since surface cracking and weight loss cannot guarantee full conversion of plastic carbon into harmless CO_2 and H_2O. In addition, practical application faces major obstacles such as incomplete mineralization, high energy consumption, difficult catalyst recovery and toxic intermediate risks. More importantly, most laboratory tests use pristine microplastics, whose behaviors differ greatly from environmentally aged counterparts. Accordingly, renewable-energy-driven hybrid systems are highly recommended for future research. Ultimately, standardized evaluation criteria, reusable catalysts and toxicity assessments are essential to translate lab-scale achievements into real-world microplastic remediation.

Keywords: Microplastics, Chemical degradation, Advanced oxidation processes, Mineralization

1. Introduction

Plastic materials are relatively inexpensive, durable and versatile, so they have been widely used. However, with the rapid development of plastic production, a considerable amount of waste has been generated and will remain in the environment for a long time. Over time, most of the large plastic waste will break down into microplastics, which are generally defined as plastic particles smaller than 5 mm [1].

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Microplastics are divided into primary and secondary according to their origins. Primary microplastics are intentionally produced in a small size, and secondary microplastics result from the fragmentation of larger plastic items due to UV radiation, abrasion, oxidation, etc., in the environment [1]. Microplastics have many sources and are distributed widely in the environment of land and water, posing a threat to the transfer of food chains. Figure 1 shows the main sources of entry, transport routes and biological accumulation of primary and secondary microplastics in the environment.

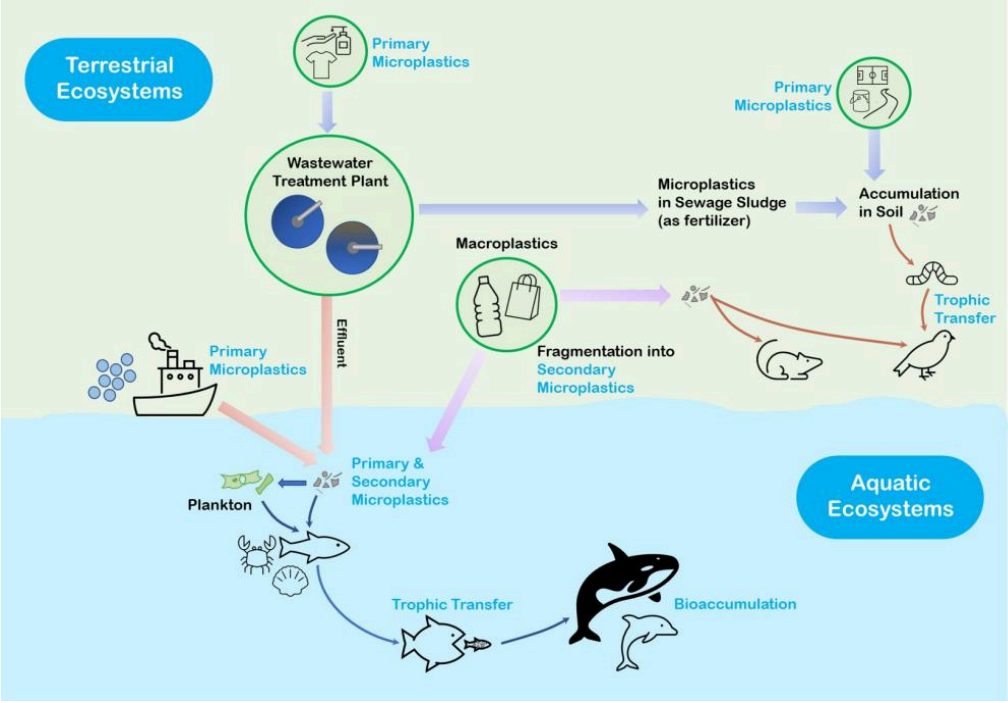

Figure 1. Entry pathways and trophic transfer of microplastics within terrestrial and aquatic ecosystems

Scheme of Sources for Microplastics, Transport in Wastewater Systems and Bioaccumulation in Food Webs in Terrestrial and Aquatic Environments. Note. Adapted from Wasser 3.0. Retrieved from https://wasserdreinull.de/en/blog/impact-of-microplastics-on-wildlife/ [2].

Their Durability is also associated with polymer chemistry. Common microplastics are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) and polyvinyl chloride (PVC); all have stable molecular structures and are resistant to natural decomposition. The surface of the microplastic can also accumulate heavy metals and organic pollutants to spread them in the environment [1].

The previous ways to remove microplastics are mainly filtering, settling, coagulation, adsorption and so on. However, the above ways usually transfer the particles to sludge or other waste; they do not degrade the polymer. Therefore, some attention has started to be given to chemical degradation technology that directly alters the polymer structure.

Among the above technologies, advanced oxidation processes (AOPs) are relatively good because they can produce strong oxidants to break down stable polymer chains. The above are photocatalysis, Fenton-based oxidation, ozonation, electrochemical oxidation and persulfate activation [3].

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Polymer damage is not to be confused with total degradation. Therefore, a good treatment should ideally convert polymer carbon into simple products such as carbon dioxide and water [3].

This paper will present the main mechanisms and technologies currently being used in the study of chemical degradation of microplastics. In addition, the advantages, limitations, environmental concerns, and future development of these approaches are discussed.

2. Chemical characteristics and degradation mechanisms of microplastics

The chemical structure of a polymer strongly influences its degradation behavior. Figure 2 presents the repeating-unit structures of five widely-detected plastic polymers in aquatic environments. PE and PP are particularly resistant because their backbones mainly contain stable carbon–carbon and carbon–hydrogen bonds. PET, in contrast, contains ester groups that can be more susceptible to chemical attack [1]. Therefore, degradation efficiency varies considerably among polymer types.

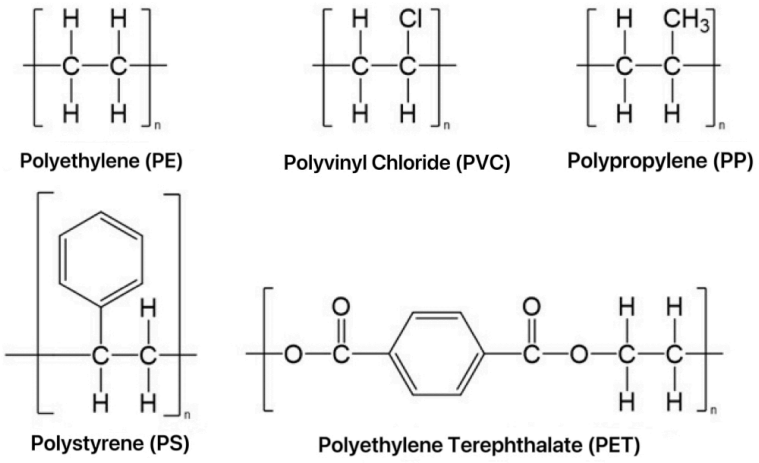

Figure 2. Chemical repeating-unit structures of common plastic polymers found as microplastics

Structural formulas of polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET), the most frequently identified microplastic polymers in aquatic ecosystems. Note. Adapted from "The structure of plastic," by Biotech Academy, 2025, https://www.biotechacademy.dk/en/high-school-projects/plastic-degradation-high-school/the-structure-of-plastic/ [4].

Chemical degradation usually begins at the microplastic surface. Reactive species damage polymer chains and produce radicals. Oxygen then reacts with the radicals to form hydroxyl, carbonyl and carboxyl groups. With the progression of oxidation, polymer chains are cleaved, the molecular weight declines, and the material becomes more brittle [3].

The two are not the same; they refer to different things. Although there is cracking and a decrease in particle size, it does not mean that the plastic has been destroyed. Partial oxidation can produce nanoparticles and dissolved organic matter. Therefore, all kinds of degradation can be monitored by measuring how much of the material is degraded using various methods [3].

In short, chemical decomposition is a slow process of surface oxidation, chain scission, the generation of smaller intermediates, and ideally, complete mineralization.

3. Advanced oxidation processes for microplastic degradation

Advanced oxidation processes are one of the main chemical ways to break down microplastics. First of all, these are very reactive species that can damage the structure of stable polymers; they include

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hydroxyl radicals and sulfate radicals [3].

Many AOPs have been studied, including photocatalysis, Fenton and Fenton-like reactions, ozonation, electrochemical oxidation, persulfate activation, etc. Although these ways have different activation modes, they all aim to oxidize polymer chains and promote chain scission.

AOP Performance will vary with different operating conditions. Oxidant concentration, pH, temperature, catalyst dosage, irradiation intensity, polymer type and particle size can all affect the degradation efficiency [3]. Natural organic matter and inorganic ions in real wastewater can consume reactive radicals and thus reduce the treatment efficiency.

Another problem is the production of degradation products. Partial oxidation will result in smaller plastic particles or dissolved organic matter. High particle removal is not the same as complete mineralization or environmental safety.

AOPs are still good choices because they can chemically change the microplastic polymer rather than just separating it from water. Among the above, photocatalysis has been given more attention due to its use of light energy. Therefore, the following section will introduce photocatalytic degradation in more detail.

3.1. Photocatalytic degradation

Photocatalysis is a relatively well-known chemical route for the degradation of microplastics, and it achieves this by producing reactive oxygen species under light. In a typical photocatalytic system, semiconductor catalysts absorb light and produce electron–hole pairs. These charge carriers react with oxygen and water to generate highly reactive species, such as hydroxyl radicals and superoxide radicals, and thus damage polymer chains through oxidation [3]. Figure 3 shows the general working principle of heterojunction photocatalysis and the free-radical and singlet oxygen-driven oxidation path of microplastics.

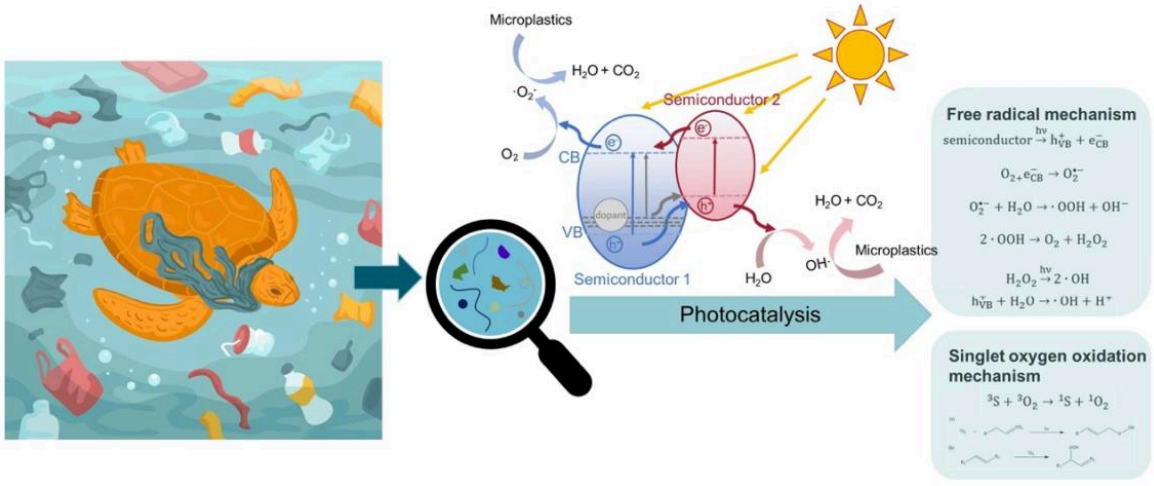

Figure 3. Mechanism of heterojunction photocatalytic degradation of aquatic microplastics

Schematic diagram showing microplastic pollution in aquatic environments and the photocatalytic degradation process via heterojunction semiconductors, including free-radical mechanism and singlet oxygen oxidation reactions. Note. Adapted from " Photodegradation of Microplastics through Nanomaterials: Insights into Photocatalysts Modification and Detailed Mechanisms," by Y. Xiao, Y. Tian, W. Xu, and J. Zhu, 2024, Materials, 17(11), Article 2755. https://doi.org/10.3390/ma17112755 [5].

Titanium dioxide (TiO_2) and zinc oxide (ZnO)are two of the most studied photocatalysts. Reference [6] used ZnO nanorods to reduce the microplastic residue of low-density polyethylene

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(LDPE) under visible light. After a long time, the surface of LDPE developed cracks and cavities, became more brittle, increased in carbonyl index, and showed oxidation of the polymer structure. Therefore, this paper has determined that visible-light photocatalysis can chemically modify polyethylene and not just separate it from water.

The other reason is that the catalyst is not very photocatalytic. A high surface-area catalyst has more sites for radical generation and will therefore increase the number of such reactions. To improve the charge-separation efficiency and expand the range of light absorption to include visible light, other ways are to modify catalysts, add metals or construct heterojunctions [3]. Therefore, in recent years, more and more attention has been paid to developing catalysts that can use a larger proportion of solar radiation.

Photocatalysis is not without its flaws. Firstly, there is a weak contact between solid microplastics and the surface of photocatalysts, so a radical reaction cannot take place. Second, most of the absorbed light by traditional TiO_2 is in the ultraviolet range. Photocatalyst nanoparticles may be pollutants themselves; therefore, they should not be discarded after use [3].

The other is partial mineralization. Surface oxidation, cracking and mass loss do not necessarily mean that all polymer carbon has been converted into carbon dioxide and water. Therefore, photocatalytic degradation should be judged by all the above indicators.

In general, photocatalysis has a great potential since it can be conducted in rather mild conditions and can potentially utilize solar energy as the primary driving force. However, there is still a need to improve catalyst recovery, visible-light activity, catalyst-plastic contact, and mineralization efficiency.

3.2. Fenton and Fenton-like oxidation

Besides photocatalysis, another significant route of chemical microplastic degradation is Fenton-based oxidation. Traditional Fenton chemistry consists of reactions between iron ions and hydrogen peroxide which result in the formation of highly reactive hydroxyl radicals. These radicals are able to attack stable polymer chains, introduce oxygen-containing groups and facilitate chain scission [3].

The high oxidative potential is one of the key benefits of Fenton oxidation. In addition, iron salts and hydrogen peroxide are readily available and comparatively cheap as opposed to certain sophisticated catalyst systems. Nevertheless, traditional Fenton treatment tends to perform optimally in acidic conditions and can produce sludge containing iron which poses another disposal challenge [3].

Heterogeneous and photo-Fenton systems have been developed to overcome these drawbacks. In heterogeneous systems, iron is immobilized on solid supports, which can help to minimize iron leaching and enhance catalyst recovery. Moreover, photo-Fenton systems use light to promote the generation of radicals and iron cycling.

Reference [7] studied the use of iron-modified TiO_2 aerogel powders to photo catalytically and photo-Fenton degrade polystyrene microplastics. Notably, it was demonstrated that the modification with iron affected the photocatalytic and Fenton activity, whereas the interactions between the catalyst and the plastic surface also influenced the efficiency of degradation.

More recently, the combined Fenton and persulfate systems have shown to be especially effective. Reference [8] came up with a heterogeneous electro-Fenton-activated persulfate system of PET microplastics. After 12 hours the system was able to remove about 91% of PET.

In general, Fenton and Fenton-like technologies offer strong oxidation reactions to microplastics. However, the issues of acidity, chemical usage, catalyst stability, and sludge are still relevant. Some

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of these limitations can be overcome by hybrid approaches such as photo-Fenton and electro-Fenton systems.

3.3. Ozonation

Besides Fenton-based systems, ozonation is another chemical oxidation process that has been explored to degrade microplastic. Ozone is a powerful oxidizing agent and can directly react with polymer structures. Moreover, the decomposition of ozone in water can produce hydroxyl radicals, which further enhances oxidation potential [3]. Figure 4 shows SEM morphological comparisons, radical-driven degradation pathways, molecular-weight change curves and reactor performance data of polystyrene micro/nano plastics after catalytic ozonation.

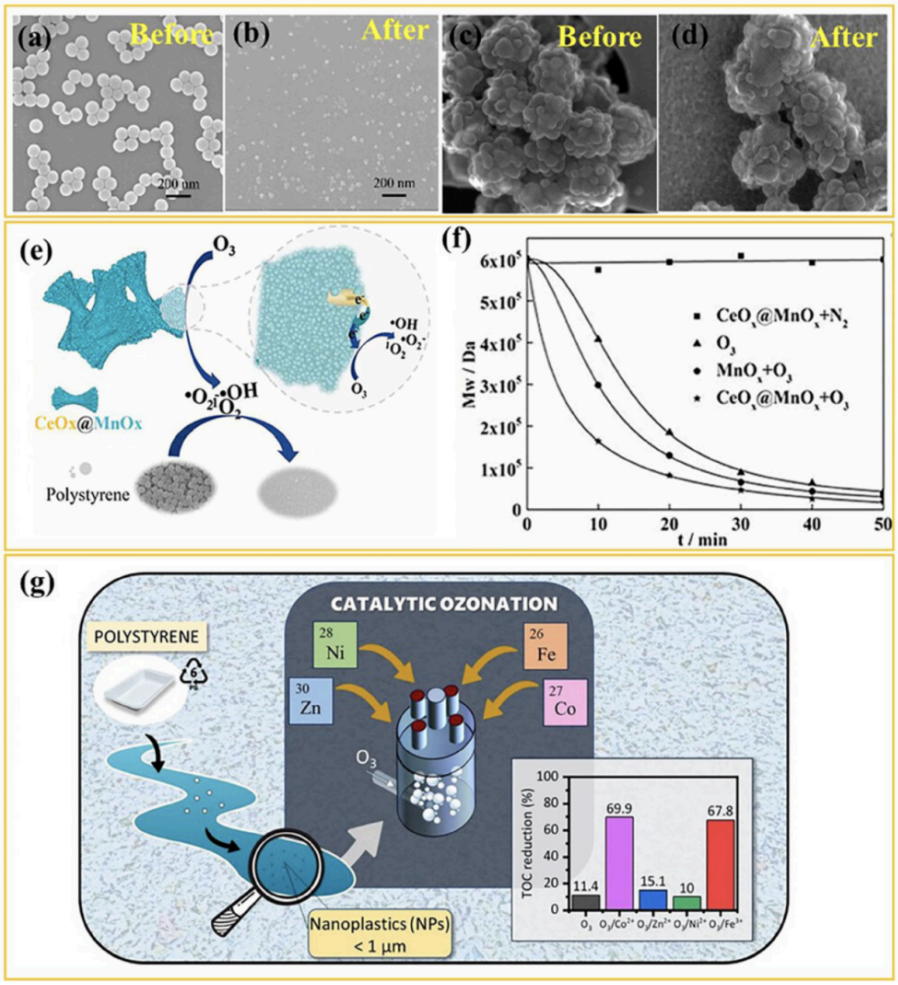

Figure 4. Degradation of polystyrene micro- and nanoplastics by catalytic ozonation

Panels (ad): SEM images of plastic surface morphology before and after oxidation treatment; (e): Schematic diagram of radical generation mechanism over CeOx@MnOx catalyst; (f): Molecular-weight reduction curves under different reaction conditions; (g): Overview of continuous-flow catalytic ozonation reactor and TOC removal performance for nanoplastics. Note. Adapted from "Current approaches and challenges in advanced oxidation processes for nanoplastic degradation," by A. Fazli, Athanassiou, A., & Fragouk, D., 2025, Advanced Science, 12(30), e04352. https://doi.org/10.1002/advs.202504352 [9].

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During ozonation, polymer surfaces gradually become oxidized and develop oxygen-containing functional groups. As a result, microplastics become more hydrophilic and chemically unstable. Continued oxidation may lead to chain scission, reduced molecular weight, and eventual formation of smaller organic compounds.

One practical advantage of ozonation is that ozone is already widely used in drinking-water and wastewater treatment. Consequently, existing treatment infrastructure may facilitate future application of ozone-based microplastic degradation. Moreover, ozone can be generated on-site and decomposes after treatment rather than leaving a persistent chemical residue.

However, several limitations remain. Ozone transfer from the gas phase into water can be inefficient, while hydrophobic microplastic surfaces may limit direct contact with dissolved ozone. Moreover, the production of ozone is energy intensive, which may raise the cost of operation. Similar to other AOPs, incomplete oxidation can also yield smaller particles or intermediate organic products instead of complete mineralization [3].

In general, ozonation has a significant benefit as it is already an established water-treatment technology. Nonetheless, better ozone utilization, less energy use, and more mineralization will be required before it can be an effective single solution to microplastic degradation.

3.4. Electrochemical oxidation

Electrochemical oxidation is another potential method to chemically degrade microplastics after ozonation. Reactive species can be produced directly at or close to electrode surfaces in electrochemical systems. Thus, electrochemical oxidation may be less dependent on the constant input of external oxidants and offer more control over treatment conditions than certain traditional chemical treatments [3].

The direct and indirect electrochemical oxidation can be used to degrade microplastic. Direct oxidation is a reaction between the pollutants and electrode surface, but indirect oxidation relies on reactive species generated by electrochemistry. Such species, especially hydroxyl radicals, are capable of attacking polymer chains, adding oxygen-containing functional groups, and facilitating chain scission. This leads to gradual reduction in polymer molecular weight and smaller degradation products may be obtained [3].

Degradation efficiency is highly dependent on electrode properties and operating conditions. Indicatively, the production of reactive species can be influenced by current density, electrolyte composition, treatment time, and electrode material. Reference [10] studied electrochemical and photoelectrochemical degradation of PET microplastics and measured degradation through weight loss, total organic carbon (TOC), HPLC, and FTIR measurements. Notably, they have investigated both the alterations in the remaining polymer and intermediates released into solution. This method gives a more comprehensive evaluation of degradation as compared to just measuring particle removal.

Moreover, the interactions between microplastics and reactive species can be enhanced by changing the solution around them. As an example, Reference [11] studied how various surfactants influenced electrochemical degradation of PET microplastics. They found that surfactants had the potential to boost redox reactions, generate reactive-species and enhance interactions between reactive species and PET surfaces. Therefore, proper adjustment of the reaction conditions can potentially enhance the efficiency of electrochemical degradation considerably.

However, there are several drawbacks to electrochemical oxidation. Power usage may raise the cost of treatment, especially in cases where lengthy reaction times are necessary. In addition, long-term performance can be diminished by electrode fouling and deterioration. Microplastics can also

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compete with natural organic matter and other contaminants in wastewater to react with reactive species [3]. Thus, findings achieved in simplified laboratory conditions might not reflect the actual treatment performance in environmental waters.

In general, electrochemical oxidation is highly controllable and allows the formation of reactive species in situ. Moreover, it can be used in conjunction with other AOPs to enhance efficiency of treatment. An important example is the activation of persulfate that adds sulfate radicals yet another route of polymer degradation.

3.5. Persulfate-based and hybrid chemical degradation

Besides oxidation with hydroxyl-radicals, persulfate treatment has gained more interest in the degradation of microplastics. Ultraviolet radiation, heat, ultrasound, transition metals or electrochemical processes can be used to activate persulfate to produce highly reactive sulfate radicals [3]. These radicals are able to attack polymer structures and facilitate oxidative chain scission.

The benefit of persulfate-based treatment is that various activation techniques can be integrated. Indicatively, Reference [12] created a system that uses ultraviolet irradiation and electrical activation of persulfate to concurrently degrade PVC microplastics and p-aminobenzoic acid. The degradation of PVC was about 37% and the degradation of the organic contaminant was about 99.22% under the conditions studied. Thus, this paper shows that hybrid systems can potentially deal with microplastics and other contaminants in polluted water at the same time.

The treatment of polyester microfibers with persulfate has also been studied. The light-, heat- and ultrasound-activated persulfate systems were compared in reference [13]. Optimized UVC/peroxydisulfate treatment gave a mass loss of about 18.5% after nine hours and clear surface pitting and cracking. But when the treatment was extended to 24 hours there was no corresponding increase in the amount of mass lost. This implies that significant surface conversion may take place without full mineralization.

Fenton chemistry can also be combined with persulfate activation. As mentioned earlier, Reference [8] came up with a heterogeneous electro-Fenton-activated persulfate system of PET microplastics. The synergistic effect of sulfate and hydroxyl radicals facilitated the degradation and mineralization of PET. Therefore, the combination of various radical pathways can address certain shortcomings of single oxidation processes.

However, hybrid systems have their own complexity as well. Additional catalysts, energy sources or chemical reagents might be needed, which will raise the cost of operations. Thus, degradation percentage should not be used to assess treatment performance alone. Other factors that should be taken into account include energy consumption, catalyst recovery, chemical demand, intermediate formation and environmental impacts.

In general, persulfate-based and hybrid systems offer good prospects to enhance microplastic degradation. Nonetheless, their implementation will be based on the balance between increased degradation efficiency and cost, energy consumption, and complexity of operations.

4. Comparison of chemical degradation technologies

A number of chemical advanced-oxidation processes have been explored to degrade microplastic pollutants in water. These degradation technologies have their unique mechanisms, advantages and limitations. The characteristics of photocatalysis, Fenton/photo-Fenton oxidation, catalytic ozonation and conventional ozonation for the treatment of microplastics are compared in Table 1.

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Table 1. Comparison of major advanced-oxidation-based chemical degradation technologies for aquatic microplastics

Technology	Advantages	Limitations
Photocatalysis	mild conditions, solar-energy potential	poor contact, incomplete mineralization, catalyst recovery difficulty
Fenton-based oxidation	fast polymer modification, abundant hydroxyl radicals	acid requirement, iron waste, high complexity for modified systems
Ozonation	mature water-treatment application, on-site ozone generation	low mass transfer, incomplete mineralization, poor standalone performance
Electrochemical oxidation	good controllability, in-situ reactive species	high energy cost, electrode fouling and high cost
Persulfate-based systems	sulfate radicals, compatible with hybrid processes	complex setup, higher energy and reagent consumption

All these comparisons show that the efficiency of degradation should not be used as a sole criterion to decide which technology is the most effective. Other considerations such as energy use, cost, catalyst recovery, treatment time, production of nano plastics or organic intermediates and performance in real wastewater must also be considered [3].

5. Current challenges and future perspectives

While there has been substantial advancement in the chemical degradation of microplastics, there are still some challenges that hinder its practical use. To begin with, full mineralization is not easy. Numerous reports describe surface oxidation, cracking, reduction in particle-size or loss of mass but such changes do not always imply that polymers have been entirely transformed into non-toxic products. Thus, future research must explicitly differentiate between fragmentation, degradation and complete mineralization.

Second, natural environments are not completely reflected in laboratory conditions. Most experiments involve the use of pristine microplastics and purified water when environmental microplastics have already been subjected to sunlight exposure, oxidation, mechanical abrasion and interaction with other contaminants. Reference [14] compared environmentally aged microplastics sampled in urban hydro systems with artificially aged materials that were produced by accelerated photo-oxidation. Their research emphasizes the need to take realistic aging into account in assessing the degradation of microplastics. Future experiments should therefore be more inclined towards using environmentally aged particles and realistic water matrices as opposed to just using pristine laboratory plastics.

Another challenge is the energy consumption. The artificial UV irradiation, ozone generation and electrochemical processes may demand a lot of electricity. Thus, degradation based on renewable energy has emerged as a significant future trend.

Moreover, the combination of various degradation mechanisms can be useful in future technologies. A hybrid system was developed by reference [15]. Notably, it shows how photocatalysis and Fenton chemistry driven by light can be combined to enhance polymer

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degradation. Thus, hybrid systems can address certain shortcomings of single oxidation technologies.

However, higher degradation efficiency does not necessarily imply sustainability. Hybrid systems can involve the use of extra catalysts, equipment or energy. In addition, degradation products need to be closely controlled since partial oxidation may produce smaller particles and dissolved substances. Future researches are thus to incorporate structural characterization along with mineralization measurements, identification of degradation products and toxicity [3].

In general, future studies should go beyond the laboratory demonstrations to scalable and environmentally realistic treatment systems. The necessary measures will include standardized degradation measurements, environmentally aged microplastics, renewable energy, reusable catalysts, toxicity testing, and pilot-scale experiments. Finally, chemical degradation technologies need not only be highly efficient in terms of degradation but also environmentally safe, economically viable, and low-energy-consuming.

6. Conclusion

The problem of microplastic pollution is significant due to the fact that traditional polymers are durable and do not easily decompose naturally. Thus, chemical degradation is a valuable alternative to physical removal since it can directly alter and degrade polymer structures.

In this review, various key chemical degradation processes such as photocatalysis, Fenton based oxidation, ozonation, electrochemical oxidation and persulfate-based oxidation were reviewed. Though each technology has certain benefits, none of the methods at the moment offers a perfect solution. Photocatalysis has the potential to utilize solar energy, whereas Fenton and persulfate systems can offer powerful radical oxidation. In the meantime, ozonation enjoys the experience of proven water-treatment uses, and electrochemical oxidation offers more control over operations [3].

Nevertheless, incomplete mineralization, energy expenditure, recovery of catalysts, treatment expenses and formation of degradation-products are still significant constraints. Therefore, the future studies must not only aim at enhancing the efficiency of degradation but also environmental safety and economic viability.

In general, the most promising future trend can be integrated chemical treatment systems in conjunction with renewable energy. The progress in solar-powered photocatalysis and hybrid photocatalytic/Fenton processes shows that more efficient and sustainable degradation of microplastics is possible [15, 16]. Finally, additional work and realistic environmental testing will be required before these technologies can be extensively used to remediate microplastic.

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