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Review

Aging Process of Microplastics in the Aquatic Environments: Aging Pathway, Characteristic Change, Compound Effect, and Environmentally Persistent Free Radicals Formation

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Abstract: Plastic wastes are becoming one of the most serious environmental pollutants because of their high antidegradation properties and the damage they cause to human health. More seriously, plastics can become smaller in size and form microplastics (MPs), attributing to the oxidation, weathering, and fragmentation processes. The influx of MPs into water bodies seriously affects the quality of the aquatic environment. Therefore, it is necessary to summarize the aging process of MPs. In this review, we first provided an overview of the definition and source of MPs. Then we analyzed the potential aging pathways of MPs in the current aquatic environment and elaborated on the changes in the physicochemical properties of MPs during the aging process (e.g., particle size, crystallinity, thermodynamic properties, and surface functional groups). In addition, the possible synergistic contamination of MPs with other pollutants in the environment is illustrated. Finally, the mechanisms of generation and toxicity of environmental persistent free radicals (EPFRs) that may be generated during the photoaging of MPs were described, and the feasibility of using photoaged MPs as photosensitizers to catalyze photoreactive degradation of organic pollutants is proposed. Overall, this review provides a comprehensive and objective evaluation of the behavior of MPs in the aquatic environment.

Keywords: microplastics; aging pathways; characteristic change; combined pollution; environmental persistent free radicals

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1. Introduction

Plastics have the characteristics of durability, affordability, and convenience, and have been widely used as materials in industrial, commercial, and municipal applications [1,2]. According to recent statistics, 400 million tons of plastic are produced every year, and of that, about 70% will transfer to solid plastic. Additionally, the global plastic recycling rate is only 15%, and about 90 million tons of solid plastic are converted to plastic waste per year. More than 80% of plastic wastes are disposed of by incineration, landfill, and other methods, however, about 10 million tons of plastic waste per year enter the aquatic environment via littering, landfill leakage, wind effect, and hydrodynamic effect [3]. In the 1990s, some countries and relevant international organizations developed a series of control measures to prevent plastic waste from entering the aquatic environment, and reduce the total amount of plastic waste in the aquatic environment. However, the persistence of plastic has led to a continuous rise in the total amount of plastic in the aquatic environment, and the formation of large plastic waste belts. In 2004, Thompson et al. firstly observed microplastics (MPs) debris and fibers under the microscope confirming that MPs are widely present in the aquatic environment [4,5]. This research has drawn the attention of scholars to MPs and promoted the current academic boom in MPs research.

The morphology of MPs is various, including irregular debris, fibrous debris, granular debris, and spherical debris. Furthermore, the chemical composition of MPs such as polyethylene (PE), polystyrene (PS), polypropylene (PP), phenol-formaldehyde (PF), polyamide (PA), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyester, etc., are diverse, resulting in different density, crystallinity, melting point, mechanical strength, hydrophobicity and chemical stability of MPs [6]. The sources of MPs are divided into primary MPs and secondary MPs. Primary MPs are the plastics produced in microscopic size (e.g., microplastic balls in personal care products, and tire dust), and secondary MPs are the plastics obtained by fragmenting large plastic pieces [7]. Due to the high mobility, high chemical stability, and high hardness of MPs, they can be dispersed and accumulated in the aquatic environment under the hydraulic migration of water [8].

Once MPs enter the aquatic environment, they are subjected to continuous physical and chemical reactions (e.g., photooxidation, hydraulic flushing, biodegradation, etc.) that cause weathering of the microplastic [1]. Compared to the original MPs, the physical and chemical properties of aged MPs are changed. Previous research indicated that the mechanical strength, thermal stability, and crystallinity of MPs continuously decreased during the aging process. Additionally, the oxygen-containing functional groups were formed on the surface of MPs, which leads to an increase in the carbonyl index of MPs and changes the hydrophilic nature of MPs. Hence, the interface reaction between MPs and other pollutions (e.g., heavy metal [9], organic compounds [9], and pathogenic microorganisms [10], etc.) in the aquatic environment will vary with the properties of MPs, resulting in the formation of compound pollutants. However, it has been recently reported that under certain external conditions, MPs produce persistent free radicals (EPFRs) on their surfaces and can induce reactive oxygen species (ROS), which can have adverse effects on human health as well as other organisms. It has also been researched that MPs can act as photosensitive initiators to catalyze photodegradation reactions and have the potential to degrade organic pollutants in the aquatic environment.

The aging process of MPs is crucial. However, a comprehensive description of the aging process of MPs is still lacking. Therefore, this review describes in detail the aging process of MPs in the aquatic environment, including the causes of MPs aging, changes in the material properties of MPs during aging, and the combined contamination of aging MPs with other contaminants in the aquatic environment. In addition, the recent studies on EPFRs on aging MPs are also reviewed, and it pointed out that aging MPs can, to some extent, act as photosensitizers for photocatalytic reactions to degrade organic pollutants. This review provides theoretical guidance for a comprehensive and objective evaluation of the behavior of MPs in the aquatic environment.

2. MPs in The Aquatic Environment

2.1. Definitions of MPs

Size is the main criterion for plastic debris definition. In 2008, the National Oceanographic and Atmospheric Agency defined MPs as plastic debris from 1 µm to 5 mm in size [11], while nanoplastics are categorized as plastic debris smaller than 1 µm [12–14]. Nonetheless, on the issue of size, another work suggested that categorize MPs into three size levels (1~100 µm, 100~350 µm, and 350 µm~5 mm), resulting in an easier comparison of different studies [15]. Plastic debris flowing into the environment have different physicochemical properties, while the classification of plastic debris only by particle size cannot describe all the properties of MPs. A classification of MPs based on physicochemical properties (including size, shape, color, origin, polymer composition, degree of polymerization, crystallinity, solubility, etc.) was proposed to refine the classification of plastic debris [16]. Despite the many voices raised on the issue, there is still no consensus on how to define and categorize plastic debris.

2.2. Sources of MPs

Plastics that are manufactured to be of a microscopic size are defined as primary MPs [17]. MPs can enter the environment through different sources, such as municipal solid waste, composting, flooding, wastewater treatment plants (WWTPs), and other human activities (Figure 1). Daily plastic products are the main source of MPs, which are easy to be ignored and difficult to treat and avoid. Primary MPs include not only intentionally added MPs (e.g., pharmaceutical and personal care products) but also by-products during the use of related plastic products (such as microfibers detached from clothing, tire dust from running cars, MPs discharged from artificial turf and paints, etc.) [18–20]. WWTPs can efficiently remove MPs from sewage, preventing their entrance into aquatic environments. However, MPs separated from wastewater will concentrate in sludge, resulting in a potential hazard in the following sludge treatment. Although a large number of MPs in domestic sewage can be efficiently removed in WWTPs, municipal effluent is a significant emission of MPs into the environment [21]. It has been reported that the daily discharges of MPs from WWTPs ranged from 50,000 up to nearly 15 million particles in the United States, which is far beyond the treatment capacity of the environment [22].

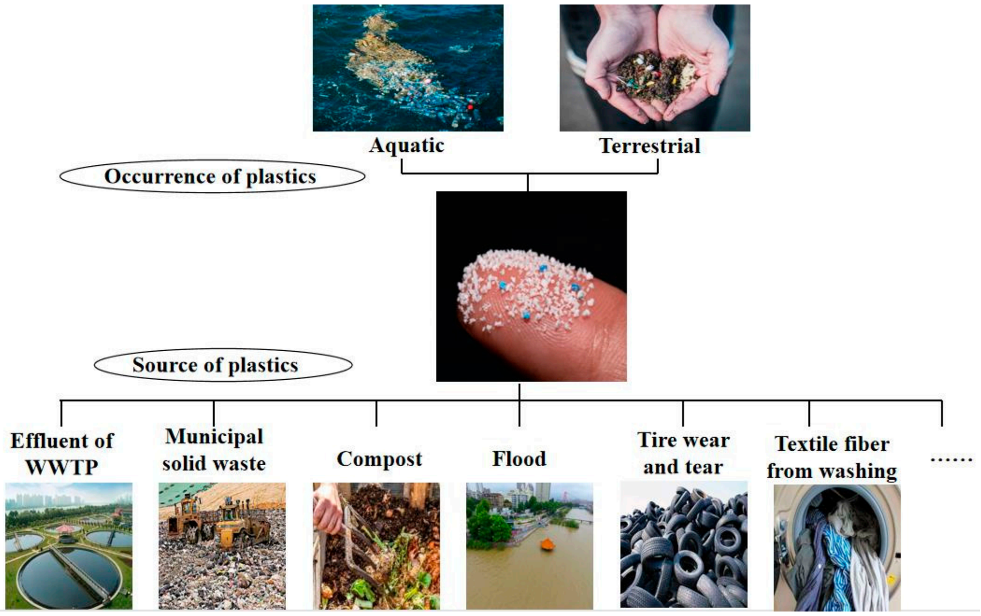

Figure 1. Occurrence and sources of MPs in the environment.

Secondary MPs refer to the plastic particles originating from the fragmentation of larger plastics [23]. Fragmentation is a process, by which macroplastics or larger plastic debris split are reduced in volume through physical, chemical, and biological reactions, including UV radiation, biodegradation, hydraulic shock, etc. Therefore, improperly disposed plastic waste is the main source of secondary MPs.

MPs can spread with water and airflow, interacting with other substances in the environment. Therefore, microplastic particles can spread everywhere in the world, even on the north pole, south pole, and no man's land, and microplastic particles with their small size have a strong migration ability [24]. According to a survey, MPs are frequently present in freshwaters as well as drinking water, and number concentrations spanned ten orders of magnitude (1×10^{-2} to 10^8 pcs/m^3) across different water types [25]. More seriously, MPs can also be detected in salt, and the number concentrations of MPs are up to 7–204 pcs/kg, 550–681 pcs/kg, and 43–364 pcs/kg in 15 brands of rock/well salts, sea salt, and lake salt, respectively [26]. The presence of microplastic particles in drinking water and edible salt has seriously threatened human health, therefore, it is very necessary to control the discharge of MPs in the environment.

The deposition, retention, and transport of MPs will depend on many factors including human behaviors (such as producing, littering, recycling, etc.), particle characteristics (such as density, shape, composition, size, etc.), weather (such as wind, rainfall, flooding, etc.), environmental topography, and hydrology, leading to difficulties in predicting the transport of MPs [27]. The aquatic environment is the main route of MPs transport. Figure 2 shows the main flows of MPs within and between the three environmental compartments: freshwater, marine, and terrestrial [28]. The figure indicates that water flow is the significant media that mediate the spread of MPs between the aquatic and terrestrial environments. For example, MPs will not only be transported by rivers from land to sea but also return to land during high tide or flooding events. In addition, the properties of MPs will be significantly changed during the transport process because of the fragmentation and aging reaction, such as photodegradation, weathering, biodegradation, etc. [12].

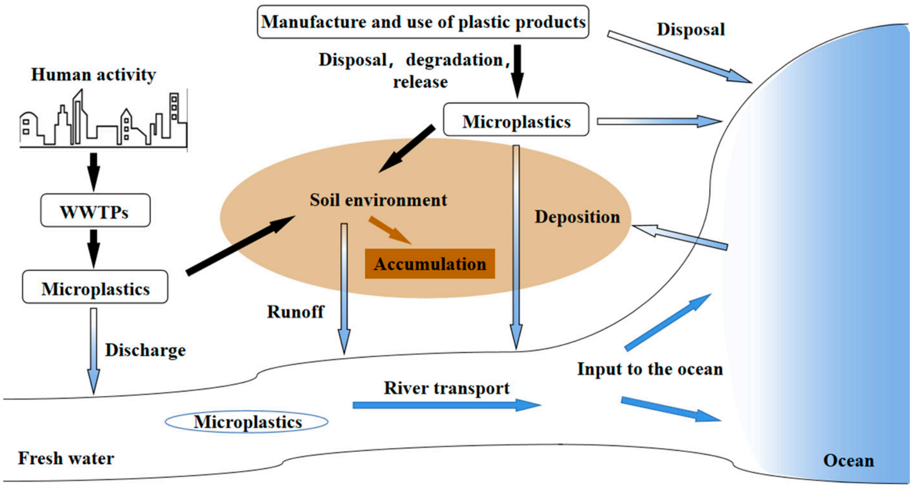

Figure 2. Transportation of microplastic particles within and between anthropogenic, terrestrial, freshwater, and marine environment. Reprinted with permission from Ref. [28]. 2017, Horton, A.A.; Walton, A.; Spurgeon, D.J.; Lahive, E.; Svendsen, C.

2.3. Analytical Methods

Many analytical techniques have been applied to detect, identify and quantify MPs particles in environmental samples. Generally speaking, MPs analysis consists of two steps: physical characterization of potential plastics followed by chemical characterization for confirmation of plastics [29].

Visual sorting is a legitimate and rapid approach used to separate and identify MPs particles with the naked eye or under a dissecting microscope [30]. Though it has been used in many studies, visual sorting is not very reliable because the obtained values for MPs occurrence strongly depend on the observer who performs the separation [31]. To make values more reliable, various chemical identification techniques including Fourier-transform infrared spectroscopy (FT-IR), Raman microspectroscopy (RM), thermoextraction desorption gas chromatography-mass spectrometry (TED-GC-MS), and pyrolysis gas chromatography (Pyr-GC-MS) are mostly applied [32]. The spectroscopic methods (FT-IR and RM) are the most popular techniques for the chemical identification of MPs as they were applied in 90% of studies [33]. FT-IR and RM identify MPs via vibrational fingerprinting, which is unique for each polymer type, while other methods rely on MS information of monomers/oligomers or additives and provide information on polymer mass.

2.3.1. FTIR

FTIR spectroscopy enables efficient and accurate analysis of MPs samples and the identification of polymer types for a wide range of sizes. FTIR spectroscopy provides information on the specific chemical bonds of particles. In FTIR analysis, all wavelengths can be collected simultaneously and then processed by Fourier-transform. Carbon-based polymers can be easily identified by this method, and different bond compositions produce unique spectra that distinguish MPs from other organic/inorganic particles [29].

Single-element detectors, which have been frequently applied in MPs analysis [34], were used in the first setups of chemical imaging [35]. Their major drawback is the high measurement time required for large field sizes. Recently, FTIR imaging has been improved through the application of focal plane array (FPA) based detection [36], where several detectors are placed in a grid mode. FPA allows for the rapid acquisition of several thousand spectra within an area with a single measurement, which enables the analysis of entire filters at high resolution [37].

FTIR has three different modes of operation, namely transmission, reflection, and attenuated total-reflectance (ATR) mode. The resolution of IR is diffraction limited (theoretically ca. 1.7 μm at 4000 cm^{-1} to 13 μm at 500 cm^{-1}) [31], consequently, smaller particles cannot be analyzed. For smaller particles, FTIR has to be applied combined with a microscope, the so-called micro-FTIR, which can be used in all three modes. Using FPA-based micro-FTIR imaging in the transmission mode, Löder et al. demonstrated that particles could be quantified down to 20 μm depending on the types of MPs. However, when the thicknesses of samples are below 5 μm (e.g., foils or fibers), enough absorbance might not yield interpretable spectra [37]. Moreover, water is very IR-active and will interfere with the analysis, so all MPs samples must be carefully dried.

2.3.2. RM

Similar to FTIR, RM shows the vibrational information of the molecular structure of samples. Modern devices have horizontal and vertical resolutions below 1 μm. It complements FTIR measurements. FTIR can identify polar groups more clearly, while RM spectroscopy can respond better to non-polar symmetric bonds [30].

Compared to FTIR micro-spectroscopy, RM spectroscopy offers many advantages such as lower minimum particle size and a full spectral range available for identification. In addition, RM can analyze dark, non-transparent particles [38]. RM is especially applicable to small MPs particles, which are numerous, but of low mass and have the potential to exhibit the largest environmental threat [31,39]. Such an analysis allows the investigation of all Raman-active particles in a sample, which makes it widely applicable to the whole particle research, and enables the investigation of a ratio of anthropogenic to natural substances in environmental samples [40]. Furthermore, RM measurements do not depend on the transmission of exciting light through the sample material, which allows the identification of thicker or strongly absorbing particles.

However, one of the biggest drawbacks of RM is the fluorescence interference from organic (e.g., humic substances), and (micro)biological and inorganic (e.g., clay minerals) contaminations, which hinders the identification of MPs. Therefore, the samples should be purified prior to RM analysis [31,41]. At the same time, the selection of appropriate acquisition parameters (photobleaching, laser power, laser wavelength, measurement time, confocal mode, magnification of objective lens) is also very important to avoid the problem of strong fluorescence background [31].

2.3.3. Thermoanalytical Methods

Chemical characterization may be affected by selection bias since the isolation of the MPs depends on the researcher’s skills [42]. The thermal analysis of MPs is a completely different approach that is being increasingly used for the characterization of MPs. The methodology is based on the identification of the polymer according to its degradation products. The thermal analysis includes different analytical techniques such as thermogravimetry (TGA), pyrolysis gas chromatography-mass spectrometry (py-GC-MS), hyphenated TGA such as TGA-mass spectrometry (TGA-MS), TGA-differential scanning calorimetry (DSC), DSC and TGA-based thermal extraction-desorption gas chromatography-mass spectrometry (TED-GC-MS). The development of thermal methods is the key to characterizing MPs with low solubility and additives that cannot be readily dissolved, extracted, or hydrolyzed.

TGA is a thermal analysis that monitors the dependence of the mass of a sample on time or temperature while the temperature is programmed under a specific atmosphere (inert or air). The thermal analysis also includes other variants, such as differential scanning calorimetry (DSC) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), all of which have regular applications in polymer analysis. Fundamentally, TGA and TGA-based methods differ from other variants because their capabilities include measuring the weight loss of the sample at a controlled rate of heating. Generally speaking, TGA analysis has well-known advantages such as ease of use, fast speed, and the ability to adapt to different sample sizes. TGA has long been used to study the thermal properties of polymers. The combination of TGA with analytical instruments, such as FTIR spectroscopy or GC-MS can effectively characterize polymers based on their gaseous decomposition products [43,44].

Differential scanning calorimetry (DSC) is a useful method for studying the thermal properties of polymeric materials [45]. The method requires reference materials to identify the polymer type, since each MP particle has different characteristics in DSC. DSC can only be used to identify PP and PE since other common polymers (PVC, PES, PET) cannot be discriminated against due to the overlap of their phase transition signals [46]. Two types of information are required for their determination: melting point temperature is used for identification, and areas of melting peak for quantification. There are three main challenges in measuring MPs in environmental samples compared to pure polymer samples: organic matter matrices may produce broad signals that overlap with the melt peaks of polymers [47]. Secondly, the peaks of the polymers may overlap each other, depending on the individual melting points of the polymers. In this case, identification may be possible, but quantification may yield incorrect values. Lastly, although MPs are ubiquitous in the environment, their mass concentrations may be below the detection limits of DSC measurements [45].

Py-GC-MS is based on the thermal decomposition of samples normally under an inert atmosphere. Py-GC-MS is based on the thermal decomposition of samples usually in an inert atmosphere. The thermal degradation of samples with masses up to 350 mg in an inert atmosphere results in pyrolytic fragments of the polymer structure that can be separated by GC and characterized by MS [48]. Each polymer has characteristic degradation products and indicator ions that can be used for identification and/or quantification [49,50]. Py-GC-MS is not dependent on the shape, size, or presence of organic/inorganic contaminants in MPs particles.

In addition, samples usually do not require any pre-treatment for analysis. This analytical technique eliminates the need for the pre-treatment of samples, as it enables the direct analysis of small molecules and/or polymers, whether they are liquid or solid, but it is compatible with most pre-treatments used to extract (macro)molecules from environmental samples [48]. However, this method is not suitable for routine analysis, as only one single particle can be analyzed per run [51]. Moreover, since the particles are placed in the tube using tweezers, they have to be large enough for easy management. Py-GC-MS is limited to a minimum particle size of about 50–100 µm due to the manual transfer of unknown particles into the pyrolysis tube [52]. Furthermore, the analysis of whole environmental samples is not desirable due to the strong matrix effects and the method is very sensitive to impurities.

Ümichen et al. developed a TGA-based thermal extraction-desorption gas chromatography-mass spectrometry (TED-GC-MS) method for the quantification of MPs in environmental samples [53]. This method has the advantage of being able to accommodate a large number of samples and avoid extensive pretreatment of environmental samples. Following this proof-of-concept work, the TED-GC-MS method was shown to be able to identify MPs in aquatic samples from different rivers and fermentation residue samples from biogas plants.

The method was extended to theoretically handle the detection and quantification of PS, PP, PET, PA, and PE by identifying characteristic decomposition products [53].

An alternative to the TED-GC-MS method is the TGA-MS method in which gaseous degradation products are transferred into a quadrupole MS without chromatographic separation by GC. In their proof-of-concept work, David et al. investigated the applicability of TGA-MS for the quantification of PET-spiked soil without prior separation of PET from its environmental matrix. The addition of PET to soil samples containing 1.61 ± 0.15 wt% organic matter revealed that the characteristic decomposition products of PET could be discriminated from the characteristic decomposition products and organic matter content of the soil due to the difference in decomposition temperatures [54]. Specifically, the use of TGA-MS allowed the detection of PVC, which is not available in TED-GC-MS analysis [55].

Table 1 provides an overview of the above techniques applied in recent studies that characterize and identify MPs in freshwater ecosystems.

Table 1. Overview of thermal methods used for analyzing MPs with advantages and drawbacks.

Analytical Method	Type of Microplastics	Analysis	Advantages	Drawbacks	Ref.
FTIR	All types	Infrared spectra of the samples were recorded for their characteristic vibrational bands; chemical composition of the samples.	Non-destructive; a minimal amount of sample is needed; no need to prepare samples; small particles (~25 µm) can be detected;	Expensive instruments; laborious work; the whole particle identification takes a long time; signal overlap caused by the presence of additives or other pollutants.	[56–58]
Raman	All types	Raman spectra of the samples recording their characteristic vibrational bands; chemical composition of the samples.	Non-destructive; a minimal amount of sample is needed; no need to prepare samples; small particles (1~2 µm) can be detected; particle size distribution information.	Interference of fluorescence; expensive instruments; laborious work; long time for the whole particle identification; signal overlap caused by the presence of additives or other pollutants.	[40,41,59]
TGA-DSC	PE, PP	Weight loss of the samples under specific conditions; achieve qualitative and quantitative information.	Simple, fast, and easy; widely available instrument.	Destructive; operational challenges; MPs may be limited to those with unique absorption bands; pre-concentration may be needed.	[46]
TED-GC/MS	PE, PP, PS, PET, PA	Weight loss of the samples under specific conditions; quantitative and qualitative information on polymers and organic additives may be achieved.	Higher selectivity and sensitivity; potential to have fully automated systems; higher sample volumes vs py-GC-MS; may be used to get more representative samples; minimal potential for blocking along the system connections; independent on MPs size and shape.	Destructive; long expenditure time; operational challenges; complex data analysis.	[53,60–63]

Table 1. *Cont.*

Analytical Method	Type of Microplastics	Analysis	Advantages	Drawbacks	Ref.
py-GC-MS	All types	Provides information related to the chemical composition of the polymers and organic additives present, based on the degradation products of the sample pyrolysis; achieves qualitative and quantitative information.	No pre-treatment required; independent on MPs size and shape; fully automated system.	Destructive; inorganic additives cannot be detected; complex data Interpretation; may not be representative for heterogeneous samples; small sample amounts (5–200 µg)	[48,64,65]
TGA-MS	PE, PP, PS, PET, PVC	Weight loss of the samples under specific conditions; characterization of the evolved gases; achieve qualitative and quantitative information.	Capable of one-step analysis; provides additional chemical information during the same TGA run; independent on MPs size and shape.	Destructive; connection between the TGA and the detector may be blocked; potential of interference from high organic matter content; overlapping events on complex samples present a challenge to data interpretation.	[62,63]
TGA-FTIR-GC/MS	PE, PP, PS, PVC	Quantify the broadest scope of polymers in real samples.	Pyrolysis products at any given temperature can be examined by MS; pyrolysis products at any given temperature can be carefully examined by MS; it is feasible to use standards and calibrate characteristic mass peaks at distinctive composition temperatures for quantitative analysis.	Operational challenges; complex data analysis; long expenditure time; instruments are not widely available.	[43]

3. Aging of Microplastics in the Aquatic Environment

In recent years, MPs have accumulated in the aquatic environment in large quantities, far exceeding the self-cleaning capacity of the environment, and are regarded to be a potential health hazard [66,67]. The self-cleaning of MPs in aquatic environments mainly depends on the aging or weathering processes, such as photooxidation by ultraviolet (UV), mechanical abrasion, hydrolysis, and biodegradation. So, to solve the MPs problem in the aquatic environment, it is necessary to investigate the aging process of MPs. Recent studies about MPs aging are reviewed in Table 2 Biological methods are more effective in the aging of MPs than chemical methods [68].

Table 2. Recent studies of microplastic aging using different methods.

MPs	Methods	Mass Loss Rate	Experimental Conditions	Ref.
PE	Mechanical fragmentation	—	With the increase in weathering time (30 d), the proportion of secondary MPs (1–2.4 μm^2) increases.	[69]
^{14} C-PS	Photo-degradation	17.1 ± 0.55% in water, 6.17 ± 0.1% in air.	^{14}C-PS nanoplastics under UV irradiation after 48 h in water and air.	[70]
PVC	Fenton	No degradation, but 100% recovery of PVC	Optimum conditions: molar ratio (H_2O_2/Fe^{2+}) = 7500, concentration of H_2O_2 = 0.2 M/L, reaction time = 2 min, T = 25 °C, pH = 5.8, frother concentration = 15 mg/L, flotation time = 4 min.	[71]
PE	Ag/TiO_2/reduced graphene oxide (rGO)	76%	Under UV radiation for 4 h	[72]
MPs	Activated sludge	16.6%	Wastewater, [influent] = 47.4 ± 7.0 n/L, [effluent] = 34.1 ± 9.4 n/L.	[73]
PLA	Biodegradation	>202.7 mg PLA 100 larvae-1·d-1	Feed yellow mealworms (larvae of Tenebrio molitor) with PLA-bran mixtures (50% PLA)	[74]
PET, PE, PS	Biodegradation	3.0%, 6.2%, 5.8% for PE, PS and PET	Different MPs as the sole carbon source to promote the growth of Bacillus gottheilii in synthetic media	[75]
PVA	Biodegradation	50~80%	Two bacterial strains and mixed cultures isolated from compost loaded with PVA-based material fed with PVA1799 and PVA1788	[76]

3.1. Photooxidation

Light is one of the most important environmental factors affecting the transformation and aging of MPs in the aquatic environment [77]. Under the irradiation of natural light, the color of MPs gradually changes, and cracks slowly appear, which leads to the decrease in its elasticity, ductility, impact resistance, and other properties, reflecting the aging of MPs [78].

The surface functional groups of MPs can adsorb the light energy of the natural light, especially the UV light, contributing to the generation of free radicals, which will break bonds on the polymer backbone, and result in the spontaneous depolymerization and degradation of MPs. The photooxidation process can be divided into three steps: chain initiation, chain transfer, and chain termination [79,80]. In the chain initiation process, unsaturated chromophoric groups on the MPs surface will adsorb the light energy to break the C-C and C-H bonds on the polymer backbone, generating a free radical. The macromolecular structure of PE and PP do not contain any unsaturated chromophoric groups in their polymer backbone and are unable to absorb light energy. However, with the introduction of external impurities or structural abnormalities into the macromolecular structure, non-photoreceptive MPs can absorb light and lead to chain initiation. Subsequently, the free radical can react with O_2/H_2O in the aquatic environment and forms persistent free radicals, which lead the chain transfer process. The chain transfer process not only forms hydroperoxides, but also leads to complex radical reactions. Olefins, aldehydes, and ketones are generated in the chain transfer reaction, and they are more likely to initiate photooxidation because they contain unsaturated double bonds. The chain termination occurs when two radicals react and form inert products. Therefore, the reaction of random chain scission, branching, crosslinking, and formation of oxygen-containing functional groups are taken place due to the combination of radicals. Some MPs such as PVC are chlorine-containing polymers, when exposed to light, they undergo a dechlorination reaction first, producing hydrochloric acid and polyene polymers [79]. Then, polyene polymers participate in the reaction of photooxidation. In WWTPs, UV is commonly used for disinfection. Nonetheless, the recommended UV dose for WWTPs has little effect on MPs. In contrast, excessive UV irradiation (20 times) can significantly alter the surface morphology, chemical feature, and hydrophobicity of MPs, including cracks, wrinkles, and protuberances [81].

It was found that the adsorption capacity of photo-aged MPs for hydrophilic pollutants was higher than that of virgin MPs, and their main adsorption mechanisms included partitioning, electrostatic interactions, and intermolecular hydrogen bonding [82]. The improved hydrophilic and migration properties of photo-aged MPs would not only enhance the adsorption capacity of some hydrophilic contaminants but also further enhance the migration capacity of the adsorbed contaminants. The results show that the significant enhancement of the adsorption affinity of photo-aged PS-MP for 4-nonylphenol is due to the fact that PS-MP can make polar compounds more strongly adsorbed to their surface by enhancing hydrogen bonding. In contrast, for non-polar pollutants, such as pyrene, photo-aged MPs enhance the adsorption of pollutants mainly through their increased pore volume [83]. Moreover, the adsorption capacity of aged MPs for heavy metals (e.g., Cu^{2+} and Zn^{2+}) was higher than that of the original MPs [84]. This may be related to the increase in specific surface area and the increase in oxygen-containing functional groups of MPs after the aging process [85]. At the same time, photo-aging MPs also promote the release of additives, which mainly include antioxidants, flame retardants, and colorants. The opacity and yellow coloration of the MPs increased significantly, which may be due to the oxidation of additives and adsorbed substances. A comparison of the leaching properties of photo-aged MPs revealed that the types of leachate varied greatly [86,87]. After UV photo-aging of PP-MPs, the antioxidant subunit diphosphonic acid 168 was found to be the main releasing substance [88]. A study comparing the release of hexaBDE from PS-MP surfaces under light and dark conditions showed that the release of hexaBDE from PS surfaces under light was 34.4 mg/g, which was greater than the release of hexaBDE under dark conditions (25.6 mg/g), suggesting that light aging accelerates the release of hexaBDE [89]. It was also found that the release of total organic carbon, Ca, Cu, and Zn increased significantly after photoaging MPs [90]. Therefore, changes in the surface properties of photo-aged MPs have an important impact on the release of plastic additives and the adsorption ability to pollutants in the environment.

After photoaging, both the enhanced adsorption capacity for contaminants and the accelerated release of additives may cause greater adverse biological effects. The toxicity of pristine and photo-aged polyvinylchloride-microplastics (PVC-MPs) to green algae in freshwater was investigated by Wang et al. Both pristine and photo-aged PVC-MPs at concentrations ranging from 10 mg/L to 200 mg/L had negative effects on the growth of green algae, and exposure to PVC resulted in a decrease in intracellular chlorophyll A. Moreover, the photo-aged PVC-MPs were more toxic due to the carbonyl groups formed on the surface of the aged PVC and the increased zeta potential that affected the interaction between the MPs and the algae [84]. Researchers investigated the leachate toxicity of additive-free PE, PET, PP, and PS versus two MPs obtained from electronic devices by leaching chemicals from plastics into artificial seawater in a simulated UV-induced weathering process. It was found that all plastic leachates activated oxidative stress response, and in most cases, UV-treated samples induced stronger oxidative stress effects compared to dark controls [91]. All these studies suggest that photoaged MPs may lead to stronger biotoxicity.

3.2. Mechanical Stress

Scientists have reached a consensus that the aging of MPs on beaches and water surfaces is mainly caused by photooxidation. Nevertheless, the aging process of MPs not exposed to light is still unclear. It has been considered that mechanical stress plays an important role in the aging process of MPs.

MPs are frequently subjected to the mechanical action of the surrounding environmental forces, such as the wear and tear of stones, gravel, water flow, etc. These actions will result in the physical aging of MPs [92]. Physical aging can change the physical and chemical properties of the MPs, such as crystallinity, degree of polymerization, thermal stability, hydrophilic, etc. The process then makes MPs smaller and more fragile [93].

Residual stresses can be produced during the process of plastic items production such as cold drawing, bending, cutting, rolling, etc., which can reduce the mechanical stability of plastic items and decrease their lifespan [94,95]. Once plastic items enter the aquatic environment, the residual stresses in plastic items will be superimposed on mechanical stress, resulting in the fragmentation of plastic items and the generation of MPs [96].

The molecular structure can determine the density and tensile strength of plastic items, influencing the fragmentation process under environmental stress. It has been proved that PE and PP are minimally fragmented under the environmental stress of sand abrasion; however, expanded polystyrene (EPS) is susceptible to sand abrasion, and easily decomposed into MPs [97]. Nevertheless, to improve the mechanical stability of plastic items, additives are frequently added to plastic items. Therefore, recent plastic items can be more resistant to environmental stress and release fewer MPs [98].

There exist C-C bonds (375 kJ/mol) and C−H bonds (420 kJ/mol) in the molecular structure of MPs. The thermal energy caused by mechanical abrasion is too low to break the C-C bonds and C-H bonds of plastic items. A previous study proved that the interaction of high-intensity ultrasonic irradiation and water can form violent shock waves with a high temperature (5000 K) and a high pressure (1000 bar), which can attack the bond of C-C and C-H, resulting the depolymerization and chain breaking of MPs [99]. High shear strength will generate radicals in the aquatic environment, which can react with oxygen and result in radical recombination [80]. The recombined radical has a higher oxidation potential that can efficiently degrade MPs. Moreover, the mechanical stress of the ball mill with oxide powders such as CaO, Fe_2O_3, SiO_2, and Al_2O_3, facilitates the dechlorination process of PVC, leading to a reduction in the molecular weight of PVC [100]. Nonetheless, the energy consumption of high-intensity ultrasonic irradiation is so high that cannot apply in actual engineering [99]. In addition, mechanical stress will destroy the original surface morphology of MPs, which causes the fracture of MPs and the formation of more cracks, presenting a higher specific surface area [92].

3.3. Advanced Oxidation Processes

Recently, advanced oxidation processes (AOPs) such as chlorination and ozone oxidation are frequently applied in WWTPs. Chlorine as a disinfection agent is widely used in WWTPs. Chlorine has a strong oxidizing ability that can affect the physical and chemical properties of MPs. MPs with different molecular structures have different resistant abilities to chlorination. It has been reported that PP is most resistant to chlorination, followed by high-density polyethylene (HDPE) and PS. Moreover, C-Cl bands can be introduced on the polymer backbone of MPs, altering the physical and chemical properties of MPs, such as toxicity and hydrophobia. Chlorination can also cause the redshift of the Raman spectroscopy of MPs, resulting in a better photo-sensitivity for MPs [101].

The ozone system is an advanced tertiary treatment technology for disinfection and the removal of emerging contaminants. Ozone has stronger oxidizing properties and can directly oxidize MPs and introduce C=O functional groups in the polymer backbone. Furthermore, hydroxyl radicals ($HO^\bullet$) can be generated from the decomposition of ozone in the aquatic environment, which have a stronger oxidation potential than ozone and may boost the aging process of MPs [102]. For PE and PP, after the oxidation process of ozone, ketones groups can be detected on the surface of MPs. However, except for the formation of the ketone groups, the hydroxyl group also can be detected on the surface of PS with the treatment of ozone, indicating the formation of carboxyl acids and alcohols. The hydrophobics of PE, PP, and PS were changed after ozone treatment, affecting the adsorption of pesticides [103].

Fenton and persulfate treatments are other oxidation methods. $OH^\bullet$ produced in the Fenton reaction has a high standard redox potential (E_0 ($OH^\bullet/H_2O$) = 2.80 V/SHE) that can break the C-C bonds and C-H bonds of plastic items. It has been reported that hydrophilic functional groups (C-O-H and O=C-O) can be introduced on the surface of PS and PC after Fenton treatment, increasing the surface wettability, and decreasing the floatability of PC and PS. Nonetheless, Fenton treatment has little effect on PVC. So, separation of hazardous PVC from plastics mixture can be achieved through Fenton treatment [71]. The size of MPs can be significantly decreased by the treatment of Fenton and heat-activated $K_2S_2O_8$. After 30 days of Fenton and heat-activated $K_2S_2O_8$ treatment, PS and PE MPs were fragmented into small pieces, and the dominant size class was reduced from 40–50 µm to 10–20 µm. The contact angles of PS and PE MPs can be decreased after the treatment of Fenton and heat-activated $K_2S_2O_8$, attributing to the introduction of oxygen-containing groups [76]. MPs can be noticeably reduced through an Mn@NCNTs/PMS system. PMS can be effectively activated to produce $SO_4^{\bullet-}$and $OH^\bullet$ in Mn@NCNTs/PMS system, which can realize 50 wt% of MPs mass lost rate by assisting with hydrolysis. In addition, the intermediates from MPs degradation had no hazard to the microorganisms, and even serve as the nutrient for waterborne algae [104].

Electrochemical advanced oxidation processes (EAOPs) can degrade MPs through electrochemical reactions without the addition of chemicals. $SO_4^{\bullet-}$ and $OH^\bullet$ can generate in situ on the surface of the electrode, attacking the surface functional group of MPs. After 6 h of electrolysis with a current intensity of 9 A, 89% of the MPs can be degraded in water. Through anodic oxidation treatment, MPs do not break into smaller particles and they degrade directly into gaseous products. So, EAOPs are a promising method for MPs degradation in water without the production of any wastes or by-products. However, the current efficiency of EAOPs is so low that the surface reaction between MPs and electrodes should be further investigated [105].

3.4. Biodegradation

The process of biodegradation refers to the conversion of organic compounds into biogas and residual biomass to support microbial activities. In this process, plastic can be used as a carbon source [106–108]. Many types of MPs degrading microorganisms have been isolated from various environmental samples, such as marine environments, activated sludge from WWTPs, landfill, plastic waste dumps, and sediments. A handful of lepidopteran species has recently come under the spotlight as exceptional 'plastivores' [109,110]. Caterpillar larva of the greater wax moth Galleria mellonella is found to be able to ingest and metabolize PE at unprecedented rates. Cassone et al. investigated the intestinal microbiome in Galleria mellonella, founding microorganisms in the genus Acinetobacter appeared to be involved in the biodegradation process [111]. Thus far there have been more than 56 species across 25 genera of bacteria and fungi associated with PE biodegradation [112].

The degradation of MPs by bacteria is a complex process that involved multiple metabolic and regulatory pathways. In the first step of MPs degradation by bacteria, polymers must be converted to monomers by extracellular enzymes excreted by bacteria. That is because the particle size of MPs is so large and cannot pass through the membrane of bacteria. As a result, the attachment of enzymes to MPs is the rate-limiting step for degradation. In order to accelerate the bacteria-degrading of MPs, the formation of biofilm onto the surface of MPs is needed. The MPs with smooth or rough surfaces, including various forms and chemical compositions, can serve as substrates for bacteria inoculation. The previous research found that the biofilm formed by Pseudomonas citronellolis and Bacillus flexus masked the surface of MPs, resulting in the apparent degradation and modification of PVC [113].

MPs degradation by bacteria is influenced by the molecular properties of MPs themselves, such as mobility, crystallinity, molecular weight, functional groups, substituents present, and the modification by adding plasticizers or additives, which all significantly influence the bacteria-degrading of MPs [80]. On the other hand, the bacteria-degrading of

MPs is also influenced by the external environment, including light, heat, humidity, and the presence of chemicals. The external environment affects the growth and metabolism of related bacteria that significantly alter the rate of MPs biodegrading. Over the past few years, researchers pointed out that the gut environments within insect larvae, including Tenebrio Molitor, is the suitable microenvironments for plastic biodegradation [114]. Insect larvae can secret emulsifying factors that increase bioavailability and accelerate the biodegradation of plastics [115].

After the biodegradation of MPs, the changing of the characteristics of MPs occurs, including weight loss, tensile strength change, surface change, and chemical change. Due to the hydrolysis reaction of MPs mediated by bacteria, the polymers degrade to monomers which results in weight loss [116]. With the biodegradation of MPs, the degree of polymerization is decreased, which reduces the tensile strength of the MPs. An investigation of PE biodegradation by bacterial strains from the guts of plastic-eating waxworms indicated a significant decrease (>50%) in tensile strength in PE exposed to Bacillus sp. YP1 or Enterobacter asburiae YT1 [117]. Attributing to the formation of biofilm and the biodegrading reaction in the microenvironment, cracks, pores, and holes emerged on the surface of MPs, changing the surface topography of MPs [118]. Furthermore, the biodegrading process also changes the surface functional group of the MPs and resulting in shifts and changes in the intensity of the carbonyl bands [119]. An increasing number of studies have examined the MPs degradation potential of different bacterial consortia [120–122]. Some recent studies proposed 'syntrophic metabolism', in which the degradation products of MPs of one species are a source of carbon for another species [123].

In addition to bacteria, fungi also have the potential to adhere to and utilize MPs [124]. Fungi can promote the formation of different chemical bonds in MPs, such as carboxyl, carbonyl, and ester functional groups. The extensive surface area of fungal hyphae can penetrate the surface of polymeric substances and thus effectively contact and degrade plastic polymers [125]. Furthermore, fungi can promote the circulation and transformation process of substances [124]. Studies on the degradation of MPs by fungi are still an area of active investigation and some progress has been made.

Yamada-Onodera et al. isolated Penicillium simplex YK for the biodegradation of PE. It was shown that this strain could be observed in a lower molecular weight form of PE after 500 h of UV irradiation and 3 months of liquid culture, indicating that ultraviolet (UV) pretreatment can promote the degradation of MPs by the fungus [126]. In another study, Russell et al. screened two Pestalotiopsis microspora isolates to test their ability to degrade polyurethane (PUR) [125]. They identified a serine hydrolase to be responsible for observing the degradation of PUR, and the results demonstrated that the enzyme secreted by this fungus could promote the biodegradation of MPs.

Fungi can also degrade hydrolyzable plastics. Deguchi et al. first reported an Oxidative attack on nylon-6,6 for the white-rot fungi IZU-154, Trametes Versicolor, and Phanerochaete chrysosporium [127]. Some high-density polyethylene (HDPE) degrading fungal strains were isolated from PE waste dumped in marine coastal areas and screened under in vitro conditions. Two isolated fungal strains (Aspergillus tubingensis and Aspergillus flavus) were shown to be effective in degrading HDPE [128]. The weight loss of HDPE observed after incubation with the above two fungi was 6.02 ± 0.2% and 8.51 ± 0.1%, respectively. The excellent ability of these fungal strains to degrade MPs under in vitro conditions was demonstrated [129]. Although the fungal degradation rate is higher than the bacterial rate [130], plastic degradation by fungi requires more stable conditions than in the case of bacteria.

In addition, large amounts of MPs enter rivers and marine environments where microorganisms including micronuclei, algae, bacteria, and archaea also interact with the exposed MPs [68,131,132]. Arossa et al. collected 24 individual Red Sea giant clams and then exposed them for 12 days to four concentrations of PE microbeads ranging from 53 to 500 μm. Only 1.59% of MPs were removed by active ingestion. However, the shells of clams contributed a much higher removal rate of 66.03% of PE microbeads through passive adhesion [133]. Filamentous blue-green algae are able to grow on the surface of PE wastes in the presence of sunlight, water, and nutrients [134,135], showing the potential of microalgae to colonize plastic surfaces. In addition, some diatom and cyanobacterial species have shown efficiency in the biodegradation of PE [136]. However, the effectiveness of microalgae as plastic degraders needs further investigation.

4. Changes in Physical and Chemical Properties of MPs in Aging Process

After the aging process, the physical and chemical properties of MPs including size, crystallinity, thermal stability, surface functional groups, etc., are changed, which leads to a significant influence on the interface reaction between MPs and other pollutions as well as the toxicity of MPs.

4.1. Size and Morphology

With the aging process of MPs, the sizes of MPs are gradually reduced. It is understood that plastic particles in the environment will continue to degrade and become smaller and smaller, eventually resulting in the formation of nanoplastics [28]. At the same time, the surface morphology of MPs becomes rough. MPs in environmental samples can currently be detected down to a size of 1 μm. However, few studies identify plastic particles <50 μm due to methodological limitations [38]. The size distribution of MPs can be analyzed based on the images measured by an emission scanning electron microscope. UV irradiation can significantly attract the bonds on the polymer backbone of MPs, which accelerates the shattering of MPs. Wu et al. indicated that the average size of PP-MPs decreased from 443.65 μm to 84.13 μm after 12 days of UV irradiation. Furthermore, with the addition of Irgafos 168 antioxidants, the oxidation effect of UV irradiation on MPs decreased and resulting in a three-times larger size compared to the MPs without antioxidants [88]. Ren et al. accelerated the mechanical abrasion process of MPs and concluded that rough, pits, microcracks, and broken edges were observed on the surface of MPs [137]. The transmittance and thickness of MPs were also decreased under mechanical abrasion.

4.2. Crystallinity

Crystallinity represents the orderliness of polymer monomer arrangement, which can influence the thermal stability, mechanical stability, chemical stability, and biodegradability of MPs. The crystallinity of MPs can be measured by XRD, TGA-DSC, and ATR-FTIR. For MPs with different molecular structures, the crystallinity varied greatly after the aging processes. Yu et al. analyzed the variation in crystallinity of MPs after 30 years of a landfill in Shanghai, and conclude that the crystallinity of PP increased from 24.9% to 56.8%, however, the crystallinity of PE decreased from 55.6% to 20.8% [138]. Bonyadinejad et al. studied the effect of photooxidation on the material properties of low-density polyethylene (LDPE) and proposed that the crystallinity of LDPE increased from 24% to 35% after 3 weeks of UVA exposure (24 h) [139]. Furthermore, humidity is not conducive to the increase in crystallinity of LDPE under UVA exposure. The different aging process has a different effect on the crystallinity of MPs, Wu et al. found that the crystallinity of PP MPs decreased from 62.04% to 56.40% after UV oxidation for 12 days [88].

4.3. Thermal Stability

Different aging processes influence the thermal properties of MPs. Luo et al. investigated the nanoscale infrared, thermal and mechanical properties of TiO_2^- pigmented MPs before and after aging using the AFM-IR technique [140]. The result showed that the average softening temperature of unaged MPs and aged MPs were about 209.50 ± 11.48 °C and 94.91 ± 4.40 °C, respectively, suggesting that the high-temperature resistance of MPs decreased a lot after aging treatment. Meanwhile, the glass transition temperature of MPs decreased by 114.59 °C after the aging treatment. Ainali et al. found that exposure to UV irradiation would induce a continuous decrease in melting temperatures of LDPE, HDPE, and PP by increasing exposure time [141]. The decrease in melting temperature was mainly due to the shortening of the average chain length of the polymer, which leads to chain cleavage and reduces the average molecular mass. Yu et al. investigated waste plastics with different landfill ages [138]. It was shown that the melting point of PE decreases with an increasing number of years of landfill and the exothermic peak moves towards the low-temperature region. Sample PE-27 (27 years of landfill) has a double-shouldered peak in the melting phase (104.2–121 °C). The breakage of the polymer carbon chain produces a low molecular weight polymer. Therefore, there are two melting endothermic peaks during the melt phase.

4.4. Surface Functional Groups

As indicated above, UV radiation and oxygen exposure are the main two factors that induce the aging process of MPs in the aquatic environment. Ainali et al. evaluated the physicochemical properties changes of LDPE, HDPE, PP, and PS aged by laboratory UV-B [141]. The research demonstrated that new functional groups, such as vinyl, carbonyl, and hydroxyl/hydroxyperoxide were formed on the surface of MPs, leading to a significant increase in the carbonyl index of MPs. In addition, owing to the chain breaking and crosslinking reaction caused by UV radiation, thermal stability, and crystallinity of the four kinds of MPs exhibited an obvious decline, and there were many defects on the surface of the MPs. Furthermore, analytical pyrolysis coupled to gas chromatography and mass spectrometry was applied to provide a sign of oxidation and degradation extent and proved that the UV-aging process can change the peak position of the pyrolytic marker compounds, which results in unreliable quantification of MPs in the aquatic environment. Luo et al. put PE-MPs in a high temperature and strong radiation (Xenon-lamp) environment to accelerate the aging process of the MPs and demonstrated that cracks and fragmentation on MPs surface facilitated the accessibility of light and oxygen to the internal layer and therefore accelerated the aging process [142]. Furthermore, the pigments in MPs were continuously leaked during the aging process, and significantly increased the toxicity of MPs. Luo et al. later exposed the MPs mixture (25 wt% LDPE and 60 wt% TiO_2) in a Xenon-lamp for six weeks to simulate natural weathering and explored the nanoscale infrared, thermal, and mechanical properties of the MPs mixture before and after aging [140]. Results showed that many wrinkles and granular domains were observed on the surface of the aged MPs, in addition, C-O and -CHs bonds were constantly formed on the surface of MPs during the aging process. The softening temperature and glass transition temperature of aged MPs were markedly decreased after the aging process, and the hardness of MPs increased in the aging process.

5. Combined Pollution of Aged Microplastics and Other Pollutions

5.1. Heavy Metal

Heavy metals are generally used in industrial production, including the field of inorganic pigment production, thermal stabilizers, catalysis, smelting, and electroplating. Moreover, industrial wastewater emission and solid waste discharge will commonly cause metal pollution in the aquatic environment. For example, Cd, Pb, Cr, and Co compounds are used as colorants for polymers; Pb and Zn compounds are used as thermal stabilizers [98]; Sb and Zn compounds also have been used as either flame retardants and smoke suppressants. Heavy metals are discharged into the aquatic environment with industrial wastewater.

MPs are the carriers of marine heavy metal pollution, which can carry heavy metals into the food chain and cause higher ecotoxicological risks through biomagnification. Yanwang et al. made the research and found that the combination of PS-MPs and typical heavy metals (Cd, Pb, and Zn) produced a higher pollution load on the gut of marine medaka and triggered significant changes in the specific bacterial species and gut function in the male marine medaka [8]. Previous studies conducted by Kalčíková et al. have demonstrated that aged MPs can adsorb up to 44% more silver ions than pristine plastic particles and that subsequent leaching of silver ions is more intense. Aged MPs adsorbed with silver ions have a higher ecotoxicological potential, affecting both Daphnia and Daphnia at environmentally relevant concentrations. In the test with water fleas D. magna, 10 mg/L of MPs did not cause any measurable effect after 48 h of incubation. However, 10 mg/L of MPs with adsorbed Ag caused 100% inhibition of mobility of daphnids. MPs with adsorbed Ag also cause a significant decrease in the specific growth rate (36% and 44% inhibition, respectively) of duckweed L. minor [143].

MPs have the characteristics of small size, high specific surface area, and high hydrophobicity; they are carriers for heavy metal adsorption in the aquatic environment. It can be confirmed that the physical and chemical properties of MPs (such as molecular structure, size, crystallinity, specific surface area, hydrophobicity, functional groups, polarity, etc.) significantly influence the adsorption behavior of heavy metals. Specific surface area is the main factor that affects the adsorption of metal on MPs. Table 3 depicts the concentrations of common heavy metals in MPs obtained from different regions of the globe. It can be seen that there is no clear limit for the concentration of heavy metals.

The adsorption of heavy metals by MPs is achieved through a complex set of mechanisms (Figure 3) [144]. Recently, research measured the specific surface area of five different types of MPs (PS, PP, PE, PVC, and PET) of the same size, and the result was obtained following the order: PS > PP > PE > PVC > PET [145]. The pore volume of PE and PS was higher than that of PP and PVC, and the pore volume of PET was the lowest of these five types of MPs. In addition, the adsorption rate of Pb, Cr, and Zn on PE and PVC was higher than that of PET. Additionally, the functional groups on the surface of MPs can also interact with heavy metals and thus affect the adsorption of heavy metals on the surface of MPs. Chlorinated PE has the characteristic of higher polarity because of the presence of polar groups containing chlorine, resulting in the high adsorption behavior of Pb, Cu, and Cd [146].

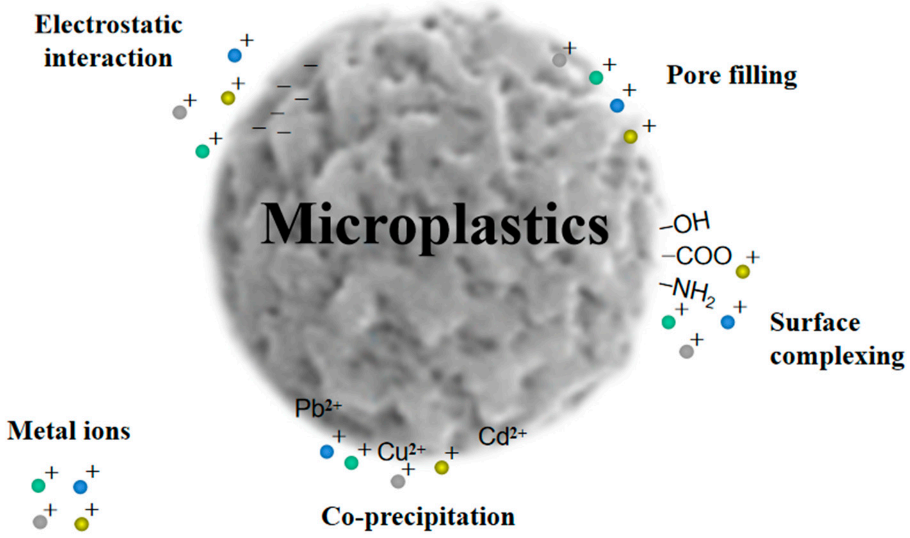

Figure 3. Possible adsorption mechanisms of heavy metals by MPs.

The presence of functional groups in different polymers affects their interactions with heavy metals, such as aromatic rings in PET and PS, CH_3 stretching in PP, terephthalate in PET, peroxide groups in PE, and a large number of common C-H stretching in all types of MPs [147]. Guo et al. observed that multiple functional groups on PVC and PP interact with Cd involving C=C, C=O, C-H, and C-O bond stretching, transformation, and bending vibrations; they concluded that different surface functional groups may play a role in the adsorption of Cd on MPs [148]. In addition, the density of MPs affects its distribution in the water column, thus indirectly influencing the interaction of MPs with heavy metals. In general, PP and PE are less dense than water and tend to float on the surface of the water, while PVC, PA, PET, and PS are denser than water and tend to sink [147].

Table 3. The range of concentrations of heavy metals is frequently detected in MPs. Reprinted with permission from Ref. [149]. 2017, Kutralam-Muniasamy, G.; Perez-Guevara, F.; Martinez, I.E.; Shruti, V.C.

	Asia (µg/g)	**Europe (µg/g)**	**South America (µg/g)**	**North America (µg/g)**	**Australia (µg/g)**
Mn	3.66–98.35	0.19–96.67	0.3–9	NA	0.0071–174.85
Cu	0.81–802.9	0.06–706.48	0.2–1	0.16–12.18	0.15–142.66
Pb	1.37–12839	0.04–227.02	<43.68	698	0.001–18.37
Ni	0.15–1958.50	0.04–131	<2.35	NA	0.0012
Zn	7.16–4303.21	0.3–23.3	0.3–8	15.57–66.9	0.17–185.39
Co	1.6–23.1	17.7–107	<0.34	NA	NA
Cd	0.02–102.81	0.001–76.7	<0.22	0.02–0.09	0.001–11.46
Cr	2.95–190	0.03–456.85	<9.83	NA	<2.76

NA = not available.

Some researchers indicated that aged MPs exhibited stronger adsorption of heavy metals than virgin MPs because of the higher specific surface area and polarity of aged MPs.

5.2. Organic Compounds

Recently, large numbers of organic compounds are used worldwide in industrial activities and daily life. Pharmaceuticals, pesticides, personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFOS), etc., are synthetic complex macromolecular organic compounds, which are difficult to degrade naturally. Additionally, the accumulation of PPCPs, PAHs, and PFOS in the aquatic environment will cause severe health and environmental problems. After prolonged exposure in aquatic environments, the organic compounds will adsorb onto the surface of MPs, and the concentration of organic compounds on the surface of MPs is a magnitude higher than those in the aquatic phase.

The hydrophobicity of organic compounds appreciably influences their adsorption behavior onto the MPs surface. In general, the octanol-water partition coefficient (K_{ow}) is an index to judge the hydrophilicity and hydrophobicity of organic compounds, and the organic compounds can be defined as weakly hydrophobic or hydrophilic ($\log K_{ow} < 3$), moderately hydrophobic ($4 \leq \log K_{ow} \geq 5$), and strongly hydrophobic ($\log K_{ow} > 5$). It was found that PE particles can serve as a carrier for the transport of PPCPs, and it was indicated that the sorption coefficient (K_d) of the four compounds followed with their K_{ow}, with the order of carbamazepine (K_d = 191 L/kg, $\log K_{ow}$ = 2.45) < 17α-Ethinyl estradiol (K_d = 312 L/kg, $\log K_{ow}$ = 3.67) < triclosan (K_d = 5140 L/kg, $\log K_{ow}$ = 4.76) < 4-methyl benzylidene camphor (K_d = 53225 L/kg, $\log K_{ow}$ = 5.1) [150]. In addition, with the aging process of MPs, oxygen-containing functional groups are formed on the surface of MPs, enhancing the hydrophilicity of MPs. Hüffer et al. accelerated the aging process of polystyrene microplastics (PS-MPs) by UV and analyzed the influence of the UV-aging process on the interaction of organic compounds with PS-MPs particles [11]. The research found that many -OH, C-O, and C-OH bonds were formed on the surface of PS-MPs after the UV-aging process, resulting in a significant increase in carbonyl index from 0.36 to 1.61. Nonetheless, compared to the changes of surface functional groups on aged PS-MPs, hydrophobic interactions play a major role during the sorption process. Due to the hydrophilic surface of aged PS after the aging process, the sorption coefficients of probe sorbates (K_{ow} = 1.15–3.90) by aged PS-MPs were up to one order of magnitude lower than for pristine particles. Furthermore, the presence of oxygen-containing surface functional groups on aged PS-MPs can form hydrogen bonds with surrounding water molecules, and hinder the sorption of organic compounds. You et al. investigated the morphology, structure, and methylene blue (MB) sorption behaviors of aged PE-MPs, and concluded that the aging process made the surface of MPs wrinkled and enlarged the specific surface area [151]. In addition, the formation of oxygen-containing functional groups on the surface of PE made PE hydrophilic, which is the main reason for the increase in the adsorption capacity of MB from 0.63 mg/g to 8.12 mg/g. Kapelewska et al. analyzed the adsorption behavior of benzophenone (BPh), 4-methylbenzylidene camphor (4MBC), benzophenone 3 (BPh3), and benzophenone 2 (BPh2) on virgin and aged HDPE, and revealing that the adsorption process for 4BMC, BPh, BPh3, BPh2 on aged HDPE were best fitted the Temkin isothermal model and the hydrophobic interactions was the main mechanisms for the sorption of BPh, 4MBC, BPh3, and BPh2 on the surface of HDPE [152]. Along with the adsorption process, the desorption process was also analyzed by some researchers. It has been proven that film/intraparticle diffusion models can be better decried than the desorption process of organic pollutants on MPs. The major stages of film/intraparticle diffusion-adsorption models contain external mass transfer, film/intraparticle diffusion and dynamic equilibrium [150]. Li et al. investigated the adsorption and desorption process of PAHs on UV-aged PE microspheres, and concluded that the desorption process of PAHs on aged PE microspheres was dominated by film diffusion, however, intraparticle diffusion also played a certain role in PAHs desorption [153].

Cheng et al. collected aged MPs from eight rivers draining into Pearl River Estuary and found that a higher average concentration of PFASs (616 ng/g) was adsorbed onto the MPs extracted in the drain outlets from urbanized cities, which was about 20 times higher than that extracted from agricultural and forested areas (29.3 ng/g) [154]. Moreover, 8:2 disubstituted polyfluoroalkyl phosphates were detected with the highest frequency (92.5%) and can be derived from a similar source as 6:2 disubstituted polyfluoroalkyl phosphates and perfluorotetradecanoic acid. Furthermore, higher concentrations of PFASs on MPs were found in dry seasons, while lower concentrations were observed in wet seasons. Llorca et al. analyzed the adsorption behavior of PFASs on MPs under environmental conditions and demonstrated that the interaction between perfluoro sulphonates/sulphonamides and MPs was stronger than other PFASs [155]. Additionally, MPs of PS and PS-COOH had more affinity for PFASs than HDPE. The aging process can reduce the particle size of MPs, and promote the adsorption of PFASs. Furthermore, salty water can change the surface charge of MPs and have a negative effect on the adsorption behavior of PFASs on MPs. A study indicated that the aging process can form dense biofilms on the surface of MPs, which significantly increased the surface area and changed the hydrophobic/hydrophilic characteristics of MPs [156]. The adsorption process of PFASs on biofilm-modified MPs can be explained by both chemisorption and physisorption, and the adsorption capacity of PFASs of MPs can be markedly increased by biofilm modification. In addition, the presence of polarized N-H bonds in biofilm-modified MPs can facilitate PFOS partitioning because of hydrophobic interactions and hydrogen bonding mechanisms.

5.3. Microorganism

With the aging process of MPs in the aquatic environment, microorganisms will attach to the surface of MPs and form biofilms, especially pathogens adsorbed on the MPs surface can drift around the world with the ocean current [157], resulting in the invasion of alien species and diseases. Mincer et al. showed that plastics entering the environment are instantly colonized by mobile biofilms and estimated that plastic marine litter harbors 1000–15,000 tons of microbial biomass [158]. Aged MPs with biofilms have the potential to adsorb large amounts of metals and further transport them to more acidic waters where they will leach at much higher rates than pristine MPs [143]. The formation and development of biofilms were influenced by many factors, such as material properties, environmental conditions, and weathering time [159]. Consequently, the community structure of biofilms on different MPs varies greatly, involving microbial selection, dispersal, diversification, and drift [160].

It can be concluded that geographical factors play an important role in microorganisms' colonization. For instance, the sequencing results showed an obvious difference in microbial community structure between the Baltic and North Seas (3%) and inferred the salinity of water may be the key factor that influences the biofilm formation and microbial community structure [161]. On the other hand, the characteristics of MPs and exposure times also significantly influence the compositions of bacterial communities on MPs. The

α-diversities and compositions of bacterial communities on MPs were marked distinct from small particle-attached communities in the surrounding water and large particle-attached communities in the surrounding water. In addition, the bacterial communities on PE and PP more closely resembled each other, however, they were quite different between PE and PET [162]. During the early colonization stages, the bacterial communities of biofilm attached to MPs are affected by the polymer type and surface parameters of the MPs, however, the communities will undergo temporal shifts from more different communities to more similar communities over time, irrespective of the MPs' characteristics [163].

Virsek et al. analyzed the bacterial community structure living on the MPs and demonstrated that 28 bacterial species including Aeromonas spp. and hydrocarbon-degrading bacterial species were identified from the biofilms on MPs [164]. Moreover, Aeromonas salmonicida as a fish pathogenic bacterium was also identified on MPs, which produces a potential threat of fish disease transmission. Some Vibrio species are identified as water-related human pathogens which cause wound infections, septicemia, or diarrhea. MPs can act as vectors for V. parahaemolyticus colonization, possibly leading to alien species invasion and disease spreading [165]. Furthermore, pathogens colonization is significantly influenced by the material properties of MPs and environmental factors. PET is more favored by pathogens than PP and PE. High temperature and high nitrite concentration in seawater can increase the colonization of pathogens in MPs [166]. As mentioned above, antibiotics can be enriched on MPs, which induces the colonization of antibiotic-resistant bacteria (ARB) and increases the abundance of antibiotic-resistant genes (ARG) [167]. Furthermore, with the migration of MPs by ocean currents, the horizontal transfer of resistance genes may have occurred, leading to the enhancement of antibiotic resistance in natural environments [168].

6. Environmentally Persistent Free Radicals (EPFRs) Formation on Aging MPs

6.1. Definitions of EPFRs

Environmentally persistent free radicals (EPFRs) are new organic pollutants with unpaired electrons that can exist in the environment for minutes or even months, as opposed to the traditional short-lived radicals [169,170]. EPFRs are widely present in a wide range of environmental media and components in the atmosphere, water bodies, and soil [171].

Some polymers are driven by external energy (e.g., heating, UV radiation, microwave radiation, and plasma action), and the covalent bonds undergo homolytic cleavage to form atomic clusters with asymmetric electrons, while the conjugation effect or spatial site resistance of the polymer stabilizes the unpaired electrons inside the macromolecule, forming EPFRs. The toxicity of EPFRs is mainly related to their reactivity. The production of reactive oxygen species (ROS) can be induced by substances carrying EPFRs in the atmospheric environment or by entering the aqueous phase system. It is generally believed that EPFRs on the particulate matter directly transfer lone pairs of electrons to oxygen molecules to form superoxide radicals ($O_2{}^{\bullet-}$), while $O_2{}^{\bullet-}$ forms H_2O_2 with hydrogen ions through disproportionation reactions, while H_2O_2 decomposes to produce •OH under exogenous catalysis on the one hand, and H_2O_2can get EPFRs on the other hand of electrons to form •OH [172].

Previous studies had shown that the formation of organic radicals always involves the transfer of electrons from aromatic hydrocarbon compounds to transition metals or the breaking of chemical bonds during UV irradiation, heating, electrical discharge, and electrolysis [173]. Among them, EPFR generation through electron transfer (redox reactions) usually occurs on atmospheric particulate matter, metal oxides, and soil inorganic minerals such as clay minerals. In these processes, light accelerates the electron transfer from organic pollutants to transition metal ions, facilitating the generation of EPFR. The breakage of chemical bonds in organic compounds or polymers during light exposure or thermal treatment can also lead to the generation of organic radicals.

6.2. The Formation Mechanism of EPFRs on Aging MPs

MPs such as PS and PF contain conjugated benzene rings in their molecule structure, which can continuously form EPFRs on their surface under light irradiation. Zhu et al. analyzed the aging process of four representative MPs (PS, PF, PE, and PVC) under solar light irradiation, and found that the EPFRs can be generated on the surface of irradiated PS and PF, rather than PE and PVC [170,174]. This research has detected transition metals such as Fe, Zn, and Pb in PF, PVC, and PE, however, no transition metals were detected in PS. Thus, Zhu et al. indicated that transition metals were not a prerequisite for the formation of EPFRs on MPs, and the chemical bond homolytic cleavage in MPs driven by light irradiation may be the main cause for the generation of EPFRs on MPs. Zhu et al. proposed a possible formation pathway of EPFRs on aged PS under UV-vis irradiation. Firstly, peroxides and other oxygen-containing chromophoric groups in MPs can absorb photons and generate reactive radicals, then, these radicals will attack the methine C−H bond in PS, and form tertiary alkyl radicals via the homolytic cleavage of methine C−H. Tertiary alkyl radicals will react with oxygen in the atmosphere, and generate tertiary peroxy radicals. Subsequently, the tertiary peroxy radicals will react with hydrogen radicals to form hydroperoxide groups (−C−OOH) [170]. Hydroperoxide groups are unstable and extremely photolabile, which can be cleaved to form tertiary alkoxy radicals and •OH under UV-vis irradiation. Finally, tertiary alkoxy radicals will be transformed into hydroxy, aldehydes, and ketones groups. The unpaired electron in all radicals has characteristics of strong delocalization because of the neighboring phenyl group, resulting in the relatively stable property of these free radicals. On the one hand, Zhu et al. suggested that reactive oxygen species, including $O_2^{\bullet-}$, $^1O_2$, H_2O_2, and •OH also play an important role in the formation of EPFRs on PS under long-term light irradiation [175]. The result showed that the correlations between the concentrations of EPFRs and the yields of total reactive oxygen species are significant positive correlations, and the correlation coefficient of $O_2^{\bullet-}$ and EFPRs was 0.94 ($p < 0.001$), which was obviously higher than that of H_2O_2 and •OH. Zhu et al. indicated that the electrons in EPFRs firstly transfer to dissolved oxygen under light irradiation, resulting in the formation of $O_2^{\bullet-}$. Then, H_2O_2 and •OH were successively generated via the disproportionation of $O_2^{\bullet-}$ and the decomposition of H_2O_2, respectively. In addition, the aged PS could absorb the energy of light irradiation transfer to the triplet states PS (^{3}PS*), which can activate dissolved oxygen to form $^1O_2$ (Figure 4) [176].

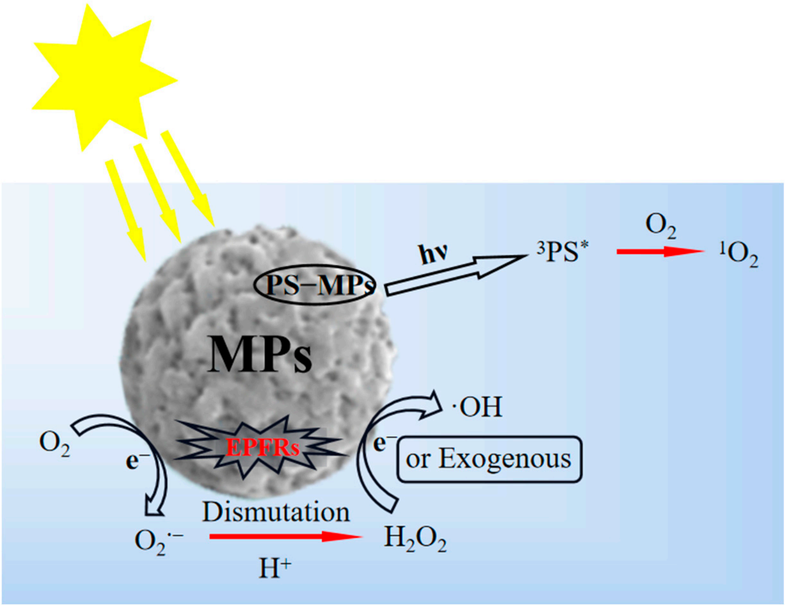

Figure 4. Proposed mechanism of MPs serving as photosensitizers for the formation of ROS in the presence of light.

Therefore, the methine C−H bond on MPs is the main target for the attack of radicals to form EPFRs, and the conjugated benzene ring structure contributes to the stability of EPFRs. Furthermore, the conversion process of EPFRs on the surface of MPs will induce different types of reactive oxygen species.

6.3. Toxicity of EPFRs on Aging MPs

EPFRs entering the organism induce the production of intracellular ROS, causing an imbalance between the cellular antioxidant defense system and free radical activity, which attacks cell membranes, lipid proteins, and DNA, resulting in oxidative stress or cellular damage. These ROS can also cause diseases in multiple tissues, such as neurological and cardiovascular diseases, damage the internal organs and immune system of the organism, increase the risk of cancer, and even cause death [176].

Liu et al. analyzed the EPFRs on photoaged tire wear particles (TWP) and evaluated their toxicity. The results showed that approximately 1.0×10^{17} spins/g of EPFRs (g-factor range 2.00308–2.00318) were formed on TWP under 60 days of light exposure, including more than 29% of reactive EPFRs (r-EPFRs). There was an obvious positive correlation between the concentration of EPFRs on TWP and the cytotoxicity of TWP. With the irradiation time increased from 30 days to 60 days, the cytotoxicity of TWP was significantly increased and resulting in the cell viability of macrophages decreasing to 73.5% and 54.9%, respectively. In addition, the EPFRs generated on TWP also cause oxidative stress response of macrophages. The macrophage engulfing photoaged TWP will cause the intracellular oxidative stress response, and the cellular membrane contacting with EPFRs on TWP will cause an excessive oxidative stress response. Furthermore, the oxidative stress by EPFRs generated on TWP may also lead to inflammation in macrophages, leading to the increase in the mRNA levels of inflammatory factors (IL-6, TNF-α). Overall, the formation of EPFRs on TWP is accompanied by ROS production, which is a major reason for cytotoxicity [177].

6.4. EPFRs on Aged MPs Enhance Photolysis of Organic Pollution

Previous studies have reported how MPs increase the persistence of pollutants and co-contamination with other pollutants, however, little research has been conducted on the promotion or degradation of organic pollutants by the formation of persistent radicals on aging MPs.

Liu et al. conducted experiments with PS as a representative plastic and sulfadimethoxine (SMT) as a target pollutant and found that the degradation rate of SMT was increased by 80.1% in the presence of sunlight irradiation compared to the control group under no light irradiation. The bursting experiments and radical trapping experiments revealed that hydroxyl radicals (•OH) were generated in the experimental system of PS-promoted oxidative degradation of SMT, which is the main ROS species affecting the oxidative degradation of SMT [178]. Ding et al. investigated the photolytic effect of PS on TC under solar irradiation and its mechanism. The corresponding results showed that PS could induce the photolysis of TC, while hydroxyl radical (•OH), singlet oxygen ($^1O_2$) and superoxide anion ($O_2^{\bullet-}$) all promoted the degradation of TC. Quantitative burst analysis showed that $^1O_2$ and $O_2^{\bullet-}$ were the major contributors with 15.25 ± 2.21% and 11.69 ± 1.84%, respectively [179]. A study investigated the photodegradation of cimetidine by aged polystyrene microplastics (PS-MPs) with different aging times (0–7 days) under simulated sunlight irradiation (700 W/m^2). PS-MPs with an aging time of 5 days degraded cimetidine much faster (>99%) than the original PS-MPs (<8%) after 2 h of irradiation. It is clear from the analyzed mechanism that the chromophore oxygen-containing groups (C-O, C-O) increase during the aging of PS-MPs and subsequently induce the formation of environmentally persistent free radicals (EPFRs) through the redshift of the absorption rate during photoaging, including •OH, $^1O_2$, and $^3PS^*$; $^1O_2$ plays a more important role in the degradation process [180].

All these studies suggest that MPs can act as photosensitizers to modify the fate of co-occurring drugs in aquatic environments. However, most of recent studies have only covered PS. In future studies, the potential of other types of MPs in forming EPFRs and catalyzing the degradation of other types of organic pollutants in aquatic environments may be the focus.

7. Conclusions and Perspectives

In the past few decades, MPs as widespread contaminants in aquatic environments have been widely reported. Therefore, analyzing the aging processes of these pollutants and monitoring the interaction of the aged MPs and other pollutions in the aquatic environment has attracted a good deal of attention. This study reviewed much of the related literature to comprehensively describe the aging process of MPs in the aquatic environment. The major conclusions of this review are shown as follows:

1. The aging processes of MPs in the aquatic environment include photooxidation, mechanical stress, AOPs, and biodegradation. Each aging process shows unique aging mechanisms. For photooxidation, the light-absorbing groups on the surface of MPs will absorb light energy to generate free radicals, and then oxidized the main chain structure of the polymer. Mechanical stresses will superimpose the residual stresses in the MPs and causing the age and break of MPs. The AOPs can generate free radicals that oxidated the surface of MPs, and introduce oxygen-containing groups. Biodegradation refers to the process that microorganisms use MPs as a carbon source to carry out their life activities.
2. The mechanical stability, thermal stability, and crystallinity of MPs exhibit an obvious declination after the aging process. Oxygen-containing functional groups are formed on the surface of aged MPs, resulting in a significant increase in the carbonyl index. Furthermore, the continuous leakage of pigments in MPs will occur during the aging process, and significantly increase the toxicity of MPs.
3. Due to the changes in the polarity, hydrophilicity, specific surface area, and surface functional groups of the aged MPs, the interactions of the aged MPs and other pollutions are significantly changed. The increase in the polarity and specific surface area of aged MPs can benefit the adsorption of heavy metals on aged MPs. With the formation of oxygen-containing functional groups in aging processes, the hydrophilicity of MPs increased, which influences the adsorption of organic pollutions with different hydrophilicity on aged MPs. Microorganisms in the aquatic environment can attach to the surface of aged MPs, and gradually form biofilms. The microbial community structure of the biofilms on aged MPs is influenced by molecular structure, surface hydrophobicity, and environmental factors.
4. Large amounts of EPFRs are produced on MPs as a result of photo-irradiation, which can induce oxidative stresses in biological systems and cause damage to cells and organisms. In addition, ROS can be generated during the formation of EPFRs on MPs, and increase the toxicity of EPFRs. However, attributing to the formation of ROS during the formation of EPFRs on MPs under photo-irradiation, the photo-aged MPs can act as photosensitizers that initiate photocatalytic reactions to degrade organic pollutants.

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