Review

Potential of Advanced Oxidation as Pretreatment for Microplastics Biodegradation

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Abstract: In the last two decades, microplastics (MP) have been identified as an emerging environmental pollutant. Due to their small size, MP particles may easily enter the food chain, where they can have adverse effects on organisms and the environment in general. The common methods for the removal of pollutants from the environment are not fully effective in the elimination of MP; thus, it is necessary to find a more suitable treatment method(s). Among the various approaches tested, biodegradation is by far the most environmentally friendly and economically acceptable remediation approach. However, it has serious drawbacks, generally related to the rather low removal rate and often insufficient efficiency. Therefore, it would be beneficial to use some of the less economical but more efficient methods as pretreatment prior to biodegradation. Such pretreatment would primarily serve to increase the roughness and hydrophilicity of the surface of MP, making it more susceptible to bioassimilation. This review focuses on advanced oxidation processes (AOPs) as treatment methods that can enhance the biodegradation of MP particles. It considers MP particles of the six most commonly used plastic polymers, namely: polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate and polyurethane. The review highlights organisms with a high potential for biodegradation of selected MP particles and presents the potential benefits that AOP pretreatment can provide for MP biodegradation.

Keywords: microplastics; biodegradation; pretreatment approaches; advanced oxidation processes

1. Introduction

Plastics have been part of human life for a long time, with global plastic production starting in 1940 [1]. The constant growth of the human population, followed by a higher standard of living, has required an increasing production of plastics. Unfortunately, this has resulted in large amounts of plastic waste entering the environment, which has become a global environmental problem. Once released into the environment, plastic items are gradually broken down into smaller pieces by natural processes or artificial activities; those pieces smaller than 5 mm are described as microplastics (MP). In addition, MP particles are intentionally produced for the needs of various industries, e.g., resin pellets and microspheres used as abrasives in cosmetics, etc. [2,3].

Nowadays, MP is present in practically all environmental constituents: water [2], soil [4], and even air [5,6], and due to the high persistence of plastics, the amount of MP in the environment is constantly increasing [7]. Unfortunately, MP has a high hazard potential [8] due to the fact that MP may easily enter the food chain; thus, the risk of biomagnification in high-level predators, including humans, is very high. MP can enter living organisms through ingestion, inhalation or skin infiltration [9]. Once MP enters the organism, it can impair fertility, cause immune responses, behavioral changes, digestive problems, various inflammatory conditions and intestinal damage, or eventually death [10–14]. The effects of MP on organisms can generally be categorized as physical (in terms of the shape or size of the MP particles) [15], chemical (in terms of the presence of

toxic additives or adsorbed chemical pollutants) [16,17] or biological (in terms of pathogens adsorbed on the surface of MP) [18]. However, despite the obvious danger posed by MP to the environment, there is still no legal regulation of the permissible concentrations of MP in the environment [19].

Large amounts of MP enter municipal wastewater treatment plants (WWTPs). Waldschläger et al. [20] conducted a comprehensive analysis of literature reports on the concentration of MP in WWTP influents and reported a range of 15–320 MP particles per liter. However, we have found reports with even higher values, e.g., 910 MP particles per liter, in the case of Dutch WWTPs [21]. Unfortunately, common WWTPs are generally unable to completely remove MP [20–23]. The average removal efficiency of MP is less than 90% and depends on the type of treatment applied and on MP characteristics such as size, density or morphology [23]. The coarser fraction of MP accumulates in sewage sludge [24], which can serve as a source of MP in the environment, primarily through the application of biosolids on agricultural land [25]. About 50% of sewage sludge in Europe is processed for agricultural use, resulting in an estimated 125–850 kg of MP per inhabitant entering European agricultural soils annually [26]. The smaller MP particles remain in WWTPs effluents and enter the aquatic environment [27]. Although concentrations of MP in the effluents are generally not too high (about one particle per liter [28], there are reports of much higher MP concentrations [21,29]), this transport route into the environment must be seriously considered because of the large volumes of water that is discharged. Considering the current state-of-the-art in MP pollution, it is necessary to find a sustainable method for the removal of MP from the environment. Among various approaches tested, biodegradation appears to be the most economically and environmentally acceptable, although it is often not favored among the scientific community for the removal of chlorinated plastics such as PVC, as this treatment poses an additional environmental hazard due to the possible formation of toxic chlorinated degradation products [30,31].

The biodegradability of MP has been tested with numerous organisms, but given the presence and importance of microorganisms in environmental biodegradation processes, it is not surprising that studies on the biodegradation of MP by microorganisms strongly dominate. For successful biodegradation of MP, three basic criteria must be met. First, the microorganisms present must be able to produce enzymes that can break down large plastic polymers into shorter chains or smaller molecules: oligomers, dimers and monomers. These molecules are small enough to pass through the semi-permeable membrane in the microorganism's cell, where they can be used as carbon and energy sources for the microorganism's growth and development [32]. Second, satisfactory process conditions such as temperature, pH, humidity, salinity, optical density, agitation speed, and/or the addition of biostimulants must be ensured [33–37]. Finally, the chemistry and morphology of MP must be such that they allow microorganisms to adhere and form a biofilm [38]. The properties of MP, such as surface roughness, surface electrostatic interactions and surface hydrophobicity are important parameters for biofilm formation [39,40]. The factors affecting the biodegradability of MP are shown in Figure 1. One of the most important factors is the chemical structure of the plastic polymer. Very small differences in the chemical structure of the polymer can result in large differences in biodegradability [32]. Thus, the possibility of microbiological degradation decreases with the increasing molecular weight of a polymer. In addition, the possibility of biodegradation decreases as the crystallinity of MP increases because the proper structure and close packing of the polymer chains prevent microorganisms from penetrating the MP particles. Therefore, semi-crystalline and amorphous polymers have a higher degree of biodegradability [41,42]. Finally, commercially available plastics usually contain a complex mixture of additives [43] that improve plastic materials' properties and extend their life. However, these additives can significantly affect the biodegradability of plastics, especially if they are designed to prevent or slow down biodegradation [44].
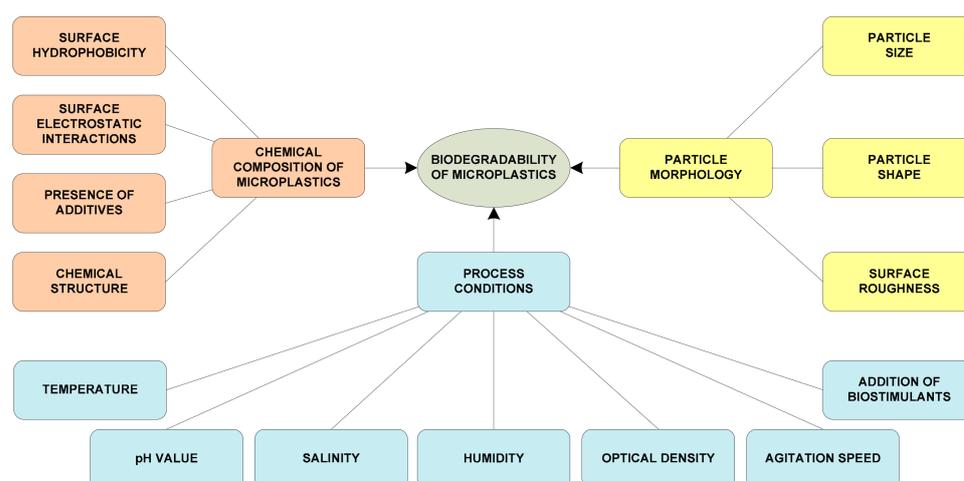
Figure 1. Factors affecting biodegradability of microplastics.

Studies addressing the biodegradability of MP have generally been conducted for the most commonly used plastic polymers (Figure 2), such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polyurethane (PUR) [45]. Auta and coworkers [46,47] exposed PE, PET and PS microparticles to the bacterium *Bacillus cereus*, PE, PET, PP and PS microparticles to the bacterium *Bacillus gottheilii*, and PP microparticles to the bacterium *Rhodococcus* sp. isolated from mangrove sediment; exposure time was 40 days in all experiments. Percent weight loss from MP for *B. cereus* was 1.6%, 6.6% and 7.4% for PE, PET and PS, respectively. Exposure to *Bacillus gottheilii* resulted in weight loss of 6.2%, 3.0%, 3.6% and 5.8% for PE, PET, PP and PS, respectively, while *Rhodococcus* sp. reduced the weight of PP by 6.4%. Yang et al. [48] showed that *Enterobacter asburiae* and *Bacillus* sp. could biodegrade low-density PE (LDPE) films with a thickness of 22.5 µm. The weight losses after 60 days of incubation were 6.1% and 10.7%, respectively. Bacteria belonging to the genus *Pseudomonas* are known to be able to degrade various oil contaminants [49,50], which also indicates their potential to degrade MP. For example, *Pseudomonas* sp. was found to be capable of degrading 4.9% to 28.6% of the low molecular weight PE (1.7–23.7 kDa) during 80 days exposure at 37 °C [51]. *Pseudomonas fluorescens* and *Pseudomonas chlororaphis* have been identified as organisms that can use PUR as a carbon source [52]. The same is valid for the bacterium *Delftia acidovorans* (formerly known as *Pseudomonas acidovorans*), which also uses PUR as a nitrogen source [53]. Lee et al. [54] investigated the potential of *Pseudomonas aeruginosa* to biodegrade PS, PE and PP microbeads. After 15 days of exposure, a decrease in the diameter of the microbeads was observed, with daily biodegradation rate values of 0.098%, 0.64%, and 0.025%, respectively. PET is generally considered non-biodegradable, but several studies have shown that some microorganisms can use PET as an energy and carbon source. For example, Farzi et al. [55] reported 68.8% biodegradation of 212 µm PET powder during 18 days of exposure to *Streptomyces* sp. at 28 °C, while Yoshida et al. [56] found almost complete biodegradation of 60 mg PET films (20 × 15 × 0.2 mm) by *Ideonella sakaiensis* after 42 days of incubation at 30 °C. PVC is also a very stable polymer that is generally not biodegradable. However, Anwar et al. [57] reported that two consortia of microorganisms isolated from landfills showed the ability to colonize and degrade PVC films (2.5 × 2.5 × 0.003 cm). The first, consisting of *Pseudomonas otitidis* and *Bacillus aerius*, reduced the molecular weight of PVC from 66.61 to 31.57 kDa, while the second, consisting of *Pseudomonas otitidis*, *Bacillus cereus* and *Acanthopleurobacter pedis*, was even more successful, with a reduction to 15.63 kDa; the exposure period was 9 months. In addition, some *Pseudomonas putida* strains can use vinyl chloride monomers as a carbon source for growth [30]. Giacomucci et al. [58] reported biodegradation of PVC by *Pseudoomonas citronellolis* and *Bacillus flexus*, but the bacterial activity was more focused on the additives present than on the PVC chains.
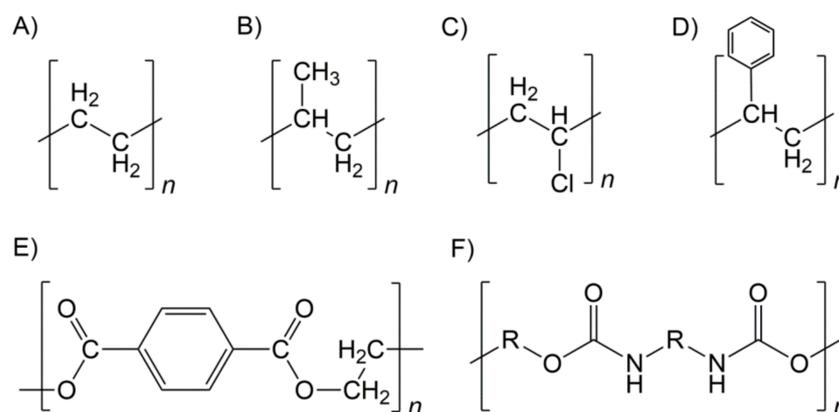
Figure 2. Chemical structures of polyethylene (**A**), polypropylene (**B**), polyvinyl chloride (**C**), polystyrene (**D**), polyethylene terephthalate (**E**) and polyurethane (**F**).

In addition to bacterial strains, the potential for biodegradation of MP was also demonstrated for some fungi. *Zalerion maritimum* partially biodegraded PE microfragments in a size range of 250 to 1000 μm. The authors' graphical representation of the data [59] shows a continuous increase in the degradation of MP during a 28-day exposure period. However, the degradation efficiency of approximately 43% reached on day 14 was the only value numerically reported within the exposure period. *Aspergillus tubingensis* and *Aspergillus flavus* were found to be capable of biodegrading 40 μm high-density PE (HDPE) films; the degradation rate after one month was 6.02% and 8.51% for *Aspergillus tubingensis* and *Aspergillus flavus*, respectively [60]. In addition, a consortium consisting of *Aspergillus niger*, *Aspergillus flavus* and *Aspergillus oryzae* degraded 14.66% of LDPE strips (the area was 2×2 cm with no information about the thickness provided) during 40 days of exposure. The experiment was performed with the addition of shredded LDPE particles (no information about the dimension of the particles was given) [61]. *Phanerochaete chrysosporium* caused a significant structural change in a starch-containing PVC film (0.05–0.07 mm thickness, surface area of 15 cm^2) followed by a decrease in the molecular weight of PVC from 80.3 to 78.9 kDa after 90 days of contact [62].

There are reports of testing the potential of various invertebrates, especially their larvae, in biodegrading MP [63–65]. In most cases, the ability of larvae to biodegrade MP is related not only to the enzymes produced in their digestive system but also to the enzymes produced by microorganisms in their gut. Larval biodegradation of MP generally does not result with mineralization, which means that smaller MP particles are formed and can be released into the environment, posing additional environmental risks. In addition, there are significant drawbacks that may limit the use of larvae as a strategy to remove MP and promote the use of microorganisms [30]. Culturing invertebrates is much more expensive than culturing microorganisms, and it is difficult to maintain the efficient production of larvae that feed on MP. Therefore, the search for new bacterial or fungal isolates with the potential for biodegradation of MP seems to be a more promising strategy.

Of course, biodegradation of MP by bacteria or fungi also has serious drawbacks, generally related to the slowness and insufficient efficiency of the process. However, since it is by far the most environmentally friendly and economically acceptable remediation approach, further research must be encouraged to find a way to speed up the process, increase efficiency and eliminate undesirable side effects. One possibility is the development of genetically enhanced microorganisms [66]. Current genetic engineering techniques offer the possibility of modifying microorganisms by introducing exogenous genes for specific enzymes involved in the degradation of MP. However, on-site experiments with genetically engineered microorganisms are limited for biosafety reasons, so evaluation of the efficiency of gene editing in the biodegradation of MP is limited to laboratory experiments [67]. Another possibility is the modification of the surface of MP particles. Since biodegradation is preceded by microbial colonization of the surface and the formation of a biofilm, it is likely

that increased colonization could lead to an overall increase in biodegradation efficiency. In addition, bacterial adhesion and biofilm formation are known to increase with increasing surface roughness [68,69]. A rougher surface can be achieved by various pretreatments.

The aim of this review is to provide an overview of advanced oxidation processes (AOPs) that can lead to surface degradation and modification of MP particles, making the particles more susceptible to biodegradation. AOPs are considered environmentally friendly because they are largely harmless to the environment and are considered effective in removing a vast array of organic pollutants [70,71]. Considering that plastics are organic pollutants, AOPs should be applicable in the remediation of MP-polluted environments. However, AOPs are associated with high process costs because they require expensive chemicals and/or energy input [72]. Therefore, it seems to be a good approach to use AOPs as a pretreatment for biodegradation, aiming to degrade only the surface of MP and make it rough and suitable for microbial colonization. AOPs usually combine the use of a strong oxidant with the use of catalysts or irradiation [70,73,74]. Accordingly, AOPs include a wide range of non-selective methods such as ozonation, photocatalysis, electrochemical oxidation, Fenton and Fenton-like processes, etc., as shown in Figure 3. These processes are characterized by generating in situ highly reactive free radicals such as hydroxyl (HO•) or sulfate (SO$_4$•$^-$) radicals. The radicals generated are capable of degrading various organic pollutants.
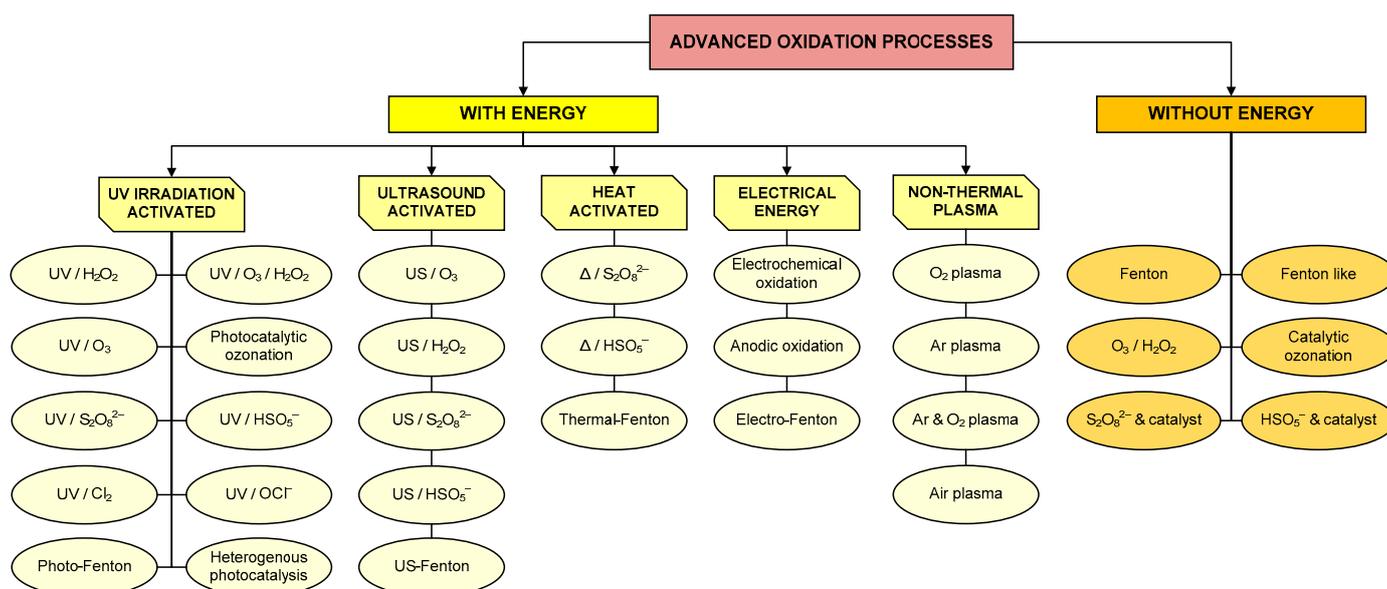
Figure 3. The main types of advanced oxidation processes.

2. Photolysis

Photolysis, although not considered an AOPs (only vacuum UV may generate in situ radical species), is a base for all photo-driven AOPs; thus, it will be discussed in context to be used alone and within AOPs for plastics degradation. Photolysis or photodegradation of polymers refers to the physical and chemical changes in polymer structure caused by light. Many organic polymers are sensitive to irradiation in the visible and especially in the UV range, as the latter has higher energy [75]. Very high irradiation energies are generally required for the photolysis of plastics. For example, longer UV wavelengths can cause the scission of C–C bonds in PET, while PP, PS and PVC require smaller wavelengths [76], such as vacuum UV irradiation (100–200 nm), which can be absorbed by all polymer bonds, especially by C–C and C–H bonds [77]. In addition, vacuum UV irradiation can lead to the degradation of the water molecule, if present, resulting in the formation of highly reactive hydroxyl radicals (HO•) and hydrogen radicals (H•), according to Equations (1) and (2) [78].

$$H_2O + h\nu \rightleftarrows HO\bullet + H\bullet \tag{1}$$

$$H_2O + h\nu \rightleftarrows HO\bullet + H^+ + e^- \qquad (2)$$
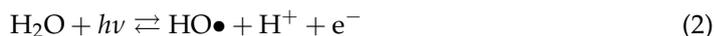
The oxygen radical and the ozone molecule can also be generated when oxygen is present in the system (Equations (3) and (4)).

$$O_2 + h\nu \rightleftarrows 2O\bullet \qquad (3)$$

$$O\bullet + O_2 \rightleftarrows O_3 \qquad (4)$$

PET strongly adsorbs UV irradiation below 315 nm [76]. Fechine et al. [79] irradiated 21 μm thick PET films at 290 nm and reported the scission of the PET chain leading to the formation of polymer radicals, as well as the intense formation of carboxyl (–COOH) end-groups known to promote further degradation of PET. In addition, irradiation of PET films (125 μm) at 254 nm resulted in a decrease in the PET contact angle, indicating a reduction of hydrophobicity of the PET surface [80].

The fact that UV photolysis can reduce the hydrophobicity of the surface of MP can be very important if the treatment is used as a pre-step to the biodegradation of MP. Namely, bacteria (with few exceptions) are hydrophilic [81]. Similarly, in fungi, only the aerial hyphae and conidia are hydrophobic, whereas yeast cells and the vegetative hyphae of filamentous fungi growing in moist environments are generally hydrophilic [82]. In contrast, MP is hydrophobic [83], so microorganisms with more hydrophobic cells adhere more strongly to the surface of MP [84]. Consequently, reducing the hydrophobicity of the surface of MP facilitates the adhesion of microorganisms to the polymer [85,86].

Some scientists consider PS to be very stable when exposed to vacuum UV irradiation because the energy absorbed by the aliphatic backbone can be transferred to the phenyl ring, and the phenyl ring is able to distribute the absorbed energy to the aromatic bonds and then relax thermally or by fluorescence. The homolytic scission of the C–C bond into two C-centered radicals, which is the first step of PS photolysis, usually ends with the recombination due to the low mobility of the PS chain [77]. However, López Gejo et al. [87] observed chemical and morphological changes on the surface of PS films (50–100 nm) irradiated at 172 nm. They reported that in the presence of air, C-centered radicals (R•) are likely to react with oxygen to form peroxyl radicals (ROO•; Equation (5)) and trigger additional reactions (e.g., the formation of HO•) that enhance polymer oxidation.

$$R\bullet + O_2 \rightleftarrows ROO\bullet \qquad (5)$$
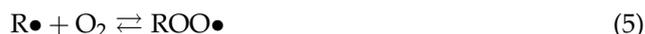
Martines et al. [88] treated HDPE, LDPE, and linear LDPE films (with a thickness of about 15 μm) with a UV irradiation source of 290–390 nm for 2, 4 and 24 h. All three polymers were commercial plastics containing antioxidants. The presence of antioxidants did not result in any changes on the polymer surface after 2 and 4 h of treatment. However, once the antioxidants were depleted, the surface began to change, as indicated by the formation of anhydride and carbonyl groups, which were detected after 24 h of treatment. Martines et al. proposed a degradation pathway that begins with the abstraction of the hydrogen atom and the formation of a C-centered polymer radical (R•; Equation (6)). However, according to Wilken et al. [77], there is another primary degradation reaction: homolytic scission of the C–C bond (Equation (7)). Highly reactive H• rapidly abstracts another hydrogen atom from the polymer and generates another polymer radical (Equation (8)).

$$RH + h\nu \rightleftarrows R\bullet + H\bullet \qquad (6)$$

$$R_2 + h\nu \rightleftarrows 2R\bullet \qquad (7)$$

$$RH + H\bullet \rightleftarrows R\bullet + H_2 \qquad (8)$$

In the presence of oxygen, R• can form a peroxyl radical (ROO•; Equation (5)) that continues the PE degradation in a chain reaction (Equation (9)) until it reacts with another radical to form a nonradical product (Equation (10)) [88].

$$\text{ROO}\bullet + \text{RH} \rightleftarrows \text{ROOH} + \text{R}\bullet \qquad (9)$$

$$\text{ROO}\bullet + \text{R}\bullet \rightleftarrows \text{ROOR} \qquad (10)$$

The main processes of PP photolysis by vacuum UV are identical to those of PE photolysis [77]. The only difference is that the scission of the C–C bond can lead to the abstraction of the methyl group, resulting in the formation of a methyl radical and a polymer radical, and not only the scission of the PP chain. Pure PVC does not adsorb wavelengths above 190 nm. Its photolysis also leads to the formation of radicals and has two main reactions: dehydrochlorination and the formation of polyene structures [89]. Radicals are also present in PUR photolysis. However, due to the specificity of the structure of PUR, it is difficult to define a universal pathway of photolysis. For example, PUR with *o*-nitrobenzyl units in the structure undergoes UV-induced photolysis leading to the formation of a nitroso compound and the release of a carboxylic acid [90], while UV photolysis of PUR polymers based on aromatic diisocyanates is associated with the formation of a diarylmethyl radical that rapidly generates peroxy radical in the presence of oxygen [91], etc.

Common to all six photolysis cases discussed is the high probability of cross-linking polymer chains by radical recombination and hydrogen abstraction from neighboring chains [92].

Since most pure plastics are susceptible to UV photolysis, commercial plastics contain photostabilizers as additives to increase the environmental stability of the plastics. Therefore, researchers are generally investigating the applicability of UV-promoted advanced oxidations, which is a much more aggressive treatment.

3. Hydroxyl-Radical Based AOPs

The hydroxyl radical (HO•) is probably the most important type of radical used in water treatment. It is a highly reactive, non-selective and short-lived oxidant that has been successfully used to degrade various organic pollutants in water [93,94]. With a high oxidation potential of (E^0 = 2.730 V; Table 1), this radical attacks organic pollutants by: (i) abstraction of hydrogen atoms, followed by subsequent hydroxylation, (ii) single electron transfer mechanism (less favorable) or (iii) by the addition to double bonds [95–97]. Due to their very short lifetime, HO• are produced in situ, either directly (vacuum UV, US, or non-thermal plasma technologies) or indirectly (through reactions between added oxidants/catalysts and/or their activation by UV or US) [93,94].

Table 1. Standard redox potentials (E^0) of the most common radical species encountered in AOP treatments [98].

Reaction	E^0/V
$\text{HOCl}^- \bullet + \text{H}^+ + \text{e}^- \rightleftarrows \text{Cl}^- + \text{H}_2\text{O}$	2.740
$\text{HO}\bullet + \text{H}^+ + \text{e}^- \rightleftarrows \text{H}_2\text{O}$	2.730
$\text{SO}_4^- \bullet + \text{e}^- \rightleftarrows \text{SO}_4^{2-}$	2.437
$\text{Cl}\bullet + \text{e}^- \rightleftarrows \text{Cl}^-$	2.432
$\text{Cl}_2^- \bullet + \text{e}^- \rightleftarrows 2\text{Cl}^-$	2.126
$\text{HOCl}^- \bullet + \text{e}^- \rightleftarrows \text{Cl}^- + \text{OH}^-$	1.912
$\text{HO}\bullet + \text{e}^- \rightleftarrows \text{OH}^-$	1.902
$\text{O}\bullet + \text{e}^- \rightleftarrows \text{O}^-\bullet$	1.6
$\text{HO}_2\bullet + \text{H}^+ + \text{e}^- \rightleftarrows \text{H}_2\text{O}_2$	1.46
$\text{OCl}\bullet + \text{e}^- \rightleftarrows \text{OCl}^-$	1.39
$\bullet\text{NO}_2 + \text{e}^- \rightleftarrows \text{NO}_2^-$	1.04
$\bullet\text{ClO}_2 + \text{e}^- \rightleftarrows \text{ClO}_2^-$	0.935
$\bullet\text{NO} + \text{H}^+ + \text{e}^- \rightleftarrows \text{HNO}$	–0.15
$\text{H}^+ + \text{e}^- \rightleftarrows \text{H}\bullet$	–2.31

3.1. AOPs with the Addition of Hydrogen Peroxide

One of the most common hydroxyl radical-based AOPs is the process involving the addition of hydrogen peroxide (H_2O_2). H_2O_2 is a strong oxidizing agent with a redox potential ranging from 1.763 V at pH 0 to 0.878 V at pH 14 [99]. Activation of H_2O_2 is usually by UV irradiation (Equation (11)) [100], although H_2O_2 is a weak absorber of UV light. Besides, metal salts and O_3 are also frequently used for activation.

$$H_2O_2 + h\nu \rightleftharpoons 2HO\bullet \tag{11}$$
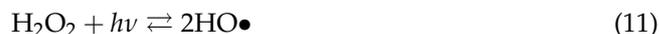
The concentration of HO• formed depends on the added dose of H_2O_2, the water matrix, and the emission spectrum and strength of the UV source [100]. An excess of H_2O_2 can reduce the oxidation rate; therefore, the optimal H_2O_2 dose must be determined and applied [101].

Considering the available studies on UV-C/H_2O_2 treatment of MP, Hüffer et al. [102] exposed PS MP (125–250 μm) to 10% H_2O_2 under 254 nm UV light. Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), scanning electron microscopy (SEM) and differential scanning calorimetry indicated significant oxidation of the particle surface after 96 h of exposure, but there was no significant change in the specific surface area. The surface area of aged MP was only 0.004 m^2/g greater than that of the initial MP. Easton et al. [103] studied the degradation of PET fibers ($\approx$40 μm) using UV-C/H_2O_2 treatment. SEM and FTIR spectroscopy showed the appearance of shallow holes, pits, and cracks on the surface of the particles, as well as changes in the relative abundance of oxygen-containing functional groups. For a 48-h treatment, the best removal efficiency of 52.7% (mass loss) was achieved with the addition of 500 mg/L H_2O_2 and UV-C irradiation of 4.0 mW/cm^2. UV/H_2O_2 treatment of PVC films (with a thickness of about 0.2 μm) [104] starts with a reaction of CH_3 end groups, which are the most susceptible to the attack of radicals. Once all CH_3 end groups are removed, the radicals attack the polymer chain, leading to chain scission, removal of chlorine, and formation of double bonds. Despite our best efforts, we have not found any reports of UV-C/H_2O_2 treatment of PP, PE or PUR. However, some of our preliminary experiments performed with MP from commercial PP and PE showed the formation of carbonyl groups at the surface of MP.

3.2. Ozonatzion

Ozonation is a general term for oxidation processes in which ozone (O_3) is used as the starting substance. O_3 is known to be a highly reactive agent with an oxidation potential of 2.07 V [105]. Therefore, ozone can directly oxidize organic pollutants, although a preferred approach is an indirect oxidation by the formation of HO• according to Equation (12). Ozone-induced formation of HO• can be easily achieved if the treatment is carried out in a basic medium [106].

$$3O_3 + H_2O \rightleftharpoons \frac{1}{2}O_2 + HO\bullet + HO_2\bullet \tag{12}$$

The reaction (Equation (12) may be accelerated by UV irradiation, especially when OH^- is not dominant, which yields the generation of H_2O_2 as an additional oxidant according to Equation (13) [107].

$$O_3 + H_2O + h\nu \rightleftharpoons H_2O_2 + O_2 \tag{13}$$

Subsequently, H_2O_2 is converted to HO• according to Equation (11). Moreover, H_2O_2 can be added to the system instead of generating it in situ. Ozonation in which H_2O_2 is added is called the peroxone process. In the peroxone process, the desired HO• are formed according to Equation (14) [108].

$$2O_3 + H_2O_2 \rightleftharpoons 2HO\bullet + 3O_2 \tag{14}$$
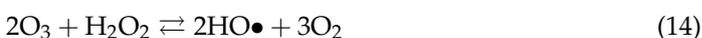
Further improvement in the production rate of HO•, and thus the efficiency of polymer ozonation, can be achieved by adding a catalyst [109]. Transition metals, such as iron, are

commonly used as catalysts for the activation of added H_2O_2 and the formation of HO•. These processes are referred to as the Fenton-based processes [93] and are discussed in detail in the next chapter.

Zafar et al. [110] studied the effect of ozonation on a mixture of microparticles of different sized PE, where 93.3% of the microparticles used were between 75 and 500 μm in size. Ozonation was performed with different O_3 doses ranging from 4 to 7 mg/min for 60, 120 and 180 min. After treatment, a decrease in crystallinity and the appearance of hydroxyl (–OH) and carbonyl (C=O) groups on the surface of MP were observed, indicating surface degradation of MP. Finally, surface oxidation was found to be affected by reaction time rather than the amount of O_3 added. Lee et al. [111] used mathematical models to investigate the mechanism of O_3-induced oxidative decomposition of nonpolar saturated molecules such as hydrocarbons and polymers, including PP, PS and PVC. The results showed that O_3 reacted with saturated hydrocarbons at room temperature or below. Moreover, these three polymers were not equally susceptible to ozonation of the C–H bond, which was most pronounced in the case of PS. A detailed schematic of the ozonation mechanism on saturated polymers can be found in the study by Patel et al. [109]. Patel et al. tested the ozonation effects on 60 μm thick LDPE films in the gas and aqueous phases (pH = 7), with and without the addition of $FeCl_3$ as a catalyst. The formation of peroxides on the polymer surface was the indicator of the efficiency of ozonation. Moreover, the formation of peroxides is a step that increases the hydrophilicity of the polymer surface and makes the surface more susceptible to microbial colonization. The results showed that the difference between ozonation in the gas phase and in the aqueous phase (in terms of peroxide formation) was almost negligible. The fact that a relevant concentration of HO• can be expected to occur only in the aqueous phase implies that molecular ozone plays the main role in the formation of peroxides on the LDPE surface. The influence of HO• is probably more pronounced in solutions with pH values above 7, since the experiments showed a negative influence of high pH values on the formation of peroxides. The addition of ferric ions (Fe^{3+}) by dissolving $FeCl_3$ in an acidic solution at pH 3 (creating a Fenton-like process) further increased the rate of peroxide formation.

Although O_3 has been shown to be able to oxidize polymers, higher doses or prolonged exposure to O_3 can have serious adverse effects on human health [112]. Therefore, its use is often avoided and replaced with less toxic species [113].

3.3. Fenton-Based Processes

Fenton-based processes are among the most popular techniques because they are carried out at room temperature and atmospheric pressure, which is an economic advantage. In addition, these processes are highly resistant to interference from background substrates, have relatively simple procedures, and generally have high mineralization rates for recalcitrant organic pollutants, such as MP [93,114].

The classical Fenton process involves electron transfer through a catalytic reaction between H_2O_2 and ferrous ions (Fe^{2+}), producing HO•, as shown in Equation (15) [114].

$$Fe^{2+} + H_2O_2 + H^+ \rightleftarrows Fe^{3+} + HO• + H_2O \tag{15}$$

On the other hand, the formation of HO• can be negatively affected by an excess of H_2O_2 (Equation (16)) or iron ions in bulk [93,105].

$$HO• + H_2O_2 \rightleftarrows HO_2• + H_2O \tag{16}$$

Therefore, it is necessary to determine the optimal molar ratio of Fe^{2+} and H_2O_2 for each treated system to avoid or minimize undesirable scavenging.

The classical Fenton process has its disadvantages, such as the low pH at which the process is carried out, the use of relatively large amounts of ferrous ions, and the formation of iron sludge, which can be a source of secondary pollution [115]. To avoid these disadvantages or to improve the efficiency of the classical Fenton process, numerous modi-

fications have been proposed [116]. These Fenton-based processes are generally divided into homogeneous and heterogeneous processes. The most important representative of the homogeneous Fenton-based processes is the photo-Fenton process, in which an additional amount of HO• is generated by reactions of formed ferric ions (Equations (17) and (18)) [109,117].

$$Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+ \qquad (17)$$

$$Fe(OH)^{2+} + hv \rightleftarrows Fe^{2+} + HO\bullet \qquad (18)$$

Therefore, compared to the classical Fenton process, the photo-Fenton process requires a lower addition of Fe^{2+} to generate the same amount of HO• [118]. Heterogeneous Fenton-based processes use solid catalysts containing iron and/or other transition metals [115].

Considering MP degradation by the Fenton process, the first step is hydrogen atom abstraction and formation of polymer radical (R•) according to Equation (19).

$$RH + HO\bullet \rightleftarrows R\bullet + H_2O \qquad (19)$$

Thereafter, mineralization can occur through a series of chain reactions [119].

Regarding applications of Fenton-based processes at MP, Ortiz et al. [120] studied the Fenton oxidation of five MP polymers: PET, PP, PVC, PE, and expanded PS; the size range was 150–250 µm. Experiments were conducted for 7.5 h under the following working conditions: T = 80 °C, pH = 3, $c(H_2O_2)$ = 1000 mg/L, and $c(Fe^{3+})$ = 10 mg/L. Fenton oxidation resulted in a decrease in the size of MP and an increase in the hydrophilicity of the particles. The values of weight loss were close to 10% regardless of the type of MP, indicating high stability of these solids against the attack of HO•. SEM showed the presence of wrinkles and holes on the MP surface, confirming surface degradation. These changes were more pronounced in PET and the expanded PS, probably due to their molecular structure. Namely, the presence of an aromatic ring in the structure of MP may increase the oxidation yield since it is known that HO• preferentially attacks aromatic rings and double bonds compared to single bonds of the alkane chain [121]. Wang et al. [122] tested the Fenton process as a pretreatment to the foam flotation in order to extract PVC microparticles from MP mixtures (particle size of 2.0–4.0 mm) consisting of equal mass ratios of PVC, PS and polycarbonate. Fenton treatment lasted 2 min and was performed under the following conditions: H_2O_2:Fe^{2+} molar ratio of 7500, H_2O_2 concentration of 0.2 M, temperature of 25 °C and pH 5.8. Fenton treatment significantly increased the surface roughness of PS. The treatment also increased the surface wettability and, accordingly, decreased the floatability of the microparticles of PS, which was related to the appearance of hydrophilic oxygen-containing groups on the surface of PS. At the same time, the treatment had no effect on the PVC microparticles. Piazza et al. [123] studied the heterogeneous photo-Fenton degradation of PVC (73 µm) and PP (155 µm) microparticles. The samples were irradiated with visible light. The catalyst used was ZnO nanorods coated with a tin oxide layer onto which Fe^0 nanoparticles were deposited. These nanoparticles were a source of Fe^{2+} trough reactions described by Equations (20) and (21).

$$Fe^0 + H_2O_2 + 2H^+ \rightleftarrows Fe^{2+} + 2H_2O \qquad (20)$$

$$Fe^0 + 2Fe^{3+} \rightleftarrows 3Fe^{2+} \qquad (21)$$
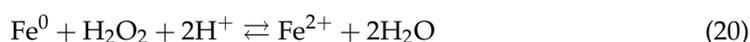
During the 7-day treatment, the particle size of PVC and PP decreased to 28 µm and 53 µm, respectively. The percentage of particle volume was also significantly reduced: 94% and 96% for PVC and PP, respectively. The treatment led to the formation of carbonyl and hydroxyl groups on the surface of PP. Interestingly, in contrast to the Fenton treatment performed by Wang et al. [122], the heterogeneous photo-Fenton treatment applied by Piazza et al. [123] resulted in changes in the PVC, including the formation of carbonyl groups, the prevalence of aldehyde or carboxylic acid groups, and finally the scission of the polymer chains. In addition, Piazza et al. [123] conducted a series of

bioassays with aquatic organisms and found no toxicity in the suspensions collected after the photo-Fenton treatment, indicating that no toxic by-products are generated during the photo-Fenton degradation of PVC and PP. Liu et al. [124] applied the Fenton treatment to PS and HDPE microgranules with an average particle size of 50.4 and 45.5 μm, respectively. During the 30-day treatment, the formation of cracks and depressions on the surface of the MP particles was observed; the longer the treatment lasted, the more pronounced these changes became. In addition, the treatment resulted in a significant reduction in the size of the microgranules, which was more pronounced in HDPE. Analysis of the X-ray photoelectron spectra showed that C−O and H−O bonds were initially formed at the surface of the two polymers studied, which were then converted to C=O and partially to O−C=O bonds. Miao et al. [125] subjected a suspension of 100 mg/L PVC particles of size 100–200 μm to electro-Fenton-like treatment with a TiO_2/graphite cathode for 6 h. The treatment was performed under potentiostatic electrolysis at −0.7 V against Ag/AgCl, continuously generating HO•. After the treatment, significant morphological changes were observed on the surface of the PVC particles using SEM analysis: a relatively smooth surface morphology at the beginning of the treatment was completely destroyed, followed by the appearance of holes and depressions. Further analysis confirmed the formation of carboxyl and hydroxyl groups on the polymer surface, the reduction of the molecular weight from 46.26 to 28.47 kDa, and a high degree of dechlorination, which was particularly pronounced at higher temperatures. All these indicate oxidation and scission of the polymer chains.

4. Sulfate-Radical Based AOPs

The sulfate radical, $SO_4•^-$, is the major reactive sulfur species in AOPs [126] and is usually obtained by physical activation (heat, ultrasound, photo-irradiation) of persulfate ($S_2O_8^{2-}$) or peroxymonosulfate (HSO_5^-) ions according to Equations (22) and (23), respectively [127,128].

$$S_2O_8^{2-} \underset{\text{PHYSICAL ACTIVATION}}{\xleftrightarrow{\hspace{2cm}}} 2SO_4^-• \tag{22}$$

$$HSO_5^- \underset{\text{PHYSICAL ACTIVATION}}{\xleftrightarrow{\hspace{2cm}}} SO_4^-• + HO• \tag{23}$$
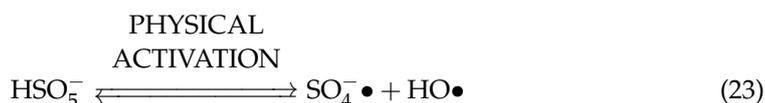
Another option for activation is chemical activation by the addition of a transition metal [93] (such as Fe^{2+} (Equations (24) and (25)), which forms a Fenton-like system [117].

$$S_2O_8^{2-} + Fe^{2+} \rightleftarrows SO_4^-• + SO_4^{2-} + Fe^{3+} \tag{24}$$

$$HSO_5^- + Fe^{2+} \rightleftarrows SO_4^-• + OH^- + Fe^{3+} \tag{25}$$
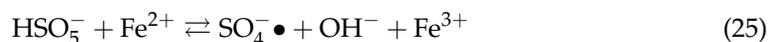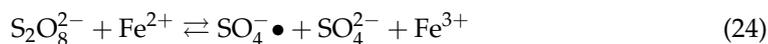
The oxides of transition metals are also commonly used as HSO_5^- activators, especially cobalt oxides such as Co_3O_4, which is a preferred HSO_5^- activator. Doping Co_3O_4 with another transition metal could further enhance the activity. For example, Cai et al. [129] tested the potential of $NiCo_2O_4$ nanosheets in activating HSO_5^- and reported that the synergistic activity of Ni and Co significantly enhanced the activation.

$SO_4•^-$ has a relatively high standard reduction potential ($E^0(SO_4•^-/SO_4^{2-}) = 2.437$ V; Table 1), making it a promising candidate for combating recalcitrant organic pollutants such as MP. Interestingly, the physical activation of peroxymonosulfate (Equation (23)) leads not only to the formation of $SO_4•^-$ but also to the formation of HO•, resulting in a dual effect on MP. In addition, the $SO_4•^-$ can react with hydroxide ions (Equation (26)) to form HO• as well, but the rate of this reaction is quite low [126].

$$SO_4^-• + OH^- \rightleftarrows HO• + SO_4^{2-} \tag{26}$$
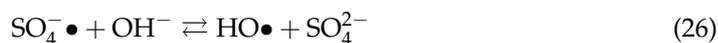
Treatments based on $SO_4\bullet^-$ have some advantages over treatments based on the formation of $HO\bullet$. First and foremost, $SO_4\bullet^-$ has a much longer lifetime than $HO\bullet$ and, therefore, a better possibility to react with MP. In addition, its potential, i.e., its oxidizing ability, is much less affected by variations in pH than the potential of the $HO\bullet$. Considering that MP is mostly found in heavy matrices in the environment, it is not unimportant that $SO_4\bullet^-$ is generally more selective for organic pollutants than $HO\bullet$. More specifically, $SO_4\bullet^-$ tend to strip electrons from organic molecules and convert them to organic radical cations, while $HO\bullet$ prefers hydrogen abstraction or addition to multiple bonds [93,126].

Photooxidation based on $SO_4\bullet^-$ is a promising approach for the degradation of MP, the potential of which is evident in the research published to date. Liu et al. [124] treated PS and HDPE microgranules using the heat-activated persulfate process and the Fenton process. They reported that cracks and depressions gradually formed on the surfaces of MP during the treatment. Within the first 10 days, comma-like shapes appeared, while within the first 30 days, multiple cracks appeared along with a ragged texture and a significant reduction in particle size. This occurred much faster compared to 20.9–40.3 years for PS and 25.2 years for HDPE, which were reported by the same authors as the expected times required to achieve equivalent roughness of PS and HDPE surfaces in nature. In addition, persulfate AOPs showed greater effects on the surface of MP than the Fenton process. Finally, Liu reported that both treatments significantly decreased the contact angles of PS and HDPE MP, i.e., decreased the hydrophobicity of the surface of the polymers. This is probably due to the formation of oxygen-containing groups on the surface of MP, such as carbonyl, carboxyl, or hydroxyl groups [85]. Zhang et al. [130] applied heat-activated persulfate treatment (30 min at 70 °C) to PS and PVC sheets (3 mm × 3 mm × 1 mm) to modify the polymer surface, and thus, change the floatability of the sheets. Similar to Liu's study [124], the treatment significantly decreased the contact angle of PS: by 12.20° and increased the surface roughness. However, in the case of PVC, the reduction in contact angle was practically negligible: only 0.13°, indicating that no hydrophilic groups were introduced on the PVC surface, which was confirmed by FTIR analysis. Obviously, treatment with $SO_4\bullet^-$ has a very limited effect on PVC.

5. UV/Chlorine Advanced Oxidation

The UV/chlorine process is considered an attractive alternative to the UV/H_2O_2 process in the remediation of polluted waters. The main advantage of UV/chlorine treatment is the lower cost of the oxidant used (chlorine gas, calcium hypochlorite or sodium hypochlorite) compared to hydrogen peroxide [131,132].

If chlorine gas is used in the treatment, chlorine in the water reacts to form two acids (Equation (27) [133]: strong hydrochloric acid and weak hypochlorous acid (pK_a value of 7.537 at 25 °C [134]).

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{27}$$

When hypochlorite salt is used, the salt dissociates in water to form the corresponding cation (usually Na^+ or Ca^{2+}) and the hypochlorite anion OCl^-, which is subsequently hydrolyzed according to Equation (28).

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \tag{28}$$
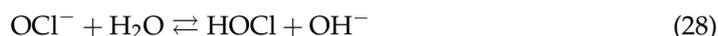
Both forms of hypochlorous acid, the nonionized and ionized forms, are susceptible to UV photolysis and form $HO\bullet$ (Equations (29), (30) and (34)) [133], but also some reactive chlorine species such as $Cl\bullet$, $OCl\bullet$ and $Cl_2\bullet^-$ (Equations (29)–(33)) [135,136].

$$HOCl + h\nu \rightleftharpoons HO\bullet + Cl\bullet \tag{29}$$

$$OCl^- + h\nu \rightleftharpoons O^-\bullet + Cl\bullet \tag{30}$$

$$HO\bullet + OCl^- \rightleftharpoons OH^- + OCl\bullet \tag{31}$$

$$Cl\bullet + OCl^- \rightleftarrows Cl^- + OCl\bullet \tag{32}$$

$$Cl^- + Cl\bullet \rightleftarrows Cl_2^- \bullet \tag{33}$$

Some other reactive chlorine species, such as $HOCl\bullet^-$, may also occur but are unstable and decompose rapidly. Decomposition by $O\bullet^-$ is generally considered negligible because a water molecule quickly captures this radical, and $HO\bullet$ is formed (Equation (34)) [135].

$$O^-\bullet + H_2O \rightleftarrows HO\bullet + OH^- \tag{34}$$

Both $HO\bullet$ and reactive chlorine species have higher reactivity to aromatic pollutants than to aliphatic pollutants [136]. Moreover, the rate constants of $Cl\bullet$ towards most aromatics are known to be higher or similar to those of $HO\bullet$, which is interesting for the degradation of PS or PET since these polymers contain benzene rings in their structure (Figure 2). The $OCl\bullet$ and $Cl_2\bullet^-$ are generally less reactive. The main reaction mechanisms of $Cl\bullet$ with most aromatic pollutants are electron transfer and addition, while reactions with $OCl\bullet$ and $Cl_2\bullet^-$ mainly involve electron transfer. With aliphatic pollutants, the reaction is mainly by hydrogen abstraction. Considering the high reactivity of chlorine species formed during UV/chlorine treatment, it is likely that halogenated by-products will be formed in waters rich in MP and other organics, posing an additional hazard to the environment. Therefore, monochoramine (NH_2Cl) or chlorine dioxide (ClO_2) is sometimes used instead of hypochlorites. Although photolysis of chloramines [131] or chlorine dioxide [137] also results in the formation of reactive chlorine species (Equations (35)–(38)), the production of thihalomethanes, haloacetic acids and total organic halogens is lower in these treatments compared to UV/chlorine treatment [138,139].

$$NH_2Cl + h\nu \rightleftarrows NH_2\bullet + Cl\bullet \tag{35}$$

$$NHCl_2 + h\nu \rightleftarrows NHCl\bullet + Cl\bullet \tag{36}$$

$$\bullet ClO_2 + h\nu \rightleftarrows O_2 + Cl\bullet \tag{37}$$

$$\bullet ClO_2 + h\nu \rightleftarrows O\bullet + OCl\bullet \tag{38}$$

It should be noted that ClO_2 is very reactive and is considered a radical due to an odd number of valence electrons [140]. Therefore, we wrote it as $\bullet ClO_2$ in Equations (37) and (38) and in Table 1. ClO_2 must always be generated on-site, as excess gaseous ClO_2 can decompose explosively [141]. Chloramines can be formed spontaneously during UV/chlorine treatment [142] if ammonia is present in the system (Equation (39)), which is very often the case with wastewater.

$$NH_3 + nHOCl \rightleftarrows NH_{3-n}Cl_n + nH_2O; n \leq 3 \tag{39}$$
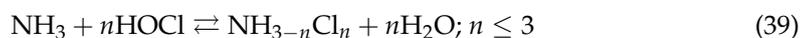
Such a scenario might be desirable for MP-polluted water because Khajouei et al. [143] consider UV photolysis of a mixture of chlorine and monochloramine to be a better treatment than UV/H_2O_2 treatment in terms of radical production: the chlorine/monochloramine mixture has higher combined molar absorption coefficients and quantum yields at 254 nm. However, the radicals present can convert ammonia to reactive nitrogen species ($\bullet NO$ and $\bullet NO_2$) [144] and highly toxic products such as nitrophenols, nitrosophenols and *N*-nitrosodimethylamine can be formed [136].

Regarding UV/chlorine, UV/monochloramine, or UV/ClO_2 treatment of selected MP, we found only one corresponding study in the literature. This was a study by Jia et al. [145] who modified the surface of PP film with UV-activated ClO_2 to increase aluminum adhesion to the film. The activation wavelength was 365 nm, and no information on film thickness was provided. The results showed that UV irradiation of the polymer surface at 365 nm did not cause photolysis of the surface but was only involved in the formation of radicals. The UV/ClO_2 treatment also did not cause significant changes in the degree of crystallinity of the PP film. However, the contact angle decreased from 107° to 86° after only 10 min of

treatment at 25 °C, indicating an increase in surface hydrophilicity. In addition, a significant increase in oxygen content, the formation of carboxyl groups, and the incorporation of a small amount of chlorine into the surface of PP were observed after treatment. In addition, Jia et al. varied the temperature of the reaction system and reported that higher temperature resulted in deeper oxidation of the film but had no significant effect on the total number of oxygen-containing groups or the contact angle. Other available studies used chlorination without UV induction of radical formation. Kelkar et al. [146] attempted to modify PP, HDPE and PS microfragments of approximately 2 × 2 × 0.05 mm in size by the oxidation with sodium hypochlorite at room temperature. The applied values of chlorine concentration–time (CT) ranged from 0.075 to 36,000 g min/L. The results of Raman spectrometric analysis showed that the chemical structures of HDPE and PP were not changed by dosages corresponding to drinking water treatment and wastewater treatment (0.075 and 0.150 g min/L, respectively). PP remained unchanged at the highest values of CT, but at 36,000 g min/L, the formation of chlorine-carbon bonds in HDPE was observed. Such formation is undesirable since organochlorine compounds are known to have increased toxicity. Raman analysis showed degradation of PS MP even at the lowest CT value (0.075 g min/L). However, no chlorine-carbon bond formation data were presented for PS at any value of CT. Although the treatment performed by Kelkar et al. was exclusively oxidation and not AOP, the degradation changes observed on HDPE and PS MP suggest that the application of a more aggressive treatment with induced radical formation may result in at least an equivalent degradation effect on the surface of MP.

PVC and HDPE account for more than 90% of thermoplastic polymers used for water pipes and fittings [147]. Since chlorination is currently the most common method of disinfecting drinking water worldwide [148], we have found numerous studies that look at the effects of chlorinated water on HDPE pipes [149–153]. Most of these studies discuss at some point the influence of radicals that occur in chlorinated water, probably considering the degradation of hypochlorite (Equations (40)–(42)), which is especially pronounced at temperatures above 40 °C [149].

$$OCl^- + HOCl \rightleftarrows OCl\bullet + Cl^- + HO\bullet \tag{40}$$

$$OCl^- + HO\bullet \rightleftarrows OCl\bullet + OH^- \tag{41}$$

$$OCl\bullet + OCl^- + OH^- \rightleftarrows 2Cl^- + O_2 + HO\bullet \tag{42}$$
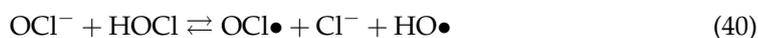
It should be noted that water pipes are made of commercial plastics that contain various additives that improve the properties of the material, such as photostability or oxidative resistance [154]. Therefore, the degradation results of samples made from commercial plastic samples can be affected by reactions with additives. Whelton and Dietrich [150] compared the effect of chlorinated water on sheets of pipe-used HDPE with 2% carbon black as an additive with the effect on sheets of prepressed HDPE resin without carbon black added. The thicknesses of the pipe-used and resin-prepressed HDPE sheets were 2.63 and 1.65 mm, respectively. The sheets were exposed to 5000 ppm chlorine at 70 °C for 28 days. The pH of the solutions was adjusted daily to 6.5, and the chlorinated water was replaced with the freshly prepared solution every 7 days. After 9 days of exposure, the surface color of both samples changed, indicating that some sort of reaction had occurred. The chlorine content of the water in each 7-day period steadily decreased from 5000 ppm to about 245 ppm for the pipe-used HDPE and 260 ppm for the resin-prepressed HDPE. These values were well below the measured chloride concentration in the blank sample, which was about 680 ppm, indicating the occurrence of reactions between chlorine and HDPE. The increased adsorption of water was observed on both treated samples after the 28th day of exposure. Whelton and Dietrich hypothesized that chlorine attacks the amorphous component of HDPE and causes some porosity, although this could also be due to the formation of hydrophilic groups on the HDPE surface. In addition, they conducted another experiment in which sheets of the pipe-used HDPE were exposed to a water solution containing significantly lower concentrations of chlorine (up to 250 ppm) at temperatures

of 25, 37, and 70 °C. After 140 days of exposure, they found carbonyl groups on the polymer surface, confirming surface oxidation. Mitroka et al. [153] conducted a similar experiment in which they exposed sheets of resin-pressed HDPE (without antioxidants) and the pipe-used HDPE to chlorinated water (up to 250 and 500 ppm Cl₂, respectively) for 160 days at 37 °C; the thickness of the sheets was 0.58 mm and 2.6 mm, respectively. Every 3 days, the chlorinated was replaced with a fresh solution, and the replaced solution was analyzed. Considering the substantial chlorine consumption reported by Whelton and Dietrich [150] over a 7-day period at 70 °C, the 3-day period chosen for treatment at a temperature of only 37 °C was probably too short to observe changes in the composition of the water used, since no statistically significant difference in reduced chlorite concentration was observed between the HDPE samples and the blank sample. However, contact with chlorinated water resulted in the formation of carbonyl groups on the surfaces of both HDPE samples, indicating oxidation. Mitroka et al. [153] proposed a pathway for the degradation of HDPE. They assumed that degradation is initiated by radical species present in chlorinated water, such as HO• or Cl•. Due to the high reactivity of these radicals, they do not diffuse into the interior of polymer material but react on its surface to form carbonyl groups. This step is followed by the auto-oxidation of HDPE, in which the formation of hydroperoxides and subsequent decomposition into carbonyls leads to the formation of further reactive species. The same conclusion was reached by Devilliers et al. [149], who analyzed the changes in unstabilized, stabilized (with carbon black as a stabilizer), and commercial pipe-used HDPE: all in the form of a film. The film thickness was 0.1 mm for unstabilized HDPE, 0.1 and 3.8 mm for stabilized HDPE, and 4.0 mm for pipe-used HDPE. Samples were exposed to 70, 40 and 4000 mg/L chlorine for 40, 15 and 5 weeks, respectively, at room temperature. In addition, Devilliers et al. made the interesting observation that the addition of carbon black had no effect on the rate of degradation under the conditions used. PVC has the best properties when used for cold water systems and has therefore been gradually replaced by chlorinated PVC (CPVC), which is suitable for both hot and cold water systems [155] and has inherent resistance to degradation by chlorinated water [156]. Therefore, we found only one report on the effects of chlorinated water on PVC, which, in addition, used samples that were above the size range of MP. Kowalska et al. [157] studied the effects of chlorinated water on the mechanical properties of PE and PVC pipes but also analyzed surface changes. They used commercially available pipes and cut them into test samples of 4 mm × 10 mm × 150 mm. The samples were exposed to water solutions containing 500 ppm chlorine at temperatures of 23 ± 2 and 70 °C for 28 days. The solutions were replaced with freshly prepared solutions every 7 days. After 28 days of exposure, the IR spectra of the outer and inner layers of the PE samples were recorded and compared, and only a slight discrepancy was found between the spectra. However, the formation of C=O bonds in the outer layer was confirmed. Similar to Whelton and Dietrich [150], Kowalska et al. [157] also observed the water penetration into the interior of the oxidized PE samples, which was more pronounced in the samples treated at 70 °C. Much stronger changes were observed in the PVC samples. The degradation occurred mainly in the outer layer, and the changes in the PVC chain were to a considerable extent conformational. Analysis of IR spectra showed the formation of C=O, C=C, and additional C–Cl bonds, confirming the oxidation and chain degradation of PVC. No additional adsorption of water on PVC was detected, suggesting that no hydrophilic groups were introduced on the PVC surface.

We did not find any recent studies on the chlorine-based degradation of PUR. However, in 1997, Kathua and Hsieh [158] exposed 20 cm long filaments of polyether-based PUR to a NaOCl solution for 10 to 540 min. The authors characterized the surface changes induced by treatment with 500 ppm active chlorine solution (unfortunately, the exact exposure time was not reported). The treatment resulted in the formation of quinoid (associated with the abstraction of hydrogen atoms from N and C atoms), azo (associated with the scission of the N–C bonds of urethane) and aldehyde groups (associated with the scission of the C–O–C bonds of ether) and the breaking of the hydrogen bonds of the urethane groups.

However, the hydrogen bonds between the urea carbonyls remained unaffected. As in the work of Mitroka et al. [153], it was assumed that the polymer degradation was initiated by the radicals present in the hypochlorite solution, most likely OCl• and HO•.

6. Glow Discharge Plasma Treatment

One of the common treatments for surface modification of thermoplastic polymers is plasma treatment. The plasmas used for this purpose are glow discharge plasma, also known as non-equilibrium plasmas, non-thermal plasmas or low-temperature plasmas. Such plasmas are capable of producing particles with very high electron concentrations at temperatures up to 10,000 K, while heavier species, such as ions and neutral molecules, are maintained at much lower temperatures (300–1000 K) [159,160]. The electrons react with the molecules present, leading to the formation of highly reactive species, such as excited atoms as described for Ar plasma (Equation (43)) [161], or radicals, as described for N_2, O_2 or CO_2 molecules (Equations (44)–(46)) [162,163]. Accordingly, some authors consider the glow discharge plasma treatment as AOP [164,165].

$$Ar + e^-_{fast} \rightarrow Ar^* + e^-_{slow} \tag{43}$$

$$N_2 + e^-_{fast} \rightarrow N_2^* + e^-_{slow} \tag{44}$$

$$O_2 + e^-_{fast} \rightarrow 2O\bullet + e^-_{slow} \tag{45}$$

$$CO_2 + e^-_{fast} \rightarrow CO + O\bullet + e^-_{slow} \tag{46}$$
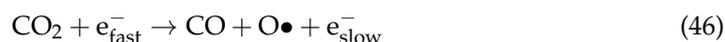
A direct current glow discharge or a high-frequency alternating current, usually radio frequency at 13.56 MHz or microwave frequency at 2.45 GHz, can be used to generate plasma [166].

Surface reactions of thermoplastic polymers by microwave-induced plasma are strongly influenced by the surface morphology of the polymer. Schmitt et al. [167] successfully applied microwave-induced oxygen plasma to modify the surface of PVC films (20 mm × 20 mm × 0.5 mm). The treatment lasted only 10 s and resulted in the scission of C–Cl bonds. This is consistent with several other reports indicating that chlorine bonds are thermally labile ("weak links") and are the site where the thermal degradation of PVC begins [168,169]. PVC degradation can occur via the ionic pathway or by radicals (at higher temperatures). There are two main degradation phases: dehydrochlorination, followed by the formation of polyene sequences, and decomposition of the polyene chains, which generally occurs at higher temperatures (up to 500 °C). Since the treatment carried out by Schmitt et al. [167] was in the presence of oxygen, surface oxidation and the formation of carboxyl groups occurred. However, this oxidation of the polymer can also lead to the formation of radicals that can potentially initiate radical-driven dehydrochlorination [168,170]. Lai et al. [171] reported the successful application of microwave-induced argon plasma to improve the hydrophilicity of PP and PET surfaces. The treatment resulted in a decrease in the contact angle of both polymers tested, which was direct evidence of increased hydrophilicity; the increase was much more pronounced for PP. The cause of the increased hydrophilicity was the formation of various oxygen-containing groups on the surfaces of the polymers, which was confirmed by X-ray photoelectron spectroscopy. The results suggested that the formation of C=O bonds was a key factor for the enhancement of surface hydrophilicity. In addition, plasma treatment resulted in a smoother surface of PET, which was considered beneficial for the surface hydrophilicity of PET, but no theoretical explanation was provided. In addition, no information was provided on the effects of plasma treatment on the surface roughness of PP. Treatment of PS sheets (5 mm × 5 mm × 0.125 mm) with oxygen glow discharge plasma [172] resulted in an increase in the concentration of oxygen atoms on the polymer surface due to the formation of various functional groups ranging from hydroxyl to carbonyl groups. At very high oxygen doses, the treatment led to the degradation of surface benzene rings, which hopefully could reduce the toxicity of the polymer surface and thus support the initial biodegradation on

the polymer surface. Dejun et al. [173] increased the surface wettability of medical PUR by glow discharge plasmas of N_2 and Ar. The samples were PUR sheets with an area of 1 cm $\times$ 1 cm and a thickness of 0.5–0.6 mm. The contact angle of untreated PUR of 78.8° decreased during exposure to N_2 plasma and reached a limit value of 61.9° after 10 min of treatment. The limit value for Ar plasma of 65.5°, reached after 2 min of treatment, shows the influence of the plasma medium and treatment duration on the reduction of the contact angle of PUR. The main reason for the improved wettability was the decomposition of COO bonds on the surface of PUR. Interestingly, no formation of new functional groups was observed.

Although glow discharge plasma treatment is an environmentally friendly process, its use as a pretreatment for the biological treatment of MP is associated with numerous disadvantages. Plasma treatment of MP, as performed in the studies previously discussed [85,163,167,171–173], exposes MP particles directly to plasma, which means that it is a dry process. Since the problem addressed in this review is the removal of MP from an aqueous medium, such an application of plasma treatment necessarily requires extensive sample preparation. There are studies on the application of plasma to wastewater samples [165,174] aimed at the degradation of organic pollutants. However, as far as we know, none of them deals with the degradation of MP, probably due to the insufficient selectivity of the approach. The basis of this approach is to bring reactive species from the plasma into contact with polluted water to generate large amounts of radical species, primarily HO• (Equations (47)–(49)) [162].

$$Ar^* + H_2O \rightarrow Ar + HO\bullet + H\bullet \tag{47}$$

$$N_2^* + H_2O \rightarrow N_2 + HO\bullet + H\bullet \tag{48}$$

$$O\bullet + H_2O \rightarrow 2HO\bullet \tag{49}$$

These radicals are then involved in the degradation of organic pollutants via the mechanisms already discussed in the chapter on AOPs. An important disadvantage of glow discharge plasma treatment is the cost of the treatment: the equipment for the treatment is expensive [122] and the process itself consumes energy. Therefore, the justification of glow discharge plasma treatment as a pretreatment for biodegradation of MP is highly questionable.

7. Studies on the Influence of AOP on the Biodegradation of MP

Despite the obvious potential of the AOP process as a beneficial pretreatment for biodegradation, the number of studies that have tested the efficiency of such a combination at MP is currently rather small. In addition, some authors investigated the biotreatment of MP particles pretreated with an AOP but without comparison with non-pretreated particles [46,47,86]. Some of the studies discussed in this chapter used UV pretreatment, which is generally not considered AOP, but in these studies, it was used in the presence of atmospheric oxygen.

Arkatkar et al. [175] pretreated 15 $\times$ 15 $\times$ 0.05 mm films of commercially available PP with UV irradiation (6-day exposure at 225 nm) and with the Fenton method (7-day treatment at pH 5.5). After pretreatment, the films were exposed to *Pseudomonas azotoformans*, *Pseudomonas stutzeri*, *Bacillus subtilis* and *Bacillus flexus* for 12 months. Statistical analysis of the bacterial growth data revealed different behavior of the four bacteria depending on the pretreatment method. Exposure to the bacterial cultures used resulted in weight losses in the range of 0.05–0.2%, 0.1–0.3%, and 0.5–2.5% for non-pretreated, Fenton-pretreated, and UV-pretreated PP films, respectively. Keto carbonyl indices showed faster degradation of UV-pretreated PP for all four bacteria used. All this suggests that the treatment strategy, i.e., selection of appropriate AOP pretreatment, plays an important role in efficiently supporting biodegradation of MP. Jeyakumar et al. [176] tested the effect of UV pretreatment (10-day exposure; $\lambda > 300$ nm) of commercial PP films (80 mm $\times$ 25 mm $\times$ 0.05 mm) on biodegradation by the fungi *Phanerochaete chrysosporium* and *Engyodontium album* (separately). After

12 months of exposure to selected fungal strains, it was reported that UV pretreatment acted in synergy with biotic treatment for both strains, resulting in higher weight loss of the pretreated PP films. Accordingly, the pretreated films had higher biomass content than the non-pretreated films.

Tribedi and Dey [177] studied the biodegradability of LDPE films (30 mm × 20 mm × 0.02 mm) placed in soil. The films were previously pretreated with a 15-W UV lamp for 100 h. After 28 days of exposure to soil microorganisms, the pretreated films were more degraded than the non-pretreated films. Interesting results were presented by Hadiyanto et al. [178]. They oxidized the surface of HDPE films (area 2 mm², 1–2 μm thick) by immersing them in a 15 M H_2O_2 solution for 72 h. The HDPE tested was a commercially available plastic with various additives. Although pure H_2O_2 oxidation is not an AOP, this oxidation was performed in a glass reactor, which means that the reaction mixture was exposed to light to some extent. After pretreatment, the films were exposed to the microalgae *Dunaliella salina* for 15 days. Although the results showed that *Dunaliella salina* could significantly degrade pretreated HDPE, Hadiyanto et al. reported that the substances (carbon and additives) released during oxidation had a negative effect on the growth rate of *Dunaliella salina*. Gilan et al. [84] studied the biodegradation of pretreated PE sheets (3 × 3 cm) by bacteria *Rhodococcus ruber* strain C208, and found that the formation of the carbonyl residues on the surface of photooxidized PE played an important role in initiating biodegradation. Pretreatment included a combination of exposure to multiple UV irradiation and water condensation cycles.

Gómez-Méndez et al. [85] pretreated LDPE films (30 mm × 10 mm × 0.016 mm) with oxygen glow discharge plasma to investigate the effect of pretreatment on the efficiency of biodegradation of LDPE by the fungus *Pleurotus ostreatus*. The treatment lasted 6 min and was performed at 0.030 mbar and 600 V. The treatment resulted in a significant increase in surface roughness and a decrease in contact angle by more than 75% (from 87° to 21°), indicating reduced hydrophobicity of the LDPE surface. Monitoring of the biodegradation experiment confirmed that the plasma treatment favored the adsorption, adherence, and growth of *Pleurotus ostreatus*, with the percentage of colonization increasing from 45.55% to 88.72%. An interesting study was reported by Scally et al. [163], who treated LDPE sheets with atmospheric glow discharge plasma and found that the addition of small amounts of CO_2 to the air used to generate the plasma promoted the formation of reactive species and enhanced the degradation of carbon bonds, which ultimately had a positive effect on the subsequent biodegradation treatment (tested on *Pseudomonas aeruginosa*).

Finally, we would like to draw attention to a study by Sullivan et al. [179] that presented a strategy for selectively converting plastic waste into useful chemical products. The study focused on the treatment of mixed plastic waste; however, the approach is likely applicable to MP. Sullivan et al. treated mixed plastic waste with a hybrid process that included metal-catalyzed autoxidation of plastic polymers as the first treatment. Autoxidation produces organic radicals in the initiation phase, which react with O_2 in the propagation phase to produce oxygenated products. The resulting mixture of small oxygenated molecules was subjected to biological treatment by an engineered bacterial strain of *Pseudomonas putida*. We assume that a more aggressive pretreatment for biodegradation of MP, e.g., the use of a strong oxidant (H_2O_2, $S_2O_8^{2-}$, or O_3) in combination with a catalyst (transition metal), should lead to an even more efficient hybrid treatment process. Of course, such an assumption has to be tested experimentally.

8. Conclusions

MP is an emerging pollutant with high adverse potential, and its concentration in the environment is steadily increasing. At the same time, conventional WWTPs are unable to completely remove MP from water. Therefore, an efficient removal method(s) is needed that is both environmentally and economically acceptable. Biodegradation is the most environmentally and economically acceptable remediation approach, but it is lengthy and relatively ineffective in terms of MP removal. One of the main reasons for this is

the inadequate properties of the surface of MP, which hinder the microbial adsorption and colonization of the surface. Therefore, appropriate modification of the surface of MP should improve the efficiency of biodegradation, and advanced oxidation is one of the most important candidates for such treatment. In this paper, the application of various AOPs as pretreatment for the biodegradation of MP was discussed.

Compared to biodegradation, AOPs also pose no threat to the environment when reagents are optimally dosed, with the exception of chlorine-based AOPs, which can produce toxic organic halogens as byproducts or where the presence of ammonia in treated water can lead to the formation of toxic nitro-compounds. Advanced oxidation is much more effective than biodegradation of MP, and the main disadvantage of AOPs drawback is basically only the economy due to energy consumption energy, relatively expensive reagents or expensive equipment as in plasma treatment. Therefore, their use to modify the polymer surface instead of degrading the whole polymer mass is very acceptable. AOP treatments usually lead to the breaking of polymer chains, which increases the roughness of the surface of MP. In addition, advanced oxidation increases the number of oxygen-containing groups on the surface of MP, leading to an increase in electrostatic interactions and a decrease in surface hydrophobicity. All these effects favor the process of MP bioassimilation, which creates conditions for more efficient biodegradation.

In this work, we did not compare the effectiveness of different AOP treatments of MP, but provided insight into the resulting surface changes that could contribute to better biodegradation of MP. This is because there is currently no standard procedure for testing the degradability of MP. Therefore, the only way to compare the performance of different AOP treatments is to perform our own tests under strictly predefined process conditions for all MP polymers of interest. However, since this is a review paper, we base our discussion on studies available in the literature. Unfortunately, we were unable to find comparable studies conducted under the same process conditions. We also did not find enough studies providing comparable information on intermediates formed during the AOP treatment of six selected MP polymers (except for the radical species formed). The analysis of intermediates is sometimes found in studies dealing with the treatment of plastics to which potentially harmful additives have been added, so that the reported intermediates result mainly from the degradation of the additives. In this work, however, we have tried to focus on the effects that the AOP treatments have on the polymer rather than on the additives.

The AOP treatments described have their own peculiarities, which makes it extremely difficult to draw a comprehensive diagram of their oxidation mechanisms. Therefore, we have focused on the main reactive forms that occur during the treatments to provide a simplified scheme of the AOP treatment mechanism, shown in Figure 4.
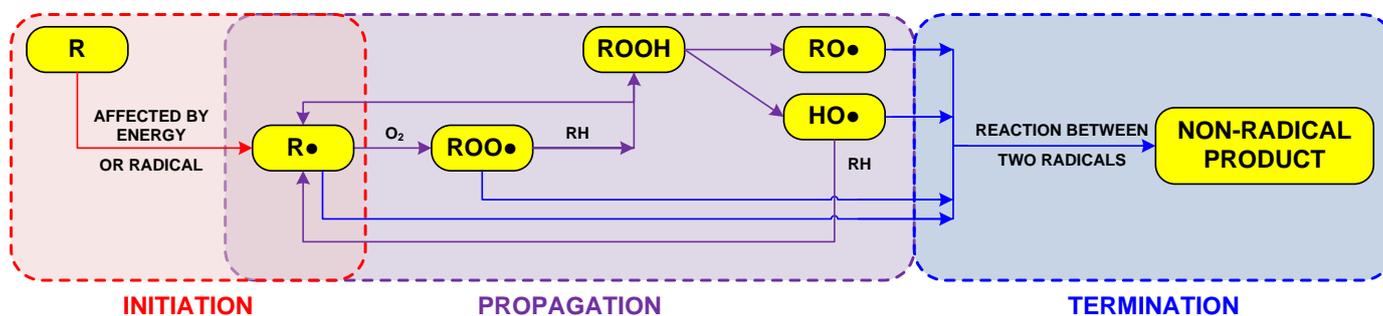
Figure 4. A generalized scheme of the AOP degradation of MP polymer (R).

To date, few studies have directly investigated the contribution of AOP pretreatment to the biodegradation of MP, and these have mainly examined the contribution of plasma treatment and UV irradiation in the presence of atmospheric air. However, given the current global efforts to develop green and sustainable technologies, it is expected that research in this area will be intensified in the coming years. An additional step to improve the process of removing MP could be the use of genetically enhanced cultures of microorganisms in the

biological part of the treatment, but it is likely that such a thing will wait until the potential safety risks of using genetically modified microorganisms in real systems are clarified.

References

1. Thompson, R.C.; Moore, C.J.; vom Saal, F.S.; Swan, S.H. Plastics, the environment and human health: Current consensus and future trends. *Phil. Trans. R. Soc. B* **2009**, *364*, 2153–2166. [CrossRef]
2. Shim, W.J.; Hong, S.H.; Eo, S. Chapter 1—Marine microplastics: Abundance, distribution, and composition. In *Microplastic Contamination in Aquatic Environments*; Zeng, E.J., Ed.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 1–26. [CrossRef]
3. Erceg, M.; Tutman, P.; Bojanić Varezić, D.; Bobanović, A. Karakterizacija mikroplastike u sedimentu plaže Prapratno. *Kem. Ind.* **2020**, *69*, 253–260. [CrossRef]
4. Boots, B.; Russell, C.W.; Green, D.S. Effects of Microplastics in Soil Ecosystems: Above and Below Ground. *Environ. Sci. Technol.* **2019**, *53*, 11496–11506. [CrossRef] [PubMed]
5. Prata, J.C. Airborne microplastics: Consequences to human health? *Environ. Pollut.* **2018**, *234*, 115–126. [CrossRef] [PubMed]
6. Liu, K.; Wang, X.; Fang, T.; Xu, P.; Zhu, L.; Li, D. Source and potential risk assessment of suspended atmospheric microplastics in Shanghai. *Sci. Total Environ.* **2019**, *675*, 462–471. [CrossRef] [PubMed]
7. Zhao, Y.-B.; Gao, P.-P.; Ni, H.-G. A Chemical Time Bomb: Future Risks of Microplastics. *Water Air Soil Pollut.* **2019**, *230*, 268. [CrossRef]
8. Alimba, C.G.; Faggi, C. Microplastics in the marine environment: Current trends in environmental pollution and mechanisms of toxicological profile. *Environ. Toxicol. Phar.* **2019**, *68*, 61–74. [CrossRef]
9. Yuan, Z.; Nag, R.; Cummins, E. Human health concerns regarding microplastics in the aquatic environment—From marine to food systems. *Sci. Total Environ.* **2022**, *823*, 153730. [CrossRef]
10. Hui, M.; Shengyan, P.; Shibin, L.; Yingchen, B.; Mandal, S.; Baoshan, X. Microplastics in aquatic environments: Toxicity to trigger ecological consequences. *Environ. Pollut.* **2020**, *261*, 114089. [CrossRef]
11. Pannetier, P.; Morin, B.; Le Bihanic, F.; Dubreil, L.; Clérandeau, C.; Chouvellon, F.; Arkel, K.V.; Danion, M.; Cachot, J. Environmental samples of microplastics induce significant toxic effects in fish larvae. *Environ. Int.* **2020**, *134*, 105047. [CrossRef]
12. Yu, Q.; Hu, X.; Yang, B.; Zhang, G.; Wang, J.; Ling, W. Distribution, abundance and risks of microplastics in the environment. *Chemosphere* **2020**, *249*, 126059. [CrossRef]
13. Rist, S.; Carney Almroth, B.; Hartmann, N.B.; Karlsson, T.M. A critical perspective on early communications concerning human health aspects of microplastics. *Sci. Total Environ.* **2018**, *626*, 720–726. [CrossRef]
14. Eltemsah, Y.S.; Bøhn, T. Acute and chronic effects of polystyrene microplastics on juvenile and adult *Daphnia magna*. *Environ. Pollut.* **2019**, *254*, 112919. [CrossRef] [PubMed]
15. Li, J.; Liu, H.; Chen, P. Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. *Water Res.* **2018**, *137*, 362–374. [CrossRef] [PubMed]
16. Prunier, J.; Maurice, L.; Perez, E.; Gigault, J.; Pierson Wickmann, A.-C.; Davranche, M.; ter Halle, A. Trace metals in polyethylene debris from the North Atlantic subtropical gyre. *Environ. Pollut.* **2018**, *245*, 371–379. [CrossRef] [PubMed]
17. Walpitagama, M.; Carve, M.; Douek, A.M.; Trestrail, C.; Bai, Y.; Kaslin, J.; Wlodkowic, D. Additives migrating from 3D-printed plastic induce developmental toxicity and neurobehavioural alterations in early life zebrafish (*Danio rerio*). *Aquat. Toxicol.* **2019**, *213*, 105227. [CrossRef] [PubMed]
18. Hou, D.; Hong, M.; Wang, Y.; Dong, P.; Cheng, H.; Yan, H.; Yao, Z.; Li, D.; Wang, K.; Zhang, D. Assessing the Risks of Potential Bacterial Pathogens Attaching to Different Microplastics during the Summer–Autumn Period in a Mariculture Cage. *Microorganisms* **2021**, *9*, 1909. [CrossRef]
19. McCormick, A.; Hoellein, T.J.; Mason, S.A.; Schluep, J.; Kelly, J.J. Microplastic is an Abundant and Distinct Microbial Habitat in an Urban River. *Environ. Sci. Technol.* **2014**, *48*, 11863–11871. [CrossRef]
20. Waldschläger, K.; Lechthaler, S.; Stauch, G.; Schüttrumpf, H. The way of microplastic through the environment—Application of the source-pathway-receptor model (review). *Sci. Total Environ.* **2020**, *713*, 136584. [CrossRef]
21. Leslie, H.A.; Brandsma, S.H.; van Velzen, M.J.M.; Vethaak, A.D. Microplastics en route: Field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. *Environ. Int.* **2017**, *101*, 133–142. [CrossRef]

22. Ngo, P.L.; Pramanik, B.K.; Shah, K.; Roychand, R. Pathway, classification and removal efficiency of microplastics in wastewater treatment plants. *Environ. Pollut.* **2019**, *255*, 113326. [CrossRef]

23. Xu, Z.; Bai, X.; Ye, Z. Removal and generation of microplastics in wastewater treatment plants: A review. *J. Clean. Prod.* **2021**, *291*, 125982. [CrossRef]

24. Cesaro, A.; Pirozzi, F.; Zafırakou, A.; Alexandraki, A. Microplastics in sewage sludge destined to anaerobic digestion: The potential role of thermal pretreatment. *Chemosphere* **2022**, *309*, 136669. [CrossRef] [PubMed]

25. Rolsky, C.; Kelkar, V.; Driver, E.; Halden, R.U. Municipal sewage sludge as a source of microplastics in the environment. *Curr. Opin. Env. Sci. Heath* **2020**, *14*, 16–22. [CrossRef]

26. Nizzetto, L.; Futter, M.; Langaas, S. Are Agricultural Soils Dumps for Microplastics of Urban Origin? *Environ. Sci. Technol.* **2016**, *50*, 10777–10779. [CrossRef]

27. Iyare, P.U.; Ouki, S.K.; Bond, T. Microplastics removal in wastewater treatment plants: A critical review. *Environ. Sci.-Wat. Res.* **2020**, *6*, 2664–2675. [CrossRef]

28. Browne, M.A.; Crump, P.; Niven, S.J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. Accumulation of Microplastic on Shorelines Woldwide: Sources and Sinks. *Environ. Sci. Technol.* **2011**, *45*, 9175–9179. [CrossRef]

29. Schmidt, C.; Kumar, R.; Yang, S.; Büttner, O. Microplastic particle emission from wastewater treatment plant effluents into river networks in Germany: Loads, spatial patterns of concentrations and potential toxicity. *Sci. Total Environ.* **2020**, *737*, 139544. [CrossRef]

30. Mohanan, N.; Montazer, Z.; Sharma, P.K.; Levin, D.B. Microbial and enzymatic degradation of synthetic plastics. *Front. Microbiol.* **2020**, *11*, 580709. [CrossRef]

31. Štefanac, T.; Grgas, D.; Marjanović, B.; Landeka Dragičević, T. Primjena i modeliranje sustava s biofilmom u obradi otpadnih voda. *Kem. Ind.* **2022**, *71*, 317–325. [CrossRef]

32. Gu, J.-D. Microbiological deterioration and degradation of synthetic polymeric materials: Recent research advances. *Int. Biodeter. Biodegr.* **2003**, *52*, 69–91. [CrossRef]

33. Karak, N. Biodegradable polymers. In *Vegetable Oil-Based Polymers*; Karak, N., Ed.; Woodhead Publishing: Cornwall, UK, 2012; pp. 31–53. [CrossRef]

34. Singh, G.; Singh, A.K.; Bhatt, K. Biodegradation of polythenes by bacteria isolated from soil. *Int. J. Res. Dev. Pharm. Life Sci.* **2016**, *5*, 2056–2062.

35. Goswami, M.; Chakraborty, P.; Mukherjee, K.; Garbita, M.; Bhattacharyya, P.; Dey, S.; Tribedi, P. Bioaugmentation and biostimulation: A potential strategy for environmental remediation. *J. Microbiol. Exp.* **2018**, *6*, 223–231. [CrossRef]

36. Skariyachan, S.; Patil, A.A.; Shankar, A.; Manjunath, M.; Bachappanavar, N.; Kiran, S. Enhanced polymer degradation of polyethylene and polypropylene by novel thermophilic consortia of *Brevibacillus* sps. and *Aneurinibacillus* sp. screened from waste management landfills and sewage treatment plants. *Polym. Deg. Stab.* **2018**, *149*, 52–68. [CrossRef]

37. Miloloža, M.; Ukić, Š.; Cvetnić, M.; Bolanča, T.; Kučić Grgić, D. Optimization of Polystyrene Biodegradation by *Bacillus cereus* and *Pseudomonas alcaligenes* Using Full Factorial Design. *Polymers* **2022**, *14*, 4299. [CrossRef]

38. Klein, S.; Dimzon, I.K.; Eubeler, J.; Knepper, T.P. Analysis, Occurrence, and Degradation of microplastics in the aqueous environment. In *Freshwater Microplastics: Emerging Environmental Contaminants? Wagner, M., Lambert, S., Eds.*; Springer Open: Cham, Switzerland, 2018; pp. 51–67. [CrossRef]

39. Rummel, C.D.; Jahnke, A.; Gorokhova, E.; Kühnel, D.; Schmitt-Jansen, M. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. *Environ. Sci. Technol. Lett.* **2017**, *4*, 258–267. [CrossRef]

40. Chandra, P.; Enespa; Singh, D.P. Microplastic degradation by bacteria in aquatic ecosystem. In *Microorganisms for Sustainable Environment and Health*; Chowdhary, P., Raj, A., Verma, D., Akhter, Y., Eds.; Elsevier: Chennai, India, 2020; pp. 431–467. [CrossRef]

41. Tokiwa, Y.; Calabia, B.; Ugwu, C.; Aiba, S. Biodegradability of plastics. *Int. J. Mol. Sci.* **2009**, *10*, 3722–3742. [CrossRef]

42. Pandey, S.P.; Shukla, T.; Dhote, V.K.; Mishra, D.K.; Maheshwari, R.; Tekade, R.K. Use of polymers in controlled release of active agents. In *Basic Fundamentals of Drug Delivery*; Tekade, R.K., Ed.; Academic Press: Chennai, India, 2019; pp. 113–172. [CrossRef]

43. Wiesinger, H.; Wang, Z.; Hellweg, S. Deep Dive into Plastic Monomers, Additives, and Processing Aids. *Environ. Sci. Technol.* **2021**, *55*, 9339–9351. [CrossRef]

44. Kubowicz, S.; Booth, A.M. Biodegradability of plastics: Challenges and misconceptions. *Environ. Sci. Technol.* **2017**, *51*, 12058–12060. [CrossRef]

45. Wilkes, R.A.; Aristilde, L. Degradation and metabolism of synthetic plastics and associated products by *Pseudomonas* sp.: Capabilities and challenges. *J. Appl. Microbiol.* **2017**, *123*, 582–593. [CrossRef]

46. Auta, H.S.; Emenike, C.U.; Fauziah, S.H. Screening of *Bacillus* strains isolated from mangrove ecosystems in Peninsular Malaysia for microplastic degradation. *Environ. Pollut.* **2017**, *231*, 1552–1559. [CrossRef] [PubMed]

47. Auta, H.S.; Emenike, C.U.; Jayanthi, B.; Fauziah, S.H. Growth kinetics and biodeterioration of polypropylene microplastics by *Bacillus* sp. and *Rhodococcus* sp. isolated from mangrove sediment. *Mar. Pollut. Bull.* **2018**, *127*, 15–21. [CrossRef] [PubMed]

48. Yang, J.; Yang, Y.; Wu, W.-M.; Zhao, J.; Jiang, L. Evidence of polyethylene biodegradation by bacterial strains from the guts of plastic-eating waxworms. *Environ. Sci. Technol.* **2014**, *48*, 13776–13784. [CrossRef] [PubMed]

49. Zhang, G.-L.; Wu, Y.-T.; Qian, X.-P.; Meng, Q. Biodegradation of crude oil by *Pseudomonas aeruginosa* in the presence of rhamno-lipids. *J. Zhejiang Univ. Sci. B* **2005**, *6*, 725–730. [CrossRef]

50. Liu, H.; Yang, G.; Jia, H.; Sun, B. Crude Oil Degradation by a Novel Strain *Pseudomonas aeruginosa* AQNU-1 Isolated from an Oil-Contaminated Lake Wetland. *Processes* **2022**, *10*, 307. [CrossRef]

51. Yoon, M.G.; Jeon, H.; Kim, M.N. Biodegradation of polyethylene by a soil bacterium and AlkB cloned recombinant cell. *J. Bioremediat. Biodegrad.* **2012**, *3*, 145. [CrossRef]

52. Cregut, M.; Bedas, M.; Durand, M.-J.; Thouand, G. New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process. *Biotechnol. Adv.* **2013**, *31*, 1634–1647. [CrossRef]

53. Nomura, N.; Shigeno-Akutsu, Y.; Nakajima-Kambe, T.; Nakahara, T. Cloning and sequence analysis of a polyurethane esterase of *Comamonas acidovorans* TB-35, and its primary structure. *J. Ferment. Bioeng.* **1998**, *86*, 339–345. [CrossRef]

54. Lee, H.M.; Kim, H.R.; Jeon, E.; Yu, H.C.; Lee, S.; Li, J.; Kim, D.-H. Evaluation of the biodegradation efficiency of four various types of plastics by *Pseudomonas aeruginosa* isolated from the gut extract of superworms. *Microorganisms* **2020**, *8*, 1341. [CrossRef]

55. Farzi, A.; Dehnad, A.; Fotouhi, A.F. Biodegradation of Polyethylene Terephthalate Waste using *Streptomyces* species and Kinetic Modeling of the Process. *Biocat. Agric. Biotechnol.* **2019**, *17*, 25–31. [CrossRef]

56. Yoshida, S.; Hiraga, K.; Takehana, T.; Taniguchi, I.; Yamaji, H.; Maeda, Y.; Toyohara, K.; Miyamoto, K.; Kimura, Y.; Oda, K. A bacterium that degrades and assimilates poly(ethylene terephthalate). *Science* **2016**, *35*, 1196–1199. [CrossRef] [PubMed]

57. Anwar, M.S.; Kapri, A.; Chaudhry, V.; Mishra, A.; Ansari, M.W.; Souche, Y.; Nautiyal, C.S.; Zaidi, M.G.H.; Goel, R. Response of indigenously developed bacterial consortia in progressive degradation of polyvinyl chloride. *Protoplasma* **2016**, *253*, 1023–1032. [CrossRef] [PubMed]

58. Giacomucci, L.; Raddadi, N.; Soccio, M.; Lotti, N.; Fava, F. Polyvinyl chloride biodegradation by *Pseudomonas citronellolis* and *Bacillus flexus*. *N. Biotechnol.* **2019**, *52*, 35–41. [CrossRef]

59. Paço, A.; Duarte, K.; da Costa, J.P.; Santos, P.S.M.; Pereira, R.; Pereira, M.E.; Freitas, A.C.; Duarte, A.C.; Rocha-Santos, T.A.P. Biodegradation of polyethylene microplastics by the marine fungus *Zalerion maritimum*. *Sci. Total Environ.* **2017**, *586*, 10–15. [CrossRef]

60. Sangeetha Devi, R.; Rajesh Kannan, V.; Nivas, D.; Kannan, K.; Chandru, S.; Robert Antony, A. Biodegradation of HDPE by *Aspergillus* spp. from marine ecosystem of Gulf of Mannar, India. *Mar. Pollut. Bull.* **2015**, *96*, 32–40. [CrossRef]

61. DSouza, G.C.; Sheriff, R.S.; Ullanat, V.; Shrikrishna, A.; Joshi, A.V.; Hiremath, L.; Entoori, K. Fungal biodegradation of low-density polyethylene using consortium of *Aspergillus* species under controlled conditions. *Heliyon* **2021**, *7*, e07008. [CrossRef] [PubMed]

62. Ali, M.I.; Ahmed, S.; Javed, I.; Ali, N.; Atiq, N.; Hameed, A.; Robson, G. Biodegradation of starch blended polyvinyl chloride films by isolated *Phanerochaete chrysosporium* PV1. *Int. J. Environ. Sci. Technol.* **2014**, *11*, 339–348. [CrossRef]

63. Kundungal, H.; Gangarapu, M.; Sarangapani, S.; Patchaiyappan, A.; Devipriya, S.P. Efficient biodegradation of polyethylene (HDPE) waste by the plastic-eating lesser waxworm (*Achroia grisella*). *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 18509–18519. [CrossRef]

64. Billen, P.; Khalifa, L.; Van Gerven, F.; Tavernier, S.; Spatari, S. Technological application potential of polyethylene and polystyrene biodegradation by macro-organisms such as mealworms and wax moth larvae. *Sci. Total Environ.* **2020**, *735*, 139521. [CrossRef]

65. Song, Y.; Qiu, R.; Hu, J.; Li, X.; Zhang, X.; Chen, Y.; Wu, W.-M.; He, D. Biodegradation and disintegration of expanded polystyrene by land snails *Achatina fulica*. *Sci. Total Environ.* **2020**, *746*, 141289. [CrossRef]

66. Kumar, V.; Sharma, N.; Duhan, L.; Pasrija, R.; Thomas, J.; Umesh, M.; Lakkaboyana, S.K.; Andler, R.; Vangnai, A.S.; Vithanage, M.; et al. Microbial engineering strategies for synthetic microplastics clean up: A review on recent approaches. *Environ. Toxicol. Pharmacol.* **2023**, *98*, 104045. [CrossRef] [PubMed]

67. Anand, U.; Dey, S.; Bontempi, E.; Ducoli, S.; Vethaak, A.D.; Dey, A.; Federici, S. Biotechnological methods to remove microplastics: A review. *Environ. Chem. Lett.* **2023**, 1–24. [CrossRef] [PubMed]

68. Yoda, I.; Koseki, H.; Tomita, M.; Shida, T.; Horiuchi, H.; Sakoda, H.; Osaki, M. Effect of surface roughness of biomaterials on *Staphylococcus epidermidis* adhesion. *BMC Microbiol.* **2014**, *14*, 234. [CrossRef] [PubMed]

69. Yu, P.; Wang, C.; Zhou, J.; Jiang, L.; Xue, J.; Li, W. Influence of surface properties on adhesion forces and attachment of *Streptococcus mutans* to Zirconia in vitro. *Biomed. Res. Int.* **2016**, *2016*, 8901253. [CrossRef]

70. Ameta, S.C.; Ameta, R. *Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology*; Academic Press: Chennai, India, 2018.

71. Feldman, D. Polymer Weathering: Photo-Oxidation. *J. Polym. Environ.* **2002**, *10*, 163–173. [CrossRef]

72. Kumar, V.; Shah, M.P. Advanced oxidation processes for complex wastewater treatment. In *Advanced Oxidation Processes for Effluent Treatment Plants*; Shah, M.P., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; pp. 1–31. [CrossRef]

73. Biń, A.K.; Sobera-Madej, S. Comparison of the advanced oxidation processes (UV, UV/H$_2$O$_2$ and O$_3$) for the removal of antibiotic substances during wastewater treatment. *Ozone Sci. Eng.* **2012**, *34*, 136–139. [CrossRef]

74. Verma, R.; Kundu, L.M.; Pandey, L.M. *Decontamination of distillery spent wash through advanced oxidation methods, In Advanced Oxidation Processes for Effluent Treatment PlantsShah, Shah, M.P., Ed*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 103–117.

75. Zielnik, A. Basics of Polymer Degradation in Weathering. Technical Guide 102; Atlas Material Testing Technology LLC: 2018. Available online: https://www.atlas-mts.com/-/media/ametekatlas/files/knowledgecenter/library/technicaldocuments/atlas_tg102_basics%20of%20polymer%20degradation%20in%20weathering_2018-03-01_az.pdf?la=en (accessed on 9 November 2022).

76. Fechine, G.J.M.; Souto-Maior, R.M.; Rabello, M.S. Structural changes during photodegradation of poly(ethylene terephthalate). *J. Mater. Sci.* **2002**, *37*, 4979–4984. [CrossRef]

77. Wilken, R.; Holländer, A.; Behnisch, J. Vacuum Ultraviolet Photolysis of Polyethylene, Polypropylene, and Polystyrene. *Plasmas Polym.* **2002**, *7*, 185–205. [CrossRef]

78. Moussavi, G.; Shekoohiyan, S. Simultaneous nitrate reduction and acetaminophen oxidation using the continuous-flow chemical-less VUV process as an integrated advanced oxidation and reduction process. *J. Hazard. Mater.* **2016**, *318*, 329–338. [CrossRef]

79. Fechine, G.J.M.; Rabello, M.S.; Souto-Maior, R.M. The effect of ultraviolet stabilizers on the photodegradation of poly(ethylene terephthalate). *Polym. Degrad. Stab.* **2002**, *75*, 153–159. [CrossRef]

80. Hurley, C.R.; Leggett, G.J. Quantitative investigation of the photodegradation of polyethylene terephthalate film by friction force microscopy, contact-angle goniometry, and X-ray photoelectron spectroscopy. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1688–1697. [CrossRef] [PubMed]

81. Hanpanich, O.; Wongkongkatep, P.; Pongtharangkul, T.; Wongkongkatep, J. Turning hydrophilic bacteria into biorenewable hydrophobic material with potential antimicrobial activity via interaction with chitosan. *Bioresource Technol.* **2017**, *230*, 97–102. [CrossRef] [PubMed]

82. Bayry, J.; Aimanianda, V.; Guijarro, J.I.; Sunde, M.; Latgé, J.-P. Hydrophobins—Unique Fungal Proteins. *PLoS Pathog.* **2012**, *8*, e1002700. [CrossRef] [PubMed]

83. Ghosh, S.; Qureshi, A.; Purohit, H.J. Microbial degradation of plastics: Biofilms and degradation pathways. In *Contaminants in Agriculture and Environment: Health Risks and Remediation*; Kumar, V., Kumar, R., Singh, J., Kumar, P., Eds.; Agro Environ Media: Haridwar, India, 2019; pp. 184–199. [CrossRef]

84. Krasowska, A.; Sigler, K. How microorganisms use hydrophobicity and what does this mean for human needs? *Front. Cell. Infect. Microbiol.* **2014**, *4*, 112. [CrossRef]

85. Gómez-Méndez, L.D.; Moreno-Bayona, D.A.; Poutou-Piñales, R.A.; Salcedo-Reyes, J.C.; Pedroza-Rodríguez, A.M.; Vargas, A.; Bogoya, J.M. Biodeterioration of plasma pretreated LDPE sheets by *Pleurotus ostreatus*. *PLoS ONE* **2018**, *13*, e0203786. [CrossRef]

86. Gilan, I.; Hadar, Y.; Sivan, A. Colonization, biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. *Appl. Microbiol. Biotechnol.* **2004**, *65*, 97–104. [CrossRef]

87. López Gejo, J.; Manoj, N.; Sumalekshmy, S.; Glieman, H.; Schimmel, T.; Wörner, M.; Braun, A.M. Vacuum-ultraviolet photochemically initiated modification of polystyrene surfaces: Morphological changes and mechanistic investigations. *Photochem. Photobiol. Sci.* **2006**, *5*, 948–954. [CrossRef]

88. Martínez, J.G.; Benavides, R.; Guerrero, C.; Reyes, B.E. UV sensitisation of polyethylenes for grafting of maleic anhydride. *Polym. Degrad. Stab.* **2004**, *86*, 129–134. [CrossRef]

89. Rånby, B.; Rabek, J.F.; Canbäck, G. Investigation of PVC Degradation Mechanism by ESR. *J. Macromol. Sci.-Pure Appl. Chem.* **1978**, *12*, 587–608. [CrossRef]

90. Petit, C.; Bachmann, J.; Michalek, L.; Catel, Y.; Blasco, E.; Blinco, J.P.; Unterreiner, A.-N.; Barner-Kowollik, C. UV-induced photolysis of polyurethanes. *Chem. Commun.* **2021**, *57*, 2911–2914. [CrossRef]

91. Hoyle, C.E.; Ezzell, K.S.; No, Y.G.; Malone, K.; Thames, S.F. Investigation of the photolysis of polyurethanes based on 4,4′-methylene bis(phenyldiisocyanate) (MDI) using laser flash photolysis and model compounds. *Polym. Degrad. Stab.* **1989**, *25*, 325–343. [CrossRef]

92. Sang, T.; Wallis, C.J.; Hill, G.; Britovsek, G.J.P. Polyethylene terephthalate degradation under natural and accelerated weathering conditions. *Eur. Polym. J.* **2020**, *136*, 109873. [CrossRef]

93. Deng, Y.; Zhao, R. Advanced oxidation processes (AOPs) in wastewater treatment. *Curr. Pollut. Rep.* **2015**, *1*, 167–176. [CrossRef]

94. Kaur, H.; Hippargi, G.; Pophali, G.R.; Bansiwal, A.K. Treatment methods for removal of pharmaceuticals and personal care products from domestic wastewater. In *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*; Prasad, M.N.V., Vithanage, M., Kapley, A., Eds.; Butterworth-Heinemann: Chennai, India, 2019; pp. 129–150. [CrossRef]

95. Cvetnić, M.; Novak Stankov, M.; Kovačić, M.; Ukić, Š.; Bolanča, T.; Kušić, H.; Rasulev, B.; Dionysiou, D.D.; Lončarić Božić, A. Key structural features promoting radical driven degradation of emerging contaminants in water. *Environ. Int.* **2019**, *124*, 38–48. [CrossRef]

96. Du, P.; Wang, J.; Sun, G.; Chen, L.; Liu, W. Hydrogen atom abstraction mechanism for organic compound oxidation by acetylperoxyl radical in Co(II)/peracetic acid activation system. *Water Res.* **2022**, *212*, 118113. [CrossRef] [PubMed]

97. Chen, C.; Lei, P.; Ji, H.; Ma, W.; Zhao, J. Photocatalysis by Titanium Dioxide and Polyoxometalate/TiO_2 Cocatalysts. Intermediates and Mechanistic Study. *Environ. Sci. Technol.* **2004**, *38*, 329–337. [CrossRef]

98. Armstrong, D.A.; Huie, R.E.; Koppenol, W.H.; Lymar, S.V.; Merényi, G.; Neta, P.; Ruscic, B.; Stanbury, D.M.; Steenken, S.; Wardman, P. Standard electrode potentials involving radicals in aqueous solution: Inorganic radicals (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1139–1150. [CrossRef]

99. Hulea, V.; Dumitriu, E.; Fajula, F. Mild Oxidation of Organosulfur Compounds with H_2O_2 over Metal-Containing Microporous and Mesoporous Catalysts. *Catalysts* **2021**, *11*, 867. [CrossRef]

100. Elovitz, M.S.; Shemer, H.; Peller, J.R.; Vinodgopal, K.; Sivaganesan, M.; Linden, K.G. Hydroxyl radical rate constants: Comparing UV/H_2O_2 and pulse radiolysis for environmental pollutants. *J. Water Supply Res. T.* **2008**, *57*, 391–401. [CrossRef]

101. Wang, G. Destruction of humic acid in water by UV light–catalyzed oxidation with hydrogen peroxide. *Water Res.* **2000**, *34*, 3882–3887. [CrossRef]

102. Hüffer, T.; Weniger, A.-K.; Hofmann, T. Sorption of organic compounds by aged polystyrene microplastic particles. *Environ. Pollut.* **2018**, *236*, 218–225. [CrossRef] [PubMed]

103. Easton, T.; Koutsos, V.; Chatzisymeon, E. Removal of polyester fibre microplastics from wastewater using a UV/H$_2$O$_2$ oxidation process. *J. Environ. Chem. Eng.* **2023**, *11*, 109057. [CrossRef]

104. Hankett, J.M.; Welle, A.; Lahann, J.; Chen, Z. Evaluating UV/H$_2$O$_2$ Exposure as a DEHP Degradation Treatment for Plasticized PVC. *J. Appl. Polym. Sci.* **2014**, *131*, 40649. [CrossRef]

105. Shao, Y.; Pang, Z.; Wang, L.; Liu, X. Efficient Degradation of Acesulfame by Ozone/Peroxymonosulfate Advanced Oxidation Process. *Molecules* **2019**, *24*, 2874. [CrossRef] [PubMed]

106. Kovacic, M.; Kusic, H.; Loncaric Bozic, A.; Dionysiou, D.D. Advanced Oxidation Processes. In *Encyclopedia of Water: Science, Technology, and Society*; Maurice, P.A., Ed.; Wiley: Hoboken, NJ, USA, 2019; Volume 4, pp. 1925–1940. [CrossRef]

107. Gong, J.; Liu, Y.; Sun, X. O$_3$ and UV/O$_3$ oxidation of organic constituents of biotreated municipal wastewater. *Water Res.* **2008**, *42*, 1238–1244. [CrossRef]

108. Fischbacher, A.; von Sonntag, J.; von Sonntag, C.; Schmidt, T.C. The $^\bullet$OH Radical Yield in the H$_2$O$_2$ + O$_3$ (Peroxone) Reaction. *Environ. Sci. Technol.* **2013**, *47*, 9959–9964. [CrossRef]

109. Patel, D.; Wu, J.; Chan, P.; Upreti, S.; Turcotte, G.; Ye, T. Surface modification of low density polyethylene films by homogeneous catalytic ozonation. *Chem. Eng. Res. Des.* **2012**, *90*, 1800–1806. [CrossRef]

110. Zafar, R.; Park, S.Y.; Kim, C.G. Surface modification of polyethylene microplastic particles during the aqueous-phase ozonation process. *Environ. Eng. Res.* **2021**, *26*, 200412. [CrossRef]

111. Lee, R.; Coote, M.L. Mechanistic insights into ozone-initiated oxidative degradation of saturated hydrocarbons and polymers. *Phys. Chem. Chem. Phys.* **2016**, *18*, 24663–24671. [CrossRef]

112. Swanson, T.J.; Jamal, Z.; Chapman, J. Ozone Toxicity. [Updated 15 November 2022]. In *StatPearls [Internet]*; StatPearls Publishing: Treasure Island, FL, USA, 2022. Available online: https://www.ncbi.nlm.nih.gov/books/NBK430751/ (accessed on 18 December 2022).

113. Nuvolone, D.; Petri, D.; Voller, F. The effects of ozone on human health. *Environ. Sci. Pollut. Res.* **2017**, *25*, 8074–8088. [CrossRef]

114. Hamd, W.; Daher, E.A.; Tofa, T.S.; Dutta, J. Recent Advances in Photocatalytic Removal of Microplastics: Mechanisms, Kinetic Degradation, and Reactor Design. *Front. Mar. Sci.* **2022**, *9*, 885614. [CrossRef]

115. Chen, Y.; Miller, C.J.; Waite, T.D. Heterogeneous Fenton Chemistry Revisited: Mechanistic Insights from Ferrihydrite-Mediated Oxidation of Formate and Oxalate. *Environ. Sci. Technol.* **2021**, *55*, 14414–14425. [CrossRef] [PubMed]

116. Jain, B.; Singh, A.K.; Kim, H.; Lichtfouse, E.; Sharma, V.K. Treatment of organic pollutants by homogeneous and heterogeneous Fenton reaction processes. *Environ. Chem. Lett.* **2018**, *16*, 947–967. [CrossRef]

117. Ameta, R.; Chohadia, A.K.; Jain, A.; Punjabi, P.B. Fenton and Photo-Fenton Processes. In *Advanced Oxidation Processes for Waste Water Treatment: Emerging Green Chemical Technology*; Ameta, S.C., Ameta, R., Eds.; Academic Press: Chennai, India, 2018; pp. 49–87. [CrossRef]

118. Sreeja, P.H.; Sosamony, K.J. A Comparative Study of Homogeneous and Heterogeneous Photo-fenton Process for Textile Wastewater Treatment. *Proc. Technol.* **2016**, *24*, 217–223. [CrossRef]

119. Mackuľak, T.; Takáčová, A.; Gál, M.; Marton, M.; Ryba, J. PVC degradation by Fenton reaction and biological decomposition. *Polym. Degrad. Stab.* **2015**, *120*, 226–231. [CrossRef]

120. Ortiz, D.; Munoz, M.; Nieto-Sandoval, J.; Romera-Castillo, C.; de Pedro, Z.M.; Casas, J.A. Insights into the degradation of microplastics by Fenton oxidation: From surface modification to mineralization. *Chemosphere* **2022**, *309*, 136809. [CrossRef]

121. Pignatello, J.J.; Oliveros, E.; MacKay, A. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84. [CrossRef]

122. Wang, J.-C.; Wang, H. Fenton treatment for flotation separation of polyvinyl chloride from plastic mixture. *Sep. Purif. Technol.* **2017**, *187*, 415–425. [CrossRef]

123. Piazza, V.; Uheida, A.; Gambardella, C.; Garaventa, F.; Faimali, M.; Dutta, J. Ecosafety Screening of Photo-Fenton Process for the Degradation of Microplastics in Water. *Front. Mar. Sci.* **2022**, *8*, 791431. [CrossRef]

124. Liu, P.; Qian, L.; Wang, H.; Zhan, X.; Lu, K.; Gu, C.; Gao, S. New insights into the aging behavior of microplastics accelerated by advanced oxidation processes. *Environ. Sci. Technol.* **2019**, *53*, 3579–3588. [CrossRef]

125. Miao, F.; Liu, Y.; Gao, M.; Yu, X.; Xiao, P.; Wang, M.; Wang, S.; Wang, X. Degradation of polyvinyl chloride microplastics via an electro-Fenton-like system with a TiO$_2$/graphite cathode. *J. Hazard. Mater.* **2020**, *339*, 123023. [CrossRef] [PubMed]

126. Zhou, D.; Zhang, H.; Chen, L. Sulfur-replaced Fenton systems: Can sulfate radical substitute hydroxyl radical for advanced oxidation technologies? *J. Chem. Technol. Biotechnol.* **2015**, *90*, 775–779. [CrossRef]

127. Moreno-Andrés, J.; Rueda-Márquez, J.J.; Homola, T.; Vielma, J.; Moríñigo, M.Á.; Mikola, A.; Sillanpää, M.; Acevedo-Merino, A.; Nebot, E.; Levchuk, I. A comparison of photolytic, photochemical and photocatalytic processes for disinfection of recirculation aquaculture systems (RAS) streams. *Water Res.* **2020**, *181*, 115928. [CrossRef]

128. Lee, Y.; Lee, S.; Cui, M.; Ren, Y.; Park, B.; Ma, J.; Han, Z.; Khim, J. Activation of peroxodisulfate and peroxymonosulfate by ultrasound with different frequencies: Impact on ibuprofen removal efficient, cost estimation and energy analysis. *Chem. Eng. J.* **2021**, *413*, 127487. [CrossRef]

129. Cai, P.; Zhao, J.; Zhang, X.; Zhang, T.; Yin, G.; Chen, S.; Dong, C.-L.; Huang, Y.-C.; Sun, Y.; Yang, D.; et al. Synergy between cobalt and nickel on NiCo$_2$O$_4$ nanosheets promotes peroxymonosulfate activation for efficient norfloxacin degradation. *Appl. Catal. B-Environ.* **2022**, *306*, 121091. [CrossRef]

130. Zhang, Y.; Jiang, H.; Wang, H.; Wang, C. Separation of hazardous polyvinyl chloride from waste plastics by flotation assisted with surface modification of ammonium persulfate: Process and mechanism. *J. Hazard. Mater.* **2020**, *389*, 121918. [CrossRef] [PubMed]

131. Kwon, M.; Royce, A.; Gong, Y.; Ishida, K.P.; Stefan, M. UV/chlorine vs. UV/H$_2$O$_2$ for water reuse at Orange County Water District, CA: A pilot study. *Environ. Sci.-Water Res.* **2020**, *6*, 2416–2431. [CrossRef]

132. Renpenni, J. European Drinking Water Directive—An Overview of the New Drinking Water Standards. Available online: https://www.analyteguru.com/t5/Blog/European-Drinking-Water-Directive-An-Overview-of-the-New/ba-p/15286 (accessed on 30 November 2022).

133. Jin, J.; El-Din, M.G.; Bolton, J.R. Assessment of the UV/Chlorine process as an advanced oxidation process. *Water Res.* **2011**, *45*, 1890–1896. [CrossRef]

134. Carrell Morris, J. The acid ionization constant of HOCl from 5 to 35°. *J. Phys. Chem.* **1966**, *70*, 3798–3805. [CrossRef]

135. Wang, L.; Liu, X. Degradation of Aqueous Polycyclic Musk Tonalide by Ultraviolet-Activated Free Chlorine. *Processes* **2019**, *7*, 95. [CrossRef]

136. Guo, K.; Wu, Z.; Chen, C.; Fang, J. UV/chlorine process: An efficient advanced oxidation process with multiple radicals and functions in water treatment. *Acc. Chem. Res.* **2022**, *55*, 286–297. [CrossRef] [PubMed]

137. Chuang, Y.-H.; Wu, K.-L.; Lin, W.-C.; Shi, H.-J. Photolysis of Chlorine Dioxide under UVA Irradiation: Radical Formation, Application in Treating Micropollutants, Formation of Disinfection Byproducts, and Toxicity under Scenarios Relevant to Potable Reuse and Drinking Water. *Environ. Sci. Technol.* **2022**, *56*, 2593–2604. [CrossRef] [PubMed]

138. Hua, G.H.; Reckhow, D.A. Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water Res.* **2007**, *41*, 1667–1678. [CrossRef] [PubMed]

139. Liu, Z.; Xu, B.; Zhang, T.-Y.; Hu, C.-Y.; Tang, Y.-L.; Dong, Z.-Y.; Cao, T.-C.; El-Din, M.G. Formation of disinfection by-products in a UV-activated mixed chlorine/chloramine system. *J. Hazard. Mater.* **2021**, *407*, 124373. [CrossRef]

140. Ganiev, I.M.; Timergazin, Q.K.; Kabalnova, N.N.; Shereshovets, V.V.; Tolstikov, G.A. Reactions of chlorine dioxide with organic compounds. *Eurasian Chem.-Technol. J.* **2005**, *7*, 1–31. [CrossRef]

141. Sodium Chlorite Chlorine Dioxide Generators. Available online: https://www.oxy.com/globalassets/documents/chemicals/products/other-essentials/chlorine-dioxide-generators.pdf (accessed on 30 November 2022).

142. Rayson, M.S.; Altarawneh, M.; Mackie, J.C.; Kennedy, E.M.; Dlugogorski, B.Z. Theoretical Study of the Ammonia-Hypochlorous Acid Reaction Mechanism. *J. Phys. Chem. A* **2010**, *114*, 2597–2606. [CrossRef]

143. Khajouei, G.; Finklea, H.O.; Lin, L.-S. UV/chlorine advanced oxidation processes for degradation of contaminants in water and wastewater: A comprehensive review. *J. Environ. Chem. Eng.* **2022**, *10*, 107508. [CrossRef]

144. Tian, F.-X.; Ye, W.-K.; Xu, B.; Hu, X.-J.; Ma, S.-X.; Lai, F.; Gao, Y.-Q.; Xing, H.-B.; Xia, W.-H.; Wang, B. Comparison of UV-induced AOPs (UV/Cl$_2$, UV/NH$_2$Cl, UV/ClO$_2$ and UV/H$_2$O$_2$) in the degradation of iopamidol: Kinetics, energy requirements and DBPs-related toxicity in sequential disinfection processes. *Chem. Eng. J.* **2020**, *398*, 125570. [CrossRef]

145. Jia, Y.; Chen, J.; Asahara, H.; Asoh, T.-A.; Uyama, H. Polymer surface oxidation by light-activated chlorine dioxide radical for metal–plastics adhesion. *ACS Appl. Polym. Mater.* **2019**, *1*, 3452–3458. [CrossRef]

146. Kelkar, V.P.; Rolsky, C.B.; Pant, A.; Green, M.D.; Tongay, S.; Halden, R.U. Chemical and physical changes of microplastics during sterilization by chlorination. *Water Res.* **2019**, *163*, 114871. [CrossRef]

147. Walsh, T. The Plastic Piping Industry in North America. In *Applied Plastics Engineering Handbook: Processing, Materials, and Applications*, 2nd ed.; Kutz, M., Ed.; William Andrew: Oxford, UK, 2017; pp. 697–716. [CrossRef]

148. Anand, S.S.; Philip, B.K.; Mehendale, H.M. Chlorination Byproducts. In *Encyclopedia of Toxicology*, 3rd ed.; Wexler, P., Ed.; Academic Press: Amsterdam, Netherlands, 2014; pp. 855–859. [CrossRef]

149. Devilliers, C.; Fayolle, B.; Laiarinandrasana, L.; Oberti, S.; Gaudichet-Maurin, E. Kinetics of chlorine-induced polyethylene degradation in water pipes. *Polym. Degrad. Stab.* **2011**, *96*, 1361–1368. [CrossRef]

150. Whelton, A.J.; Dietrich, A.M. Critical considerations for the accelerated ageing of high-density polyethylene potable water materials. *Polym. Degrad. Stab.* **2009**, *94*, 1163–1175. [CrossRef]

151. Yu, W.; Azhdar, B.; Andersson, D.; Reitberger, T.; Hassinen, J.; Hjertberg, T.; Gedde, U.W. Deterioration of polyethylene pipes exposed to water containing chlorine dioxide. *Polym. Degrad. Stab.* **2011**, *96*, 790–797. [CrossRef]

152. Castagnetti, D.; Scirè Mammano, G.; Dragoni, E. Effect of chlorinated water on the oxidative resistance and the mechanical strength of polyethylene pipes. *Polym. Test.* **2011**, *30*, 277–285. [CrossRef]

153. Miroka, S.M.; Smiley, T.D.; Tanko, J.M.; Dietrich, A.M. Reaction mechanism for oxidation and degradation of high density polyethylene in chlorinated water. *Polym. Degrad. Stab.* **2013**, *98*, 1369–1377. [CrossRef]

154. D'Elia, E. Characteristics of Drinking Water Polyethylene Pipes Tested with the Purpose of Quality Certification—Historical Data, Trends and Their Potential Consequences. Master's Thesis, Chalmers University of Technology, Gothenburg, Sweden, 2017.

155. Samarth, N.B.; Mahanwar, P.A. Degradation of Polymer & Elastomer Exposed to Chlorinated Water—A Review. *Open J. Org. Polym. Mater.* **2021**, *11*, 1–50. [CrossRef]

156. How Does Chlorine Affect Plastic Piping Systems? Available online: https://www.corzan.com/blog/how-does-chlorine-affect-plastic-piping-systems (accessed on 6 December 2022).

157. Kowalska, B.; Klepka, T.; Kowalski, D. Influence of chlorinated water on mechanical properties of polyethylene and polyvinyl chloride pipes. *WIT Trans. Built Environ.* **2016**, *165*, 63–74. [CrossRef]

158. Kathua, S.; Hsieh, Y.-L. Chlorine degradation of polyether-based polyurethane. *J. Polym. Sci. A Polym. Chem.* **1997**, *35*, 3263–3273. [CrossRef]

159. Johansson, K.S. Surface Modification of Plastics. In *Applied Plastics Engineering Handbook: Processing, Materials, and Applications*, 2nd ed.; Kutz, M., Ed.; William Andrew Publishing: Cambridge, MA, USA, 2017; pp. 443–487. [CrossRef]

160. Domonkos, M.; Tichá, P.; Trejbal, J.; Demo, P. Applications of Cold Atmospheric Pressure Plasma Technology in Medicine, Agriculture and Food Industry. *Appl. Sci.* **2021**, *11*, 4809. [CrossRef]

161. Takamatsu, T.; Uehara, K.; Sasaki, Y.; Miyahara, H.; Matsumura, Y.; Iwasawa, A.; Ito, N.; Azuma, T.; Kohno, M.; Okino, A. Investigation of reactive species using various gas plasmas. *RSC Adv.* **2014**, *4*, 39901–39905. [CrossRef]

162. Bolouki, N.; Kuan, W.-H.; Huang, Y.-Y.; Hsieh, J.-H. Characterizations of a Plasma-Water System Generated by Repetitive Microsecond Pulsed Discharge with Air, Nitrogen, Oxygen, and Argon Gases Species. *Appl. Sci.* **2021**, *11*, 6158. [CrossRef]

163. Scally, L.; Gulan, M.; Weigang, L.; Cullen, P.J.; Milosavljevic, V. Significance of a Non-Thermal Plasma Treatment on LDPE Biodegradation with *Pseudomonas Aeruginosa*. *Materials* **2018**, *11*, 1925. [CrossRef] [PubMed]

164. Rwahila, T.S.; Sugai, T.; Tokuchi, A.; Jiang, W. The Effect of Oxygen and Argon Gas Flow Rate on OH Radical Production and Dye Decolorization by Pulsed Discharge in Spray Droplet Reactor. *IEEE Trans. Plasma Sci.* **2019**, *47*, 4560–4566. [CrossRef]

165. Mitrović, T.; Tomić, N.; Djukić-Vuković, A.; Dohčević-Mitrović, Z.; Lazović, S. Atmospheric Plasma Supported by TiO$_2$ Catalyst for Decolourisation of Reactive Orange 16 Dye in Water. *Waste Biomass Valor.* **2020**, *11*, 6841–6854. [CrossRef] [PubMed]

166. Rauschenbach, B. Plasma-Immersion-Implantation. In *Encyclopedia of Materials: Science and Technology*; Buschow, K.H.J., Cahn, R.W., Flemings, M.C., Ilschner, B., Kramer, E.J., Mahajan, S., Veyssière, P., Eds.; Elsevier: Amsterdam, The Netherlands, 2001; pp. 7023–7027. [CrossRef]

167. Schmitt, B.R.; Kim, H.; Urban, M.W. Microwave Plasma Reactions of Imidazole on Poly(vinyl chloride) Surfaces: A Spectroscopic Study. *J. Appl. Polym. Sci.* **1999**, *71*, 1–6. [CrossRef]

168. Braun, D. Thermal degradation of polyvinyl chloride. *Pure Appl. Chem.* **1971**, *26*, 173–192. [CrossRef]

169. Wypych, G. Principles of thermal degradation. In *PVC Degradation and Stabilization*, 4th ed.; Wypych, G., Ed.; ChemTec Publishing: Toronto, ON, Canada, 2020; pp. 79–167. [CrossRef]

170. Yao, Q.; Wilkie, C.A. Thermal Degradation of PVC in the Presence of Polystyrene. *J. Vinyl Addit. Technol.* **2001**, *7*, 26–36. [CrossRef]

171. Lai, J.; Sunderland, B.; Xue, J.; Yan, S.; Zhao, W.; Folkard, M.; Michael, B.D.; Wang, Y. Study on hydrophilicity of polymer surfaces improved by plasma treatment. *Appl. Surf. Sci.* **2006**, *252*, 3375–3379. [CrossRef]

172. Vesel, A.; Zaplotnik, R.; Mozetič, M.; Primc, G. Surface modification of PS polymer by oxygen-atom treatment from remote plasma: Initial kinetics of functional groups formation. *Appl. Surf. Sci.* **2021**, *561*, 150058. [CrossRef]

173. Dejun, L.; Jie, Z.; Hanqing, G.; Mozhu, L.; Fuqing, D.; Jianfang, H. Surface Modification of Medical Polyurethane by Plasma Treatment. *Chin. Phys. Lett.* **1992**, *9*, 79–82. [CrossRef]

174. Ma, S.; Kim, K.; Chun, S.; Moon, S.Y.; Hong, Y. Plasma-assisted advanced oxidation process by a multi-hole dielectric barrier discharge in water and its application to wastewater treatment. *Chemosphere* **2020**, *243*, 125377. [CrossRef] [PubMed]

175. Arkatkar, A.; Juwarkar, A.A.; Bhaduri, S.; Uppara, P.V.; Doble, M. Growth of *Pseudomonas* and *Bacillus* biofilms on pretreated polypropylene surface. *Int. Biodeterior. Biodegrad.* **2010**, *64*, 530–536. [CrossRef]

176. Jeyakumar, D.; Chirsteen, J.; Mukesh, D. Synergistic effects of pretreatment and blending on fungi mediated biodegradation of polypropylenes. *Bioresour. Technol.* **2013**, *148*, 78–85. [CrossRef] [PubMed]

177. Tribedi, P.; Dey, S. Pre-oxidation of low-density polyethylene (LDPE) by ultraviolet light (UV) promotes enhanced degradation of LDPE in soil. *Environ. Monit. Assess.* **2017**, *189*, 624. [CrossRef]

178. Hadiyanto, H.; Khoironi, A.; Dianratri, I.; Huda, K.; Suherman, S.; Muhammad, F. Biodegradation of oxidized high-density polyethylene and oxo-degradable plastic using microalgae *Dunaliella salina*. *Env. Pollut. Bioavail.* **2022**, *34*, 469–481. [CrossRef]

179. Sullivan, K.P.; Werner, A.Z.; Ramirez, K.J.; Ellis, L.D.; Bussard, J.; Black, B.A.; Brandner, D.G.; Bratti, F.; Buss, B.L.; Dong, X.; et al. Mixed plastics waste valorization via tandem chemical oxidation and biological funneling. *Science* **2022**, *378*, 207–2011. [CrossRef]