Review article

Photocatalytic processes as a potential solution for plastic waste management

Aida M. Díez [a,b,*], Nadia Licciardello [a], Yury V. Kolen'ko [a]

[a] *International Iberian Nanotechnology Laboratory, Avenida Mestre José Veiga s/n, Braga 4715-330, Portugal*
[b] *CINTECX, Universidade de Vigo, BIOSUV group, Department of Chemical Engineering, 36310 Vigo, España*

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ABSTRACT

Plastics have become a critical environmental problem due to their widespread use, high physico-chemical stability and the inefficiency of wastewater treatments. Despite the efforts to reduce production and to increase reuse and recycling, the current strategies for plastic waste treatment are not suitable to handle with the growing demand of plastics and the concomitant waste in an environmentally friendly manner.

Herein, we review the existing strategies for the treatment of plastic waste, highlighting photocatalytic processes as a potential solution for the degradation of plastics. The possibility of incorporating photocatalysts to plastics during the production process could enhance their light-activated biodegradability. Parallelly, photocatalysts can be employed during waste treatment processes of non-biodegradable stable plastics. The scarcely studied factors affecting plastic photocatalytic degradation, namely catalyst type, reactor configuration, and radiation source (intensity and wavelength), are discussed, highlighting the role that photocatalytic processes can play in the future of plastic management. Finally, relevant quantification methods for measuring the photo-degradation of plastics are overviewed.

We believe that photocatalysis can be an environmentally friendly strategy both to increase the biodegradability of plastics and to treat plastic waste. With this novel comprehensive overview, we hope to stimulate further research and innovation in this field.

1. Introduction

Plastics are the most widely produced materials because of their appealing properties such as transparency, lightness, durability and facile cleaning [1]. However, the exorbitant production of unsustainable plastic goods has caused accumulation and fragmentation of plastic waste [2]. Moreover, during the wastewater treatment process, some microplastics are not retained during the filtration step and they are resistant to the biological treatment due their stability and chemical inertness [3]. Thus, the degradation by natural factors once they have survived the wastewater treatment process is extremely difficult and slow, so they persist hundreds of years [4].

This phenomenon causes the accumulation of plastics in the environment [5]. Lau et al. [6] simulated the plastic content in the environment in two possible scenarios, the one in which corrective measures are not taken or the one in which reduction of plastics production and recycling is applied. Respectively, that would generate 29 and 5.3 Mt/year of plastic in waters. Consequently, several researchers have

reviewed the last trends for plastic recycling [7,8], being biological degradation of greener plastics and photocatalytic degradation of plastics both the less studied and environmentally friendly alternatives.

Amongst plastics, microplastics have been lately a hot topic. However, there are some discrepancies on the size of the plastic that is so-labelled. Some authors consider microplastics each plastic fragment smaller than 5 mm [9] although the preferred definition englobes 1–10 μm sizes [10]. Thus, microplastics are not easily detectable and are increasing their presence in the environment. Indeed, plastics, which are present in the environment due to undesirable behaviours, are being fragmented and partially modified by weather and environmental conditions (rocks, waves, sun, etc. [11]) leading to microplastics generation. On the other hand, microplastics are added to cosmetic products (exfoliating creams, toothpaste, etc.), ending up in waters due to inefficient wastewater treatments [9].

Lately, the plastic environmental problem has been perceived and different restrictions have been set [6,9]. For instance, some effort has been put in producing biodegradable plastics. However, they are not

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100% environmentally friendly and they are still a minor option due to their worse characteristics in terms of resistance and their higher production costs [12]. Nevertheless, using these biodegradable plastics in a minor fraction has been proved to favour the photo- and bio-degradation of typical plastics. For instance, adding 10% of polylactic acid to Low Density Polyethylene (LDPE) films favoured the subsequent photo-degradation under solar radiation [13].

This review represents a comprehensive critical overview of the so far known main issues connected with the plastic threat to environmental and human health, and of the traditional plastic waste management options with a special focus on the overlooked photo-based degradation processes (including the factors influencing them) as a greener alternative for plastic treatment. Moreover, this review is set as a starting point for those willing to start to treat microplastics, as the up-to-date quantification techniques are explained as well as the other treatment alternatives which could be still used as pre- or post-treatment.

Consequently, this review poses for the first time a deep evaluation of plastic photo-degradation processes, with the combination of providing information on plastic quantification as well as the presentation of more traditional plastic treatment alternatives. Indeed, as it can be seen in Fig 1, the number of reviews focused on plastic degradation is considerably low (around 80). What is more, those mentioning quantification alternatives or other treatment options are less than a half of the total. When searching for the combination presented in this review (Fig. 1-green column), only 7 references happened to be focused on the quantification of plastics, where the plastics photo-degradation is only mentioned, without the deep study hereby presented.

1.1. Environmental issues

Plastic pollution in marine and terrestrial environment is a menace to life [1]. Moreover, the by-products generated through natural degradation can produce more toxic compounds [14]. Microorganisms, plants, animals and humans can be exposed to different harmful materials throughout the lifetime of a plastic [11]. For instance, polystyrene (PS) debris are moved through the wind and can be lethal to birds and other animals.

Plastic debris end up in water and land, where they are brought to the food chain (Fig. 2) [15]. Indeed, microplastics have been detected not only in food but also in salt or even in bottled water [10]. Consequently, microplastics can reach the gut or the lungs of mammals, if ingested through food, drink on water or inhaled from air [16,17]. Once they have reached the body, the hydrophobic nature of plastics increases their retention in lipophilic tissues (brain or liver), causing their accumulation, favouring the development of diseases. Moreover, microplastics usually have some additives which can be released to the media (bisphenol A, phthalates, flame retardants, etc.) which are known to
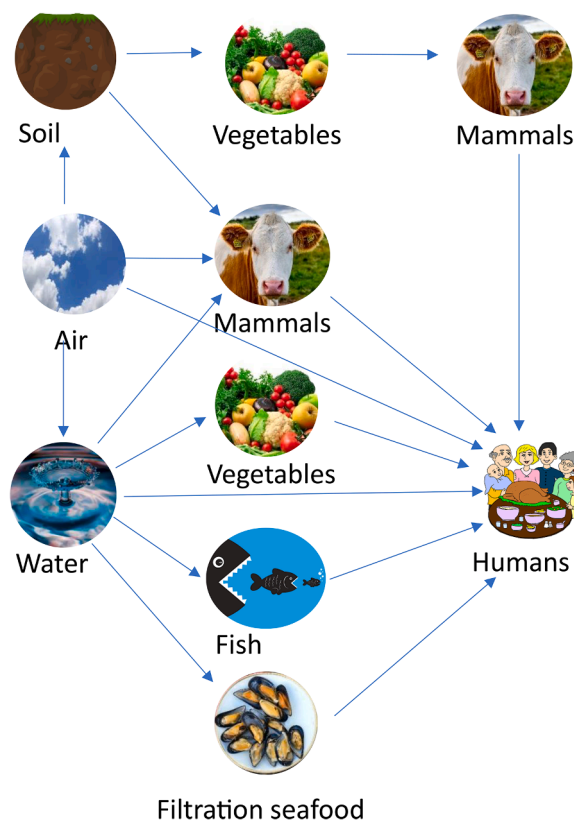

Fig. 2. Schematic representation of the microplastics fate throughout the food chain.

have endocrine disruptor effects [2]. For instance, polyvinyl chloride (PVC) release compounds (vinyl chloride) which might be carcinogenic [10].

Plastics and microplastics have been detected even in soils where they can be ingested by animals, most likely affecting the health of the carrier animal and entering the food chain (Fig. 2). In this scenario, also the soil is affected because the presence of microplastics (the smaller, the worse) promotes soil water evaporation and cracking, favouring the leaking of other pollutants [18].

Regarding the aquatic environment, plastics change the hydrological regime of water and sediments, destroy the plankton and phytoplankton and, in general, change the habitat of the aquatic species [11].

1.2. Recent insights on the microplastics interaction with other toxic pollutants

As pointed out by Zhang et al. [19], the effects of microplastics on human health are still an open debate and more research is needed. Puskic et al. [20] found only 34 papers about the effects of plastic ingestion on marine vertebrate animals (excluding fish). Increasing attention has been given to microplastics and their effects towards the environment, in particular, the marine one. Nevertheless, little attention was given to the composites that microplastics can create with other biological and chemical pollutants and that can surely have negative effects on human and environmental health. Several studies have been performed on the capacity of microplastics to act as vehicles of other toxic pollutants.

Indeed, the smallest plastic debris are strong absorbents of hydrophobic pollutants and thus they affect the fate and toxicity of each other [9]. This fact could influence the transport of toxic pollutants to environments in which they would normally not end up, affecting environmental and human health. For instance, Yu et al. [21] reported the capacity of PVC microplastics to adsorb the antibiotic levofloxacin and
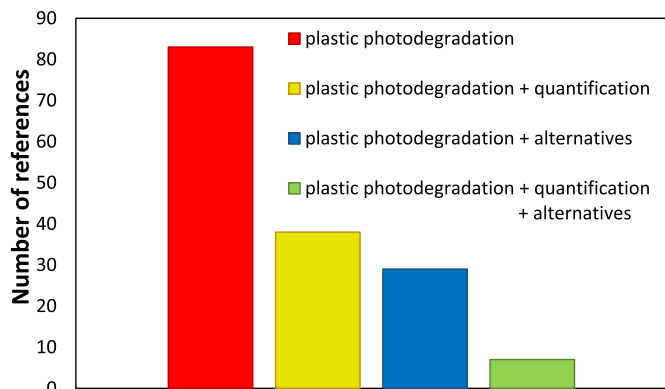

Fig. 1. References found in Google Scholar by February 2023 depending on the topic.

on how this ability is increased or inhibited depending on the heavy metal ions present in the solution, the ionic strength and the presence or absence of fulvic acid. In particular, they pointed out that the amount of adsorbed levofloxacin increases in the presence of Cu^{2+}, Zn^{2+} and Cr^{3+}, while the adsorption is inhibited in the presence of Cd^{2+} and Pb^{2+} ions. Mammo et al. [22] reviewed the latest results on the adsorption of microorganisms and chemicals on the surface of microplastics. They reported recent studies that showed how several metal ions (such as copper, arsenic, chromium, cadmium, lead) or persistent organic pollutants (pesticides, drugs) can be easily adsorbed by microplastics in real environment. Zhang et al. [23] investigated the combined toxicity of cadmium and PS microplastics on zebrafish embryos. When the amount of microplastics was increased above 0.05 mg/L, the lethal toxicity on zebrafish embryos increased. On the other hand, a lower concentration of microplastics reduced the lethal and sub-lethal toxicity of cadmium.

Zhang et al. [24] investigated the effects of cadmium and microplastics on the fruit-fly Drosophila. Both cadmium and microplastics caused gut damage and locomotor dysfunctions, which increased when a combination of the two pollutants was administered and when microplastics size was reduced. The authors believe that some of the effects caused by the co-exposure might be due to the favoured transport of cadmium in the body using microplastics as vehicle. Wang et al. [25] studied the adsorption of cadmium on polyethylene (PE) beads (2–4 μm) and how this composite could affect the health of the cladoceran Moina monogolica Daday. The microplastics were left in seawater for 7 days and the adsorption and accumulation of cadmium was significant. They observed especially how the surface of PE beads aged in water and became a very good adsorbent for cadmium. When the cladoceran was exposed for 21 days to the PE beads, negative effects on survival time and reproduction arose. When the cladoceran was exposed to the PE/cadmium composite, the negative effects were greater. With this work, they demonstrated that microplastics could act as vectors for toxic metals. They underlined how there is still a gap in research to better understand the interactions of microplastics with other pollutants and their consequent effects on environmental and human health.

1.3. Types of plastics

Another associated problem to the plastic waste treatment is that there are many types of plastics with diverse properties. The most found in waters are PE, followed by polypropylene (PP) and then by PS [26, 27]. Actually, these three polymers together with PVC and the typical bottle plastic (polyethylene terephthalate or PET), make 74% of all plastic wastes [28]. Due to their common use, these plastic types have been assigned with plastic resin identification codes (Fig. 3).

Two kinds of PE can be found depending on the degree of branching of the polymer. Thus, LDPE has a higher degree of branching which makes it less compact and, therefore, more flexible. For these properties, LDPE is one of the most widely used plastics, especially for short-time applications such as packaging [29]. Sadly, the typical plastic (LDPE based) bags, can last around 450 years [12]. This may be the reason why PE is one of the most found plastic in wastewaters after conventional treatments [30].

In contrast, High Density Polyethylene (HDPE) possesses a more linear chemical structure and lower degree of branching, and consequently it is more crystalline, rigid and with higher mechanical resistance.

Table 1 shows the main used plastics, their recyclability and their photodegradation ability under radiation. The existing capability to recycle these plastics does not unequivocally mean that they will be recycled. For instance, Mihut et al. [31] reported different ways of recycling nylon. However, the need of a complex cleaning process can make this process difficult and, consequently, nylon is not being recycled. Another example was brought by Brennan et al. [32] who demonstrated that although the copolymer acrylonitrile butadiene styrene is recyclable, there is a worsening of some characteristics in the recycled polymer, such as strain to failure and impact strength.

Polymethlyl methacrylate (PMMA), one of the most used acrylic plastics, is recyclable but the procedure, patented by Jeon et al. in 2011 [33], might not have been used yet because it is an expensive process (several batches of heating at 450 ºC). The main recycling process used nowadays for PMMA is pyrolysis and, in this process, the monomer (methyl methacrylate) may be attained [34]. However, pyrolysis does not only involve the use of high temperatures, but it also presents some additional disadvantages such as the generation of by-products which may affect negatively the polymerization step and reduce the quality of the recycled polymer. Thus, a consecutive separation process, which increases costs and pollution generation, is needed to isolate the monomers from the pyrolysis by-products [34]. Finally, thermoset plastics (such as polyurethane, PU) which are stable to incineration are not recycled and are usually eliminated by simple accumulation in landfills [35].

Table 1 summarizes also the photo-reactivity of the reported plastics under radiation. It is to be noted that the photodegradation here is
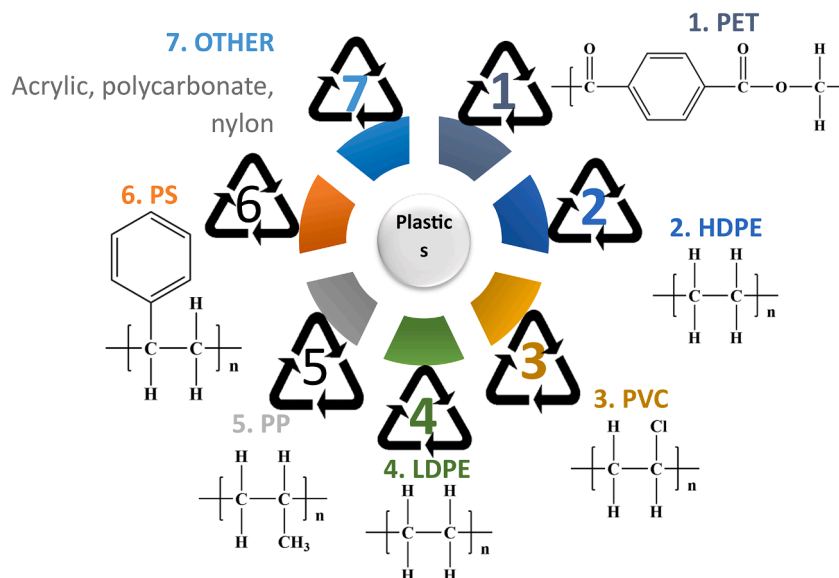

Fig. 3. Regulated labelling of the most used plastics.

Table 1

List of most used plastics with their recyclability, their presence in waterbodies, and reported photo-degradation conditions.

Plastic	Uses	Recyclable	Reference	Detected on waterbodies Example	Reference	Photo-degradation Working wavelength	Refs.
PET	Water bottles and other containers, clothes fibres	YES	[39]	Treated water in a wastewater treatment plant	[40]	254 nm	[39, 41]
PE	Exfoliating creams. LDPE (bags); HDPE (bottles for liquids: milk, washing agents, etc.)	YES	[27]	Spanish sea, Treated water in treatment plant	[26]	295–320 nm	[37]
PVC	Tubing, construction	YES	[42]	Treated water in a wastewater treatment plant	[43]	Sunlight	[44]
PP	Packaging for consumer products, automotive, exfoliating creams	YES	[27]	Spanish sea, Treated water in a wastewater treatment plant	[26,45]	253.7 nm	[44]
PS	Packaging, toys, medicines	NO	[15]	Spanish sea	[26]	Sunlight	[46]
Nylon	Electronic devices	YES	[31]	Fish tracks	[47]	Sunlight	[48]
Acrylonitrile butadiene styrene	Automotive industry, computers	YES	[32]	Treated water in a wastewater treatment plant	[30]	UV light	[49]
Acrylic	Windows, screens	YES	[33]	Fish tracks	[47]	UV lamp (λ>220 nm)	[36]
PMMA	Microbeads in creams	YES	[34]	–	–	260–300 nm	[50]
Silicone	Machines, electric devices and silicones	YES	[51]	Treated water in a wastewater treatment plant	[30]	Sunlight	[52]
PU	Footwear, automotive industry	NO	[35]	Treated water in a wastewater treatment plant	[30]	280 nm	[53]

namely photolysis, i.e. the capacity of the polymer to be degraded under direct light irradiation. Most of the reported plastics are photo-degradable under sunlight. However, the treatment times are extremely long [15]. For instance, although acrylics have been reported to be photo-degradable, Melo et al. [36] reported the need of 600 h under irradiation with an UVC (minor portion of the sunlight) lamp to completely eliminate the acrylic content. Likewise, some papers have demonstrated PE is photo-degradable [37], although there are some ambiguities. For instance, Oldak and Karzmarek [38] demonstrated how under UV (254 nm) the Raman spectra of PE remained stable, showing that no morphological changes occurred after 28 weeks irradiation time.

2. Plastic waste management options

2.1. Current status

An overview of the different existing options for the plastic waste treatment will be given in the following paragraphs. It is important to note that often these plastic waste treatment processes are used in combination.

2.1.1. Separation processes

Usually, an initial plastic separation is mandatory and thus, processes such as adsorption, filtration or coagulation-flocculation are used, being the two latter methods also suitable for microplastics [54]. However, nano-filtration is often not used because it is an expensive alternative which could lead to fouling of the filters [9]. Generally speaking, plastics are difficult to treat by physical processes due to their hardness and flexibility [55]. Indeed, an interesting review on micro-filtration of plastics [56] highlights how it should be noted that micro-plastics are even more fragmented during physical processes such as sand filtration and consequently, it is important to have a secondary treatment of the produced sewages.

2.1.2. Recycling

Not all types of plastics are thermoplastic and display big enough sizes to be suitable for recycling. In addition, even if these requirements are fulfilled, recycling is not always cost-effective [57,58]. Up to now, less than 20% of the total plastic waste is recycled [4]. Amongst the plausible usages, there exist the utilization of the plastics as material for 3D printers or construction uses [7]. Mechanical recycling may seem a good alternative, but the need for sorting, cleaning, shivering and agents (to make the plastic re-usable) addition makes the process not so

conceivable [59].

2.1.3. Disposal

Approximately 50% of the plastic waste is landfilled since recovery and recycling are difficult due to the high heterogeneity of the collected wastes [11]. However, one of the main drawbacks of landfilling is the high demand for space which could have been used for more productive aims [42]. Moreover, the landfill conditions avoid the natural ageing of the plastics, where oxidation takes place. For instance, the lack of oxygen in the landfill extends plastics life, preventing thermo-oxidative degradation [14]. Likewise, the lack of solar radiation also slows down the plastic degradation. For instance, Tu-Morn et al. [13] buried LDPE for 4 weeks and no-biodegradation was detected even if the conditions were ideal (temperature, humidity and aeration). Besides, the leaching of toxic plastic additives and the worsening of the soil quality [18] make this process an undesired option.

2.1.4. Incineration

This process overcomes the volume demand of the landfill and in the vast majority of cases, allows to recover of some energy in the form of heat [42]. For instance, PE has shown a calorific value similar to fuel oil [59]. Nevertheless, toxic gases (dioxins, furans…) can be formed during the process [28,60]. Indeed, the gases liberated by PS incineration cause suffocation and many diseases [15]. Regarding environmental aspects, it should be also mentioned that the incineration process contributes to the global warming [11].

2.1.5. Pyrolysis

This procedure consists of the plastic waste transformation at high temperatures (290–850 °C [61]) and low air concentrations into oil, carbonaceous solid residues (char) and gases [4]. In this area, there are interesting reviews which point out the influence of temperature and reactor design on the obtention of by-products, which could be hopefully, fuels [8]. However, not all the plastics are suitable for pyrolysis and this process contributes to greenhouse gases generation [58]. For instance, PET or PVC are non-suitable for this process because of the presence of heteroatoms which produce some toxic compounds when they undergo a pyrolytic procedure [4]. Other plastics are difficult to be treated under pyrolysis due to their cross-linked stable structures (PP, PE) [4]. Catalytic pyrolysis can improve the treatment performance, reduce the diversity of the attained products and the energy expenditure [59]. However, the catalysts should be eliminated at the end of the treatment and catalyst usage stimulates coke generation. Moreover,

although the catalyst can be reused several times, it usually loses efficiency with the number of cycles [61]. All of the above makes both pyrolysis and catalytic pyrolysis undesired alternatives regarding environmental and economic aspects.

2.1.6. Biodegradation

The vast majority of the used plastics are non-biodegradable. An approach for favouring biodegradation consists on applying an oxidation pre-treatment, so the mechanical fracture of plastics [62] as well as the carbonyl groups formation, favour microbial attack [63]. Thus, the application of the different hereby presented degradation processes as a pre-treatment process prior to biodegradation is an alternative in order to have biologically weak points or assimilable carbon within the plastic [12,64].

Other approaches are based on the isolation of species which are found in plastic-rich areas or the bioengineering of enzymes that promote olefin cleavage [7]. Padervand et al. [54] reported several organisms such as planktonic crustaceans, zooplankton or marine fungi which digested micropalstics, attaining nanoplastics due to fragmentation. Moreover, the Red sea giant clam has been used to remove microplastics by sorption on the shell (removing 66% of PE).

Some studies are currently being focused on creating more biodegradable plastics, thus biodegradation may be a plausible future alternative [5]. The addition of small quantities of biodegradable compounds such as stearate or polyactic acid to non-biodegradable plastics can trigger the biodegradation [13,65].

This process is environmentally friendly and unexpensive, and consequently, more effort should be focused on the overcoming of its drawbacks by the search of acceptable pre-treatments alternatives such as the overlooked photo-based processes.

2.2. Photo-based processes

The following paragraphs will be focused on photolysis and photocatalysis. It is important to make a distinction between the two mechanisms. In the case of photolysis, the plastics are simply photo-degraded by light irradiation. The UV light or sunlight is absorbed by the plastics and generate excited states leading to chain scissions, branching crosslinking and oxidation reactions, which in turn will end up in the decomposition of the plastics [66]. However, as we described in Paragraph 1.3, this is an extremely slow process for the majority of plastics. Therefore, the photocatalytic mechanism becomes of outermost importance. In the photocatalytic degradation, the presence of an additional material, normally a semiconductor oxide, namely a photocatalyst, is fundamental. The photocatalyst is excited with light of proper wavelength and generate electron-hole pairs which, depending on the environment and the specific polymers will trigger the formation of radicals and a series of chain reactions. More specifically, the degradation of plastics in the presence of a photocatalyst goes through three main steps: (i) electron–hole pairs are generated by light irradiation, (ii) charge is aggregated from the interior homogeneous dispersal of the photocatalysts to the surface, and (iii) redox reactions are triggered between reactants and photocatalysts [67]. More generically, photocatalysis is based on the light-activated production of radical species able to oxidize the pollutants, in this case the plastics and the radical species that will form will strictly depend on the environment in which the photocatalytic degradation takes place.

Both the photolysis and photocatalysis processes have several advantages, namely low cost, easy application, possibility of using sunlight, use of ambient conditions, etc. [68]. Moreover, photo-based processes can be also used for generating useful by-products or as a biological pre-treatment [7,64]. However, these processes also have some disadvantages such as the fact that radiation may cause crosslinking [69] due to the radical nature of the process, the requirement of long treatment times, the high cost of some artificial light sources, etc. Research is being carried out to diminish these drawbacks [3,9,70]. This

review points out some relevant data which could be useful for the enhancement of future research based on plastic degradation under photo-based processes.

2.2.1. Sustainability of photo-based processes

Photo-based degradation processes can be considered a sustainable alternative for the treatment of plastic wastes on the case of using low consumption lamps or solar energy [64].

In the case of photo-catalysis processes, it is important to note that photo-catalysts are usually reusable, reducing long-term costs. Moreover, the associated costs of the catalyst addition can be worth it, considering the amelioration of the process in terms of treatment time and by-products generation (avoiding toxic by-products in advantage of useful ones).

Indeed, with a proper catalyst selection, fuels can be attained throughout the plastic degradation process. Jiao et al. [3] highlighted how converting plastics in fuels can be done at room temperature, atmospheric pressure, in air presence and with the natural energy provided by the sun. They converted plastic wastes (plastic bags, food wraps and containers) based on PE, PP and PVC into CO_2 which was photo-reduced to generate acetic acid. Initially, the aliphatic chain should be photo-degraded to generate, throughout oxidation, CO_2; then, this CO_2 is reduced to produce C_2 fuels [3]. The couple $H_2O/HO\cdot$ has a highly positive redox potential (2.32 V vs normal hydrogen electrode, NHE), while the half-reactions involving the CO_2 reduction require negative potentials (-0.6 V vs NHE). Nb_2O_5 has its valence-band maximum at +2.5V vs. NHE and the conduction band minimum at -0.9V vs. NHE. Therefore, Nb_2O_5 can stimulate, under sunlight radiation, the production from PE, PP and PVC of 47.4, 40.6, and 39.5 µg $gcat^{-1}$ h^{-1} of acetic acid (resulting from the photo-conversion of the produced CO_2), respectively [3]. The acetic acid generation performance was similar when using pure CO_2 or gases generated from plastic degradation. Oppositely, a decrease of acetic acid generation was detected when using actual plastics wastes, due to the presence of additives, requiring further research. For instance, the utilization of other photocatalyst may promote another reaction pathway (Fa et al., [65]).

Moreover, plastics can be used as electron donor for the H_2 generation with solar radiation [58,71,72] process which is so-called "photo-reforming". Nowadays, 96% of the global H_2 is attained from pyrolysis of fossil fuels, which are limited. As an alternative, Uekert et al. demonstrated how CdS/CdO_x [58] or CN_xNi_2P [71] catalysts could be used in the H_2 generation from water in the presence of plastics. Specifically, the aforementioned catalysts are excited with solar light and the generated electrons can reduce water to H_2, while the generated holes provoke the oxidation of the plastic present in water. A pre-treatment with 0.5 M KOH enhances the plastic degradation process due to the generation of breaches throughout the plastic [3,71,72]. The plastic waste is converted then, under ambient conditions, in useful by-products such as formate, pyruvate or acetate. Nevertheless, H_2 generation with this method is still low. For instance, when using CN_xNi_2P catalyst for a PET bottle photo-degradation, 2.87 µmol $H_2 \cdot g$ $cat^{-1} \cdot h^{-1}$ were attained [71], whereas higher quantities, namely 64.3, 3.42, and 0.85 µmol $H_2 \cdot gcat^{-1} \cdot h^{-1}$ for polylactic acid, PET and polyurethane, respectively, were obtained using a less green catalyst such as CdS/CdO_x [58]. This demonstrates more research should be focused on the photocatalyst degradation of plastics, for the attainment of greener and inexpensive catalysts.

Positively, this process has the potential to be scaled-up, being flat photo-catalyst-panel reactors an inexpensive and efficient alternative to avoid light scattering and catalyst sedimentation, although mass transfer can be an issue [71,72]. Indeed, Uekert et al. are nowadays leading this research and they have started scale-up tests attaining around 3.13 µmol $H_2 \cdot gcat$ $^{-1} \cdot h^{-1}$, which accounts for a 60% efficiency decrease when compared to previous experiences where they used a 25 times smaller reactor [72]. With further research, those discrepancies will be reduced and the efficient scale-up a plausible future.

This plausible energy attainment (either hydrocarbons or H_2) is highly beneficial and counteracts the fact that around 4% of the world oil consumption is used as plastic source [11].
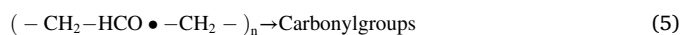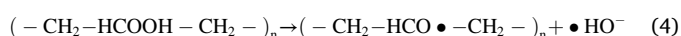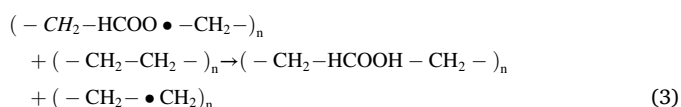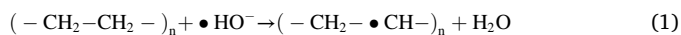
2.2.2. Degradation mechanisms

The process by which a plastic is photo-degraded consists on the irradiation of the plastic with photons with the right energy to create excited states in the plastic, which is followed by chain scission (where cross-linking may happen) and oxidation (where some oxygen groups may be incorporated favouring the subsequent degradation) [73]. Indeed, in the presence of oxygen, some oxidation (thermal- or photo-induced) can occur and aldehydes or carbonyl groups may be formed, which absorb in the range 290–400 nm. These plastics are so-called oxodegradable [29] and are prone to undergo photo-degradation. Moreover, the polar character of aldehydes and carbonyl groups may lead to degradation propagation [46].

Obviously, the impurities or other defects on the plastic matrix are weak points where the degradation process can start [74]. Likewise, the amorphous regions are more prone to oxygen diffusion through them, leading to the weakening of the intermolecular forces which favours chain scission and oxygen groups' incorporation [65]. Similarly, the presence of oxygen on the raw polymer favours the subsequent photo-degradation, hence, Alle et al. [9] degraded more easily PMMA than PS because the former has C=O and C—O groups which are more prone to breakage.

On the case of photo-catalysis processes, apart from the aforementioned photo-degradation, the catalyst is activated under a specific radiation, causing the promotion of an electron (e^-) from the valence band to the conduction band, leaving a hole (h^+) on the former. These, e^- and h^+ promote, respectively, reduction and oxidation reactions, either direct with the plastic or indirect with water and oxygen from the media, generating radical species such as $HO\cdot$, $HO_2\cdot$, $O_2^-\cdot$, etc. which attack quicky and non-selectively the organic matter (Verma et al., 2017; Nabi et al., 2020; Karim et al., 2022).

The extent of the photo-degradation and its mechanism seems to depend on the properties of the polymer, being the photo-degradation easier when having less stiffness and crystallinity [53].

The typical LDPE degradation process is depicted in Eqs. (1)–(5) from [75]. Generally, the degradation of plastics starts by the limiting step of oxygen addition to produce unstable superoxide and hydroxyl radicals, which help the propagation of the degradation process [46] Eqs. (1)–((3)). Indeed, carbon centred radicals may be formed Eq. (1) and continue chain reactions to cause more scissions or generate hydroxyl derivatives [65]. Additionally, some carbonyl by-radicals can be formed (Eq. (2)) and subtract hydrogen from nearby molecules (Eq. (3)). As reaction time passes, C—H bonds decrease due to oxidation and C=O groups are generated [76] (Eqs. (3) and ((5)), giving rise to the yellowing of the plastic. These latter groups are degraded at 290–400 nm [46]. Hopefully, many of the compounds generated throughout the photo-degradation by radicals (aldehydes, ketones, carboxylic acids) are biodegradable [12]. Furthermore, there is increasing research on the fact that a pre-treatment of plastics (e.g., heat treatment) and the optimization of the photodegradation process can both favour the complete degradation of plastics in environmentally friendly products, with lower risks of developing critical by-products and/or intermediates [67].

$$(- CH_2 - CH_2 -)_n + \bullet HO^- \rightarrow (- CH_2 - \bullet CH -)_n + H_2O \tag{1}$$

$$(- CH_2 - \bullet CH -)_n + O_2 \rightarrow (- CH_2 - HCOO \bullet - CH_2 -)_n \tag{2}$$

$$\begin{aligned} (- CH_2 - HCOO \bullet - CH_2 -)_n \\ + (- CH_2 - CH_2 -)_n \rightarrow (- CH_2 - HCOOH - CH_2 -)_n \\ + (- CH_2 - \bullet CH_2)_n \end{aligned} \tag{3}$$

$$(- CH_2 - HCOOH - CH_2 -)_n \rightarrow (- CH_2 - HCO \bullet - CH_2 -)_n + \bullet HO^- \tag{4}$$

$$(- CH_2 - HCO \bullet - CH_2 -)_n \rightarrow Carbonyl\, groups \tag{5}$$

Some aspects can favour the plastic photo-degradation. Hence, oxygen can be reduced into H_2O_2 favouring plastic degradation [3]. Moreover, common plastics have light stabilizers within their structure which presence can be even beneficial as they can react to avoid excessive radical generation, avoiding adverse effects such as cross-linking [69].

Depending on the catalyst or the applied wavelength, the degradation pathway may vary [53]. For instance, Fa et al. [65] degraded PE with TiO_2 or with $TiO_2/Fe(St)_3$ (St=stearate) and this latter catalyst performed better when analysing the carbonyl index, tensile strength and elongation. However, the weight loss was 77% smaller when using $TiO_2/Fe(St)_3$, meaning the degradation mechanism is different.

2.2.3. Typical photo-degradation setup configurations

Different factors affect the plastic photo-degradation (Table 2). Consequently, it is necessary to study each individual parameter and their combined effect on plastic degradation. As alternative, one may use a surface response software, not only for testing the best photocatalyst and its modifications but also the radiation source which may be optimal for its activation as well as other working parameters [70].

The are some examples of the conjugated effect of operational configurations. For example, PS was degraded much easily (taking into account the film piece is bigger and the treatment time quicker) when using TiO_2 as catalyst with a more powerful lamp (2.5 mW/cm^2) [77] than when using a more efficient catalyst (TiO_2/copper phthalocyanine) with a weaker lamp with broader spectrum (1.75 mW/cm^2).

Consequently, some relevant set-up aspects would be discussed next although the overall degradation performance should take into consideration the combined effect of those parameters.

2.2.3.1. Radiation source.
The selection of the lamp should be taken following Grothus-Draper law which states that only light with proper energy has the potential of causing photo-physical processes (such as bond scission) [74].

Hence, both wavelength and intensity are very important for photodegradation processes [65,78]. Indeed, Chakrabarti and Dutta [78] augmented the PVC degradation from 6 to 20% when increasing the light intensity from $0.105\cdot10^{-2}$ to $0.192\cdot10^{-2}$ W/m^2. Nevertheless, even though at low intensities, photo-degradation and light intensity are directly proportional, at higher intensities the reaction rate is proportional to the square root of light intensity [9]. Besides, the reaction mechanism is different, as longer treatment times at lower photon intensities lead to more chain scission reactions [50].

The selected wavelength also plays an important role. For instance, UV or visible radiation can promote direct photo-degradation and an increase in temperature which favours degradation. Infrared radiation promotes only thermal oxidation. [55]. UV radiation under 350 nm has the energy for breaking the covalent bonds of many polymers [49]. However, the typical bonds of polymers (C—C, C—H, C—N, C—Cl) are prone to absorb radiation under 200 nm. For instance, PMMA was degraded at 280–300 nm but with radiation above 320 nm no degradation was detected [50]. Nevertheless, some conjugated double or carbonyl bonds, which are found in commercial plastics, increase the absorption at higher wavelengths [74]. This latter fact is a positive phenomenon as UV is only a small percentage of the solar spectrum.

TiO_2 is one of the most used catalysts for UVA light degradation and its bandgap falls in this region of the electromagnetic spectrum. Indeed, doping with metals and non-metals is an usual methodology to decrease TiO_2 bandgap, favouring the utilization of visible radiation [60] and, therefore, reducing the energy requirement and operational costs.

Consequently, the influence of the radiation source depending on the catalyst selection has been reported. Zhao et al. [79] reported a two factor increase in the PE weight loss when using UV radiation instead of using solar radiation, as they used TiO_2 as catalyst. Similarly, Sawaphum

Table 2

Overview of the different operational parameters used in literature for the photo-catalytic degradation of a list of plastics with the corresponding evaluation of their degradation.

Refs.	Plastic	Radiation (time)	Catalyst (concentration)	Set-up	Weight loss (%)	Other measurements
[73]	PE	Sunlight (240 h)	polypyrrole/TiO_2 (10 wt. %)	Heterogeneous conditions: small PE fragments put in a culture dish and catalyst was added	35.4	FTIR: decrease of peak intensity at 1463 (CH_2) and 1376 (CH_3) cm^{-1} due to scissoring.
[79]	PE	254 nm, 1.0 mW/cm^2 (300 h)	TiO_2 (1 wt.%)	Homogeneous conditions: PE-TiO_2 film, 5 cm^2, lamp placed at 5 cm	42%	CO_2 concentration increase, (0.01 mM in 95 h), detection of intermediates (peak area increase in GC), FTIR (formation of bands at 1631 and 1713 cm^{-1}).
[64]	LDPE	Sunlight (200 h) 75.000–90.000 lx	TiO_2 (0.1 wt.%)	Homogeneous conditions: Film LDPE-TiO_2	68%	FTIR (carbonyl index). TGA (thermal stability is lower).
[41]	PET	254 nm, 1 mW/cm^2 (7 h)	–	Homogeneous conditions: Film 1 cm^2, distance lamp-sample 3 cm	–	Contact angle reduction from 76 to 14° 13.4% C reduction (XPS).
[55]	PP	$1.08 \cdot 10^7$–$2.19 \cdot 10^7$ J/m^2 (130 h)	TiO_2-GO-nanocomposite (0.2 wt.%)	Homogeneous conditions: Film under solar radiation (9: am-18:00 pm) 500–995 W/m^2 $1.08\ 10^7$–$2.19\ 10^7$ J/m^2	–	Deep cavities after irradiation (SEM), FTIR detection of C = O bond because of degradation and deformation of –CH_2 signal.
[78]	PVC	UV lamps 4 (4 W) and 1 (6 W) (2 h)	ZnO 0.2 g/0.2 g Erosin dye/g PVC	Homogeneous conditions: PVC-ZnO-dye film 19.2 cm^2	20%	FTIR bands modification.
[36]	Homo-methacrylic polymers	Hg lamp 220 −300 nm (35 mW/cm^2) (350 h)	–	Homogeneous conditions: Polymer coated stones	100%	Stones adsorbed water because of the protective plastic degradation, Appearance of FTIR peaks due to C = C bonds caused by chain scission.
[77]	PS	8 W ultraviolet lamps (253.7 nm). 2.5 mW/cm^2 (150 h)	TiO_2 (2 wt.%)	Homogeneous conditions: PS-TiO_2 film (100 cm^2), lamps at 5 cm away from samples	22.5%	Variation of the average MW, new FTIR bands (1217 and 1724 cm^{-1}), XPS changes concerning the elements oxidation (less bands related to reduced oxidation states)
[88]	PS	Three 8 W fluorescent lamps (310–750 nm) 1.75 mW/cm^2 (250 h)	2 wt.% TiO_2/copper phthalocyanine	Homogeneous conditions: PS-TiO_2/copper phthalocyanine film (60cm^2) 7 cm away. Containing 0.5 g of PS	7%	Detection of volatile organic compounds, CO_2 monitoring
[57]	PE	UVA (280–350 nm), 30 W (200 h)	ZnO nanoparticles grafted with 10 wt.% polyacrylamide	Homogeneous conditions: Film at 50 cm distance to the light source	25%	SEM images difference, tensile strength and elongation worsening as the photo-degradation occurs
[90]	Sulfonated PS	250 W Hg(Xe) light (250 min)	2μmol-Fe(III) and 14.1 mmol-H_2O_2/g of PS	Heterogeneous conditions: PS fragments, pH 2, 25 mL, lamp placed at 5 cm, stirring.	99	Detection of by-products
[88]	PVC	30 W UV lamp, 254 mainly and 305, 357, 384, 418, 520 and 543 nm (720 h)	2 wt.%TiO_2-aniline-ammonium persulfate	Homogeneous conditions: Films of 10 cm ø, 22 cm from light source	70	Carbonyl groups increasing and C—H decreasing (FTIR)
Ref.	Plastic	Radiation (time)	Catalyst (concentration)	Set-up	Weight loss (%)	Other measurements
[60]	LDPE	UV (15 days) 2 lamps 18 W, 315 nm	TiO_2 nanotubes (10 wt. %)	Homogeneous conditions: Films of 9 cm^2 at 5 cm from light source	78	Increase on surface roughness
[81]	PS	30 W UV lamp (288 h)	1 wt.% TiO_2-Fe stearate	Homogeneous conditions: Films 12.25 cm^2, lamp placed at 8 cm	22	Molecular weight decrease, new carbonyl groups bands in FTIR spectra
[65]	PE	30 W 254 nm (240 h)	TiO_2-Fe stearate	Homogeneous conditions: Samples of 16 cm^2 placed at 10 cm	14%	Appearance of C = O bonds (detected by FTIR), tensile strength and elongation lost (2 times and 35 times lower)
[1]	PE and PP	Solar simulator	200uL of 11,000 ppm ZrO_2	Heterogeneous conditions: Fragments of 2.25 cm^2	–	SEM superficial changes and carbonyl index increase (170%)
[15]	PS	UV, 253 nm, 30 W	3 wt.% TiO_2	Homogeneous conditions: 5 g PS in film at 8 cm of lamp	6%	MW decrease, FTIR appearance of characteristic bands for C = C and oxygenated bonds, SEM superficial changes
[62]	Polyepoxy	UV, 313 nm	10 wt.% di-benzoylperoxide	Homogeneous conditions: 45 °C, film at 25 μm of the lamp		Increase of carbonyl groups (FTIR)
[13]	LDPE	Solar radiation (4 weeks)	10 wt.% polylactic acid (biodegradable polymer)+ 1 wt.% TiO_2	Homogeneous conditions: Films of 21×30 cm, at 45° to horizontal	12%	SEM (cracks), fewer tensile properties
[82]	PE	4 UV lamps 32 W, 254 nm, 4.95 mW/cm^2, (36 h)	TiO_2 nanoparticles	Homogeneous conditions: Films with TiO_2 and triton X-100 of 1 cm^2 placed at 10 cm	100%	Raman carbon peaks disappearance
	PS	4 UV lamps 32 W, 365 nm, 3.05 mW/cm^2, (12 h)			98.4%	XPS oxidation detection, hydrophobicity reduction, TGA stable profile (meaning only TiO_2 remains on the sample)

Table 2 (*continued*)

Refs.	Plastic	Radiation (time)	Catalyst (concentration)	Set-up	Weight loss (%)	Other measurements
[9]	PMWA	UVA, 112 W/m², (7 h)	TiO$_2$ (10 wt.%)- β-SiC foams	Heterogeneous conditions: nanopalstics pH 6.3, 600 mL	50% TOC reduction	Formation of FTIR bands relative to oxidized functional groups oxidation
[83]	PVC	75 W Hg lamp (1 h)	TiO$_2$-PVC (2:1) film	Homogeneous conditions: 136 cm² film	53% PVC decomposition	XPS carbon reduction, oxygen augmentation, chloride and CO$_2$ evolution.
[69]	PS	200 W H g lamp	8 wt.% PS-block acrylic acid+11 wt.% TiO$_2$	Homogeneous conditions: Film placed at 40 cm, 60 °C	n.s.	Molecular weight reduction, gel permeation chromatography
		25 W LED lamp simulating sunlight	8 wt.% PS-block acrylic acid+11 wt.% TiO$_2$+ 0.01 wt.% copper phthalocyanine	Homogeneous conditions: Film placed at 30 cm, 60 °C	n.s	

et al. [12] noticed a better photo-degradation of PE and PP with TiO$_2$ photo-catalyst at 254 nm than under a 366 nm wavelength.

2.2.3.2. Catalysts. The key parameter for making these photo-degradation processes feasible to be used is to add a catalyst to plastics during the fabrication process in order to favour the plastic degradation. Indeed, S et al. [15] demonstrated an easier way to photo-degrade PS films when adding TiO$_2$ as photo-catalyst, improving 30% the UV degradation of original PS films. Also Camila Ariza-Tarazona et al. [80] demonstrated the addition of C,N-doped TiO$_2$ enhanced HDPE photo-degradation (Fig. 4). Moreover, as reported by Tu-morn et al. [13] the photo-degradation of LDPE modified with polylactic acid (PLA) and different amounts of TiO$_2$ proved to work much better than only biodegradation (Fig. 4). Amongst the parameters that affect the catalysts performance there are: i) the ratio pollutant-catalyst, ii) the surface area, being the larger the better for favouring the generation of active species [60] and pollutant adsorption and iii) the band gap, as for instance a higher band gap is related to better redox capacity but less activation with visible light [1].

Indeed, Zhao et al. [79] increased the PVC degradation by selecting properly the ZnO concentration to work with. They noted how the catalyst concentration was not linearly proportional to the PE degradation. Actually, Chakrabarti et al. [78] demonstrated how increasing the catalyst concentration causes more plastic degradation because of the increasing amount of active sites (i.e. Fig. 5), until a point where additional amount of catalyst caused a negative effect due to light scattering.

Obviously, in aqueous systems, the contact plastic-catalyst surface is higher in homogeneous conditions, but the use of powder catalysts is discouraged as the catalyst recovery makes the future application more difficult and causes light scattering [9]. This means that the usual high polarity of the catalysts (for instance TiO$_2$) and the low polarity of the plastics have to be overcome with the addition of some compounds such as transition metals carboxylates [81]. Thus, Nabi et al. [82] increased
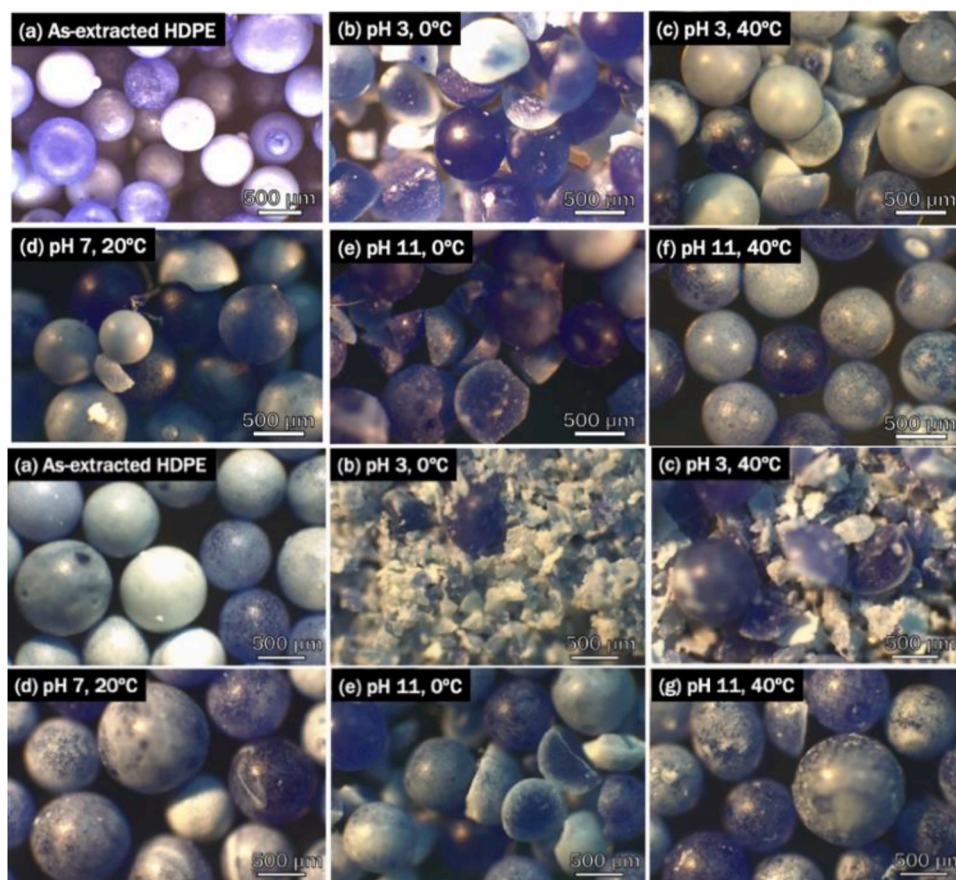

Fig. 4. Optical micrographs of HDPE microplastics after photolysis (up) and C,N-doped TiO$_2$ photocatalysis (down). Reprinted from [80], copyright (2020), with permission from Elsevier.

Fig. 5. Appearance of LDPE films in which 10 wt.% PLA or both 10 wt.% PLA and different amounts of TiO_2 have been added. The samples were imaged at week 0 and then at week 4 of irradiation with sunlight and at week 4 after biodegradation experiments. Reprinted from [13], copyright (2019), with permission from Elsevier.

from 69.25% to 91.04% and then to 98.4% the PS photo-degradation with TiO_2 by using, respectively, water, ethanol or surfactant triton X-100 as dispersing agent for PS-TiO_2-film preparation. In the case of PVC plastic film, better degradation was attained when TiO_2 particles were within the film than when they were dispersed in a solution in contact with the film (heterogeneous conditions) [83]. This demonstrates the film degradation is not only a more plausible technique for future usages but also a more easy-to-apply process overcoming plastic/photocatalyst polarity differences.

TiO_2 catalyst is one of the most used catalysts due to its efficient photo-degradation activity, high stability, low cost and relatively low toxicity [60]. Indeed, Shang et al. [77] doubled the PS weight loss until 22.5% when adding TiO_2 (2%) to a PS film (under UV), detecting three times higher CO_2 levels due to PS degradation.

Apart from TiO_2, other authors have explored the usage of other catalysts, mainly semiconductors for favouring the separation of electrons and holes. Bandara et al. [1] demonstrated how ZrO_2 performed better than TiO_2 for the film degradation of PP and PE because of the capability of this catalyst to stabilize oxygen vacancies. Kamalian et al. [57] reported how ZnO has been overlooked as catalyst, as it is widely less used than TiO_2 although it has similar properties and higher photo-activity. Indeed, ZnO has a similar band gap (3.37 eV) to TiO_2. However, ZnO has low stability due to photo-corrosion [84] and reported toxicity.

Coupled photo-catalysts are often used, that is the combination of two semiconductor catalysts. Those two compounds (A and B), are mixed and they may have different oxidation potentials, if the conduction band of A is higher than the one of B, excited electrons of A can be transferred easily to the conduction band of B. Therefore, holes in the valence band of B can easily be transferred to the valence band of A. This process decreases the e^-/h^+ recombination and thus enhances the degradation efficiency of the photo-catalytic process [73]. However, the addition of the second element should be studied, as increasing too much the concentration can lead to negative effects. For instance, Fa et al. [81] attained 14% of PE weight loss after 240 h of UV irradiation when using TiO_2 and $Fe(St)_3$ and 62% when using only TiO_2.

Modification of catalysts and their use in different conditions

There are only a few examples of modified photo-catalysts, usually so-called "doped photo-catalyst", for microplastics visible-light photo-degradation. Most of these studies are recent and led to very interesting results underlying the need of further research in this field. Regarding the metal modification of photo-catalysts, to date, only two works have been reported for the degradation of microplastics. The first one [75], is based on ZnO nanorods with 5.4% Pt nanoparticles which were used for the visible-light photo-degradation of LDPE films. In comparison to ZnO nanorods, it was found that the Pt-ZnO nanorods showed a 78% enhancement in visible light absorption. They attributed this better visible photo-catalytic efficiency to the absorption of the Pt nanoparticles and to the decreased e^-/h^+ recombination due to the photo-generated e^- diffusion from the ZnO to the Pt.

Another example of metal doped catalysts for light-induced removal of microplastics is Au@mag@TiO_2 (where mag=Ni or Fe) (Fig. 6) [85]. This removal process is not based on photo-catalysis itself. The microplastics are carried away thanks to a micromotor propulsion which happens due to a UV application. The mechanism behind the propulsion of the micromotors and the removal of microplastics lies in the interface of TiO_2 with Au. Indeed, after the excitation of TiO_2 with UV light, the electrons migrate to the metal layer where the reduction of protons takes place. The consumption of protons is what leads to the generation of a fluid flow around the metal layer and, therefore, to the propulsion. The propulsion mechanism in the presence of H_2O_2 is slightly different since the propulsion is generated by the decomposition of H_2O_2 via an oxidation-reaction mechanism on the micromotors. This novel methodology for the removal of microplastics is definitely very interesting since it opens the avenue for "smart" microplastics collectors, although it lacks in selectivity.

Non-metal doping is another strategy to enhance the photo-catalytic performance under visible-light. For instance, Ariza-Tarazona et al. [80] reported the photo-degradation, under visible-light, of HDPE extracted from facial scrubs using nitrogen-doped TiO_2. The material had a lower bandgap than pure TiO_2.

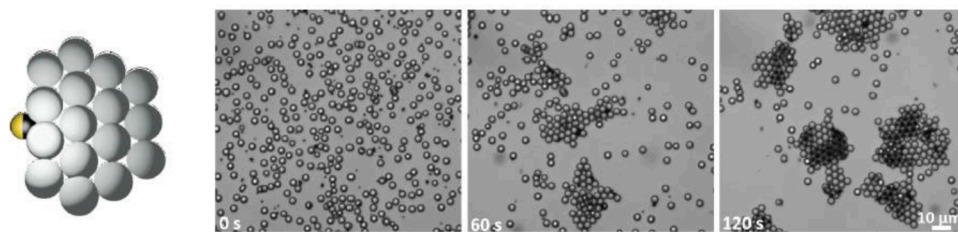Later on, the same authors [80] reported a research about *carbon and*

Fig. 6. Schematic representation of the interaction between Au@Ni@TiO$_2$ micromotors and PS particles, and optical images throughout time of the same micromotors gathering the PS particles in the presence of 1.67% H$_2$O$_2$ under UV light. Reprinted from [85], Copyright (2019) with permission from American Chemical Society.

nitrogen-doped TiO$_2$ semiconductors for the visible-light degradation of HDPE microplastics. Indeed, they reported that although in other works such as that by Tofa et al. [75] or in their previous work [86] the photocatalytic degradation of microplastics was successful under visible-light, the complete photo-degradation was not achieved. For that, low pH and temperatures may enhance the degradation performance. Hence, acid pH incorporates H^+ ions in the system facilitating the plastic degradation and the interactions of the catalysts particles with the HDPE microplastics. Low temperatures increase the fragmentation of the plastics, thus increasing their surface area and enhancing their interactions with the photo-catalyst.

Finally, Llorente-García et al. [70] reported the photo-catalytic degradation of HDPE and LDPE microplastics under visible-light in aqueous medium in the presence of a mesoporous N-TiO$_2$ coating. In this work, they focused on the issue that microplastics extracted from commercially available products have usually a big mean particle size several thousands of times bigger than the size of the commercial catalysts. In conclusions, the authors showed that the photo-catalytic degradation of HDPE and LDPE under visible-light in presence of N-TiO$_2$ catalyst is influenced by: 1) the high availability of OH• radicals generated thanks to the high surface area of the N-TiO$_2$ coating; 2) the interactions promoted by diffusion and stirring of the OH• radicals with microplastics; 3) the size of the microplastics (high surface-to-volume ratio in smaller HDPE microplastics was beneficial); 4) the shape of the microplastics (film-shaped LDPE can accumulate on the surface of the solution hindering a good illumination and oxygenation of the whole system reducing the photo-catalytic performance of the catalyst).

Amongst catalyst modifications, dye sensitization can be also used for enhancing the efficiency of semiconductor catalysts. The dye usually has a lower band gap than the raw catalyst, thus it can make an UV-active photocatalysis to extend its activation wavelength towards the visible spectra [87]. Therefore, the dye can be excited with lower energy and the excited e^- can be injected into the conduction band of the semiconductor catalyst, favouring the e^-/h^+ separation [78]. This causes the indirect activation of the semiconductor [87]. Hence, Shang et al. [88] synthesised a catalyst composed of TiO$_2$ and copper phthalocyanine. The energy of the used light should be between the band gap of TiO$_2$ (3.2 eV) and the band gap of copper phthalocyanine (1.81 eV). In this case, copper phthalocyanine is excited and an e^- is moved to a singlet state and a h^+ is formed, favouring the reduction and oxidation of pollutants. Ali et al. [60] used brilliant green dye to sensitize TiO$_2$ nanotubes, enhancing the photo-response of the latter which lead to the reduction of the half life time of LDPE plastic under visible radiation from 346 days to 231.

Another option would be the application of the photo-Fenton process which is based on the generation of oxidant species by the reaction of Fe^{2+} (or other transition metals) with H$_2$O$_2$ to generate OH• or other radicals (Fenton process). The radiation i) favours the regeneration of Fe^{2+} from the spent Fe^{3+} generated through the Fenton process, ii) can cause H$_2$O$_2$ homolytic breakage to OH• radicals and iii) promotes the photolysis of iron (or other transition metal) complexes which can be formed during the Fenton process [89]. However, few references have

been published about the photo-Fenton degradation of plastics. Nevertheless, the results reported by Feng et al. [90] are very promising, as 99% of weight loss of sulfonated PS was attained in 250 min.

2.2.3.3. Influence of photo-catalytic conditions on the plastic degradation.
The photo-catalytic process can be performed in homogeneous or heterogeneous conditions. In the first case, the catalysts are dispersed in plastic films, while in the second the catalysts are dispersed in an aqueous medium where the plastics fragments are fluctuating. Homogeneous conditions would be useful for the manufacturing of easier-to-degrade plastics [74]. However, there are researchers who have degraded the plastic by mixing the plastics and the catalysts in solid state [73] or in aqueous media dispersions [9], both processes would be useful for eliminating the plastics already present in the environment.

Homogeneous conditions allow a good contact of plastic and catalyst, nevertheless, they imply a more superficial degradation. However, Shang et al. [88] detected bigger cavities on the film as the photo-degradation proceeds, indicating that not only the surface is been attacked but also the inner part of the film.

On the case of heterogeneous photo-catalysis in water, the effect of the plastic fragments' size is a key parameter. Actually, Alle et al. [9] reported a faster PS photo-degradation for a PS diameter of 140 nm than of 508 nm. Moreover, one should consider the effect of the solution properties, such as the solubility and lifetime of the donor and acceptor species in the solution as well as the viscosity of the solvent that may affect the performance of the photo-catalytic degradation [74]. Indeed, the solution pH has an important effect which depends on the point of zero charge of the used catalyst. Thus, low pH values (4–6) are more suitable for PS photo-degradation with TiO$_2$ [9], as some oxidants' generation is enhanced at acid pH [80]. The inlet and recirculation flows are important as they are related with the residence time of the plastic in the reactor and there can be mass transfer limitations or a heterogeneous distribution of the polymer on the effluent at too low flows [9].

In Table 2 it can be seen how the set-up configuration plays an important role. Zhao et al. [79] achieved 42% weight loss in 300 h with a 1 wt.% TiO$_2$ loaded PE film when using UVA light. On the other hand, Li et al. [73] only reached 35% weight loss for the same plastic when it was placed in small fragments into a Petri dish under solar radiation and in the presence of 10 wt.% of a Polypyrrole/TiO$_2$ nanocomposite. In this latter case, a deep economic study should be carried out as the worsening of the performance may be worth it because of the energy saving when using solar radiation.

Accordingly, the application of photo-based process should be done with flexible working set-ups which allow a modification of the conditions depending on the plastic content and type to be degraded.

2.2.3.4. Plastic chemical composition. The kinetic behaviour of the photo-degradation process is also related to the chemical composition. Actually, even the same plastic with different polymerization degrees can be differently degraded. Thus, Horikoshi et al. [83] reported a much quicker PVC photo-degradation of a higher molecular weight PVC. Regarding different plastics, Myllari et al. [91] reported the

photo-degradation of PS to be linear in time whereas PP was degraded exponentially. Moreover, the photo-degradation of mixtures of plastics can be more favoured than the degradation of a single component, positive fact for future applications. For instance, the LDPE photo-catalytic TiO_2 degradation was easier when having 10% of poly-lactic acid inside the plastic composite [13], and this addition can also enhance the following biodegradation. Fa et al. [81] also evaluated the addition of thermo-degradable promoters such as $Fe(St)_3$ to favour the photo-degradation and the following biodegradation.

Moreover, some plastic modifications can enhance the plastic degradation. Hence, Feng et al. [90] sulfonated PS and this alteration allowed its degradation whereas raw PS did not undergo any modification after 300 min of photo-Fenton process. Indeed, the addition of electronegative atoms weaken the structure.

Hence, there is room for the synthesis of weaker plastics which are easily photodegraded. Indeed, those studies based on plastic film photodegradation open a path for a new generation of new photodegradable plastics, which will be easily degraded on the possible scenario of reaching the environment.

2.2.3.5. Treatment time. The degradation time plays an important role on the photo-degradation process [81]. Obviously, the longer the treatment time, the greater the extension of the degradation. Indeed, Table 2 shows how the greatest weight loss percentages are for the longer treatment times under UV TiO_2 based photo-catalysis. Thus, 15 and 30 days were needed for achieving, respectively, 78% (LDPE) and 70% (PVC) of weight loss [60,76]. Those treatment times are still quite long but they are promising, considering that the research on photo-degradation of plastics is at early stage.

However, one should select properly when to stop the reaction in order to favour the following degradation steps or to avoid the generation of toxic by-products. Indeed, even photo-degradable plastics have low efficiency to be completely photo-degraded [81].

3. Quantification methods to assess the performance of the plastic degradation process

One of the main problems connected with plastics concerns the difficulty of a proper detection method able to quantify even small quantities and to determine their state. Being plastics mainly aliphatic compounds, they usually display UV absorption bands around 200 nm, where many other chemical species absorb too. Thus, typical UV spectrophotometry cannot be used to detect plastics. Actually, the previous unawareness, caused by a lack of detection, may have been the reason of the wide accumulation of plastics into the environment. In order to avoid more plastics to be leaked to the environment and to quantify the performance of the treatment alternatives, there have been several studies which have proposed different ways of qualifying and quantifying the plastic content as well as the degradation process (Table 3). These analyses are referred to solid, liquid and gas phases as the plastics should be monitored in solid (for instance for film degradation) or liquid media (for monitoring their presence in wastewaters). Moreover, gases are undoubtedly formed because of the degradation process and their composition should be also followed.

3.1. Weight loss

Weight loss is one of the most used analysis, usually when treating plastic films, which are weighed initially and during the degradation process. Weight loss is related to the plastic fragmentation into smaller and soluble by-products (in the case of aqueous media) or into gases, such as CO_2, due to plastic mineralization (in the case of aqueous and

Table 3
Different analysis alternatives for the plastic degradation monitoring.

Refs.	Analysis	Procedure/Comments
[92, 93]	Weight loss	In heterogeneous aqueous degradation: Filter the solution, dry and weigh. In film degradation: Directly weigh.
	Size distribution (%)	Put a number of random microplastics pieces and classify by sizes.
	By-products	Extraction with toluene (x 3) and then measurement by HPLC or GC–MS
	TOC	Measure the TOC of the aqueous part after removing the and the catalyst.
	HPLC-qualitative	Comparison of the spectrum obtained for the aqueous fraction prior and after the treatment.
	HPLC-carboxylic acids	Comparison with carboxylic acids standards (formic, acetic, oxalic, butanedioic acid, propanedioic acids).
	Toxicity	The algae are exposed to different reaction solutions (after removing MP) for 14 days at 25 °C, 100 rpm and under illumination (each 12 h to mimic real-life conditions) of white fluorescent light at 50 mE. The results were compared with control test (DI water as medium).
[29, 64]	FTIR	Peaks analysis. The ratio between values of abs at 1710 cm^{-1} and 2020 cm^{-1} is related to the carbonyl concentration. One hundred times the ratio between 997 cm^{-1} and 973 cm^{-1} gives information about isotacticity.
[29]	ATR-FTIR (Attenuated Total Reflectance-FTIR)	The signals demonstrate the damage of the microplastics caused by irradiation.
	Thermodynamic mechanical analysis	Measure the storage modulus (MPa) with temperature.
	Differential Scanning Calorimetry (DSC)	Under abiotic conditions. Used to determine the thermal transitions of thermoplastics. In order to compare, the heat flow (watts/g) is plotted against temperature. Melting enthalpy can be calculated for measuring the crystallinity [45]
[64]	TGA (Thermogravimetric Analysis)	The structure modifications imply different TGA profiles.
[55]	TOF-SIMS (Time of Flight-Secondary Ion Mass Spectrometry)	Determines the chemical composition of the samples, the bonds between atoms can be reasoned, being a sensitive analysis.
	GC	The liberated gases throughout the degradation process can be analysed and quantified when using standards (methane, ethene, ethane, propane, acetaldehyde, formaldehyde and acetone).
[45]	XPS	New bands appear in the spectrum because of the degradation process.
	XRD	Provides a characteristic profile depending on the crystallinity of the plastic.
	Glass transition temperature (T_g)	The T_g may vary depending on the MICROPLASTICSdegradation reach.
[16]	RAMAN	Typical bands are characteristic of each compound. The ratio between the intensity of two typical peaks gives an idea if the compound remains unchanged or not.
[41]	Contact angle	Due to the surface oxidation, there are more oxygen species on the surface and thus there are dipole-dipole interactions which increase the hydrophilic behaviour and thus the contact angle with the water drops is reduced.
	Friction Force Microscopy	Analyses the surface chemical structure modifications.
[79]	SEM and TEM	Determine surface modifications, as cavities are formed because of the oxygen etching out.
[36]	Capillary water adsorption	If the plastic is in a porous surface, the adsorption increases as the plastic is degraded.

solid state treatments) [78]. Consequently, CO_2 liberation monitoring is, as well, one of the typical measurements to ensure plastic degradation [79]. Indeed, Nabi et al. [82] found CO_2 was the main product of the PS TiO_2-photo-catalytic degradation.

3.2. TOC analysis

The plastics fragmentation due to the photo-degradation and the conversion of these fragments in CO_2 can be monitored also by the analysis of the Total Organic Carbon (TOC) of the aqueous media before and after photo-degradation. During the photo-degradation process, TOC decreases since the plastics are broken in fragments and subsequently, into gases such as CO_2 or CH_4. Therefore, TOC analysis can provide a quantitative information on the plastics photo-degradation status. Indeed, some authors such as Alle et al. [9] have used TOC analysis for monitoring PMWA decomposition.

3.3. Chromatography

This aforementioned plastic fragmentation can be also monitored thanks to by-products analysis. For that, high performance liquid chromatography (HPLC) or gas chromatography (GC) can be used [92]. Indeed, previous authors [79] have detected methane, ethene, ethane, propane, acetaldehyde, formaldehyde and acetone after the PE-TiO_2 photo-degradation under UV radiation for 80 h.

3.4. X-ray photoelectron spectroscopy (XPS)

XPS is a surface analysis technique (measurement depth around 5 nm), nevertheless, some authors have reported that the photo-degradation takes place at the plastic-air interface, making this technique suitable. This technique provides a way of measuring the oxidation state of the compounds and one can determine if the degradation process is oxidising or reducing the structure. For instance, oxygen concentration usually increases as the plastic oxidation process happens, and C bands tend to change from the typical ones for C—C bonds to those for C=O [64]. In fact, Zhao et al. [79] suggested the formation of carbonyl and carboxyl groups due to the detection of new peaks at lower binding energies. Shang et al. [77] demonstrated slight modifications on the XPS spectra of initial and treated PS. For instance, after 130 h of irradiation with fluorescence light and using TiO_2-copper phthalocyanine as catalyst, oxygen from PS was oxidized from carbonyl or hydroxide to carbonate or carboxylic acids, demonstrating the efficacy of the oxidation process. Indeed, XPS peaks at 286.5 eV are usually attributed to the C present in alcohols and carboxylic acids [77]. This analysis can be used for quantifying the oxidation by measuring the proportion of the generated peak and estimating the percentage of degradation [79]. However, Hurley et al. [41] found difficult to resolve the peaks due to the oxygen peaks broadening as the photo-degradation process happens, so XPS may require to be complemented with other techniques.

3.5. Fourier transform infrared (FTIR) and Raman spectroscopies

FTIR and RAMAN spectroscopies have been widely used for plastic analysis due to their non-destructive character and the simplicity of the measurement [16]. With the FTIR spectrum, one can follow the photo-degradation process. For instance, C = C bonds are formed because of the scission of the carbonaceous chains. Moreover, C—H bonds decrease and C—O bonds can be detected due to the oxidation of the molecule, as well as C=O and –OH groups. All these functional groups are reflected in FTIR bands [76]. Indeed, the bands appearing at 1631, 1178, 1713 and 3050–3570 cm^{-1} are related with, respectively, the amount of C≡C, C—O, C=O and –OH [60]. Indeed, Tofa et al. [75], used FTIR spectroscopy to determine the higher performance, in the photocatalytic degradation of LDPE, of Pt-doped ZnO nanorods in

respect to a ZnO catalyst (Fig. 7). There, several peaks related to oxidized functional groups are present in the LDPE spectra after photocatalytic degradation in the presence of ZnO and Pt-doped ZnO (regarding LDPE before irradiation) and they have higher intensity in the case of Pt-doped ZnO.

In fact, several authors [13,60,64] have used the carbonyl index to quantitatively estimate the oxidation of plastics. One of the most accurate ways of calculating the carbonyl index is to divide the area of the FTIR peak in the region from 1850 to 1650 cm^{-1} (carbonyl peak) by the area of the FTIR peak in the range between 1500 and 1420 cm^{-1} (methylene scissoring peak) [94].

Raman spectroscopy is complementary to FTIR, identifying species and detecting structural or bonding modifications on polymers [38]. Actually, the C—C peaks which appeared at 1050–1150, 1300 and 1450 cm^{-1} of Raman shift for initial PS were reduced gradually as a TiO_2 photo-catalysis process was applied and the polymer degraded. This happens also with the degradation of PE, where those signals disappear as irradiation time increases [82]. Raman technique is powerful enough to be used for plastics monitoring when comparing with standards [16].

3.6. Thermogravimetric analysis (TGA)

TGA results should be carefully analysed, as the profile may have different weight losses areas which are related to the stability of the structures within the plastic. During TGA measurement, the plastic is submitted to a gradual increase of the temperature which provokes weight loss following different trends. The temperature at which the weight loss happens depends on the plastic nature and crystallinity. Thus, more amorphous plastics are more prone to photo-degradation [64]. This, this technique can be complemented with XRD.

3.7. X-ray diffraction (XRD)

XRD spectra are useful for determining the structure of crystalline materials. Since plastics have usually some crystalline parts, they can be measured by XRD. Hence, one can determine the presence of a given plastic by comparison with the spectra of the standard. Moreover, changes due to degradation can be monitored [64]. Tang et al. [45] used the intensity of some of the characteristic peaks of PP to calculate the amount of PP β-form (which is less ordered and with high melting point than the α-form, predominant in commercial PP).
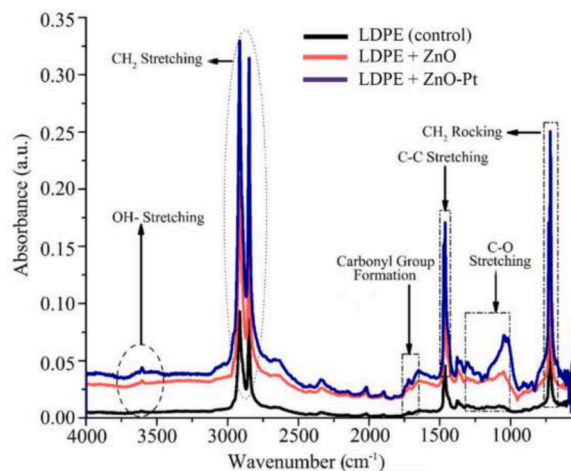

Fig. 7. FTIR spectra of LDPE films before and after 175 h visible light irradiation with ZnO and Pt-ZnO catalysts, Reprinted from [75], copyright (2019), with permission from MDPI.

3.8. Scanning electron microscopy (SEM)

As SEM is an efficient surface analysis technique, it can be used to detect all the morphological modifications on the surface of plastics due to degradation. Usually, the initial plastic surface is smooth but, after irradiation, it gets some cracks and irregularities [95]. Shang et al. [77] noticed, after 130 h of PS photo-catalytic degradation in the presence of TiO_2, that the film surface had bubbles and this was related to CO_2 release (0.25 mM after 18 h). Indeed, Tu-Morn et al. [13] showed how the holes in LDPE films with TiO_2 increased from a diameter of 4 μm to 7 μm from week 1 of solar irradiation to week 4. In the case of Nabi et al. [82], they photo-degraded PS spheres which size was reduced as the degradation processes took place.

Thomas and Sandhyarani [64] manufactured a TiO_2-PE film to study its photo-degradation. Before irradiation, it was not possible to visualize the TiO_2 particles by SEM, as they were embedded in the PE film. After the solar photo-degradation of the PE film, TiO_2 was detected via SEM images. This is in accordance with Zhao et al. [79] who detected TiO_2 on PE cavities which were formed because of the degradation process. This demonstrates both the photo catalyst is within the polymers matrix and the fact those plastics are being degraded.

3.9. Toxicity tests

Some plastics liberate toxic compounds through the degradation process, thus measuring the toxicity of the generated by-products is a good way to determine at what point the reaction should be stopped [93]. Some alternatives for toxicity evaluation are measuring the microalgae growth when compared to standard water [92], using luminescent bacteria (Microtox) [93] or measuring the mutagenicity activity [83].

Kang et al. [92] degraded microplastics contained in facial cleaners and reported that the algae growth increases with the degradation time due to the generation of assimilable carbon material used as carbon source by the bacteria. The photo-degradation of PVC with TiO_2 did not cause either mutagenic by-products [83]. However, the toxicity extremely increases in the work reported by Johnson et al. [93] as after 84 days all of the tested plastic bags (PE) have generated toxic compounds through degradation, leading to complete decease of luminescent bacteria. These authors highlighted that further tests should be done in order to know if treated bags were also toxic for more complex organisms.

3.10. Gel permeation chromatography

The variation of molecular weight is, as reported by Fa et al. [81], one of the most important factors to measure the plastic degradation and that can be measured by gel permeation chromatography. The usual decrease of the molecular weight is caused by chain scissions [15] and it happens alongside with the formation of new hydroxyl, carbonyl and other oxygen-containing groups [65]. On the other hand, the increase of molecular weight is caused because of the crosslinking of the chains during the last steps of the degradation [74]. Several authors have used the profile of gel permeation chromatography to determine the effect of the degradation process, using the initial polymer profile as reference [69].

3.11. Mechanical properties testing

The worsening of the mechanical properties is related to plastics degradation [13]. For instance, Fa et al. [65] reported a 60% loss in tensile strength and 97.7% loss in elongation of PE after 30 days of thermo-oxidative degradation. Ali et al. [60] reported an inverse relationship between elongation and carbonyl index. Another example was the tensile strength decrease reported after the degradation of LDPE films under TiO_2 photo-degradation [13]. Indeed, the

photo-degradation causes the plastic molecules to agglomerate and thus the tensile strength diminishes [60].

Table 4 collects the values of some of these analyses for the monitoring of PE, PS and PP photo-degradation, as they are the most used and detected plastics in the environment [26,27].

4. Future perspectives

With this overview of the current state-of-the-art on plastics waste issues and treatment options, some relevant points should be considered for the future research focused on plastic degradation.

·The addition of other compounds to the plastic matrix is beneficial for improving the contact between the catalyst and the polymer, but can lead to structure modifications such as the addition of defects which might modify the mechanical properties [65]. This is why the initial characterization of the target polymer should be done in order to determine properly its structure and to be able to recognize changes when the degradation process starts, so the degradation quantification is done accurately.

In order to evaluate the real effect of the catalysts, the natural photo-degradation of the plastic should be evaluated to know the extent of the direct photolysis on the final results [78].

Photo-based processes could be used as a pre-treatment option. For instance, if the photo-catalytic process reduces the melting point of the target plastics, not only its pyrolysis would be easier but also its biodegradability may be higher [5]. For instance, Fa et al. [65] noticed an enhancement on the biodegradation performance of PE after the UV photo-catalysis pre-treatment. Similarly, Nakatani et al. [69] found an easier thermal degradation of PS after a controlled photo-degradation which avoided the cross-linking thanks to the addition of light stabilizers.

In order to monitor properly plastics in the environment and to assess those degradation processes, more effort should be put on the identification and quantification of plastics [2]. Even though there are the hereby reported analytical procedures, more research needs to be done in order to ensure the correct quantification and avoid sample contamination, which is one of the most critical issues for proper plastic analysis [16].

Taking into consideration the difficulty of plastic analysis, the measurements should be done in replicates.

Taking into account Vethaak et al. [2] considerations, the effect of the plastic particles on human health should be better studied. Thus,

Table 4

Typical plastics with usual analysis results for their initial characterization.

Analysis	PE	PP	PS	Refs.
XPS	283–290 eV (C-three peaks) and 528–536 eV (O-two peaks)	283.3, 285.0, 286.8, and 288.2 eV (C-four peaks) and 527–538 eV (O-two peaks)	283–290 eV (C-three peaks) and 528–536 eV (O-two peaks)	[77, 79, 96]
XRD	Strong peak at 21.6° and a weaker one at 23.75°	Characteristic peaks for α form at 14.0°, 17.0°, 18.5°, 21.0°, and 22.0° and β form at 16°	Peaks at 9.51° and 18.88 °	[45, 95, 97]
TGA	Weight loss at 101 °C	Weight loss at 164 °C	Weight loss at 420 °C	[98, 99]
FTIR	Bands at 719, 1472, 2850, 2923 cm^{-1}	Different small bands between 800 and 1200, two big peaks at 1400, and big signal at 2900 cm^{-1}	Bands at 697, 756, 1028, 1450, 1492, 1603, 2856, 2926 and 3028 cm^{-1}	[79, 97]
RAMAN	Bands at 1063, 1127, 1294, 1417, 1439 and 1459 cm^{-1}	Bands at 800, 830, around 1000 (3), 1150, 1220(small) 1320, 1360, and 1450 cm^{-1}	Bands at 620, 1002 and 1032 cm^{-1}	[38, 100, 101]

toxicity tests with complex organisms should be done [93], in order to understand the effect of plastics and by-products on humans.

The study of the effects that plastics can have in the spread of other toxic pollutants in the environment is a crucial point to focus on in future.

As Jiao et al. [3] mentioned, taking into account the high plastic generation and the lack of truly efficient treatment alternatives, it is highly imperative to research on enhancing the selective conversion of plastic waste into carbon fuels.

The presence of different polymers or other additives such as plasticizers causes a modification on the photo-degradation rate (for instance polyvinyl siloxane was more slowly degraded when having o-dioctyl phthalate (Horikoshi et al., 1998)) and thus this should be taken in consideration for the plastic synthesis and treatment processes application.

5. Conclusions

This review highlights the increasing presence of plastics in the environment and the problems this is causing not only from the environmental point of view, but also concerning human health. The traditional treatment options have been reported and their advantages and disadvantages have been discussed. This have led to the conclusion that a new degradation process more environmentally friendly, economically feasible and easier to set-up is required.

Photo-based processes have been discussed in order to focus efforts on the upcoming research. On this context, the quantification techniques have been summarised and main aspects have been highlighted. Special attention should be put on the catalyst addition to plastics in order to reduce the treatment times and the operational costs. Additionally, other factors such as plastic chemical composition, degree of contact between the catalyst and the plastics' surfaces, degradation set-up or catalysts type and concentration have been discussed within the up-to-date research. So far, photo-Fenton processes seem to have been unnoticed as oxidative treatment option, as it has been not sufficiently reported.

Additionally, and taking into account the energy demand, the photo-conversion of plastics into fuels seems to be an efficiently plausible alternative.

Moreover, by the present time, the most viable alternative seems to couple photo-based processes with traditional treatments such as biodegradation or pyrolysis in order to overcome the disadvantages of one and another.

Declaration of Competing Interest

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

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References

[1] W.R.L.N. Bandara, R.M. de Silva, K.M.N. de Silva, D. Dahanayake, S. Gunasekara, K. Thanabalasingam, Is nano ZrO_2 a better photocatalyst than nano TiO_2 for degradation of plastics? RSC Adv. 7 (2017) https://doi.org/10.1039/C7RA08324F.

[2] A.D. Vethaak, H.A. Leslie, Plastic debris is a human health issue, Environ. Sci. Technol. 50 (2016), https://doi.org/10.1021/acs.est.6b02569.

[3] X. Jiao, K. Zheng, Q. Chen, X. Li, Y. Li, W. Shao, et al., Photocatalytic conversion of waste plastics into C2 fuels under simulated natural environment conditions, Angew. Chem. Int. Ed. (2020), https://doi.org/10.1002/anie.201915766.

[4] R. Miandad, M.A. Barakat, A.S. Aburiazaiza, M. Rehan, A.S. Nizami, Catalytic pyrolysis of plastic waste: a review, Process Saf. Environ. Prot. 102 (2016), https://doi.org/10.1016/j.psep.2016.06.022.

[5] Y. Tokiwa, B.P. Calabia, C.U. Ugwu, S. Aiba, Biodegradability of plastics, Int. J. Mol. Sci. 10 (2009), https://doi.org/10.3390/ijms10093722.

[6] W.W.Y. Lau, Y. Shiran, R.M. Bailey, E. Cook, M.R. Stuchtey, J. Koskella, et al., Evaluating scenarios toward zero plastic pollution, Science 369 (2020), https://doi.org/10.1126/science.aba9475.

[7] X. Zhao, B. Boruah, K.F. Chin, M. Đokić, J.M. Modak, H.S. Soo, Upcycling to sustainably reuse plastics, Adv. Mater. 34 (2022), https://doi.org/10.1002/adma.202100843.

[8] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, et al., Pyrolysis technology for plastic waste recycling: a state-of-the-art review, Prog. Energy Combust. Sci. 93 (2022), https://doi.org/10.1016/j.pecs.2022.101021.

[9] P.H. Alle, P. Garcia-Munoz, K. Adouby, N. Keller, D. Robert, Efficient photocatalytic mineralization of polymethylmethacrylate and polystyrene nanoplastics by TiO_2/beta-SiC alveolar foams, Environ. Chem. Lett. (2020), https://doi.org/10.1007/s10311-020-01099-2.

[10] P. Zuccarello, M. Ferrante, A. Cristaldi, C. Copat, A. Grasso, D. Sangregorio, et al., Exposure to microplastics, Water Res 157 (2020), https://doi.org/10.1016/j.watres.2019.03.091.

[11] E. Comanita, R.M. Hlihor, C. Ghinea, M. Gavrilescu, Occurrence of plastic waste in the environment: ecological and health risks, Environ. Eng. Manag. J. 15 (2016), https://doi.org/10.30638/eemj.2016.073.

[12] S. Shawaphun, T. Manangan, Thermo- and photo- degradation of LDPE and PP films using metal oxides as catalysts, functionalized and sensing materials, Adv. Mater. Res. 93 (2010), https://doi.org/10.4028/www.scientific.net/AMR.93-94.505.

[13] M. Tu-Morn, N. Pairoh, W. Sutapun, T. Trongsatitkul, Effects of titanium dioxide nanoparticle on enhancing degradation of polylactic acid/low density polyethylene blend films, Mater. Today Proc. 17 (2019), https://doi.org/10.1016/j.matpr.2019.06.253.

[14] M. Hakkarainen, Albertsson AC. environmental degradation of polyethylene, Long Term Prop. Polyolefins 169 (2004), https://doi.org/10.1007/b13523.

[15] D.l. S, S.J. T, R. C, Solid-phase photodegradation of polystyrene by nano TiO_2 under ultraviolet radiation, Environ. Nanotechnol. Monit. Manag. 12 (2019), https://doi.org/10.1016/j.enmm.2019.100229.

[16] A. Kniggendorf, C. Wetzel, B. Roth, Microplastics detection in streaming tap water with Raman spectroscopy, Sensors 19 (2019), https://doi.org/10.3390/s19081839.

[17] S. Zhang, J. Wang, X. Liu, F. Qu, X. Wang, X. Wang, et al., Microplastics in the environment: a review of analytical methods, distribution, and biological effects, TrAC Trends Anal. Chem. 111 (2019), https://doi.org/10.1016/j.trac.2018.12.002.

[18] Y. Wan, C. Wu, Q. Xue, X. Hui, Effects of plastic contamination on water evaporation and desiccation cracking in soil, Sci. Total Environ. 654 (2019), https://doi.org/10.1016/j.scitotenv.2018.11.123.

[19] Y. Zhang, S. Pu, X. Lv, Y. Gao, L. Ge, Global trends and prospects in microplastics research: a bibliometric analysis, J. Hazard. Mater. 400 (2020), https://doi.org/10.1016/j.jhazmat.2020.123110.

[20] P.S. Puskic, J.L. Lavers, A.L. Bond, A critical review of harm associated with plastic ingestion on vertebrates, Sci. Total Environ. 743 (2020), https://doi.org/10.1016/j.scitotenv.2020.140666.

[21] F. Yu, Y. Li, G. Huang, C. Yang, C. Chen, T. Zhou, et al., Adsorption behavior of the antibiotic levofloxacin on microplastics in the presence of different heavy metals in an aqueous solution, Chemosphere 260 (2020), https://doi.org/10.1016/j.chemosphere.2020.127650.

[22] F.K. Mammo, I.D. Amoah, K.M. Gani, L. Pillay, S.K. Ratha, F. Bux, et al., Microplastics in the environment: interactions with microbes and chemical contaminants, Sci. Total Environ. 743 (2020), https://doi.org/10.1016/j.scitotenv.2020.140518.

[23] R. Zhang, M. Wang, X. Chen, C. Yang, L. Wu, Combined toxicity of microplastics and cadmium on the zebrafish embryos (Danio rerio), Sci. Total Environ. 743 (2020), https://doi.org/10.1016/j.scitotenv.2020.140638.

[24] Y. Zhang, M.B. Wolosker, Y. Zhao, H. Ren, B. Lemos, Exposure to microplastics cause gut damage, locomotor dysfunction, epigenetic silencing, and aggravate cadmium (Cd) toxicity in Drosophila, Sci. Total Environ. 744 (2020), https://doi.org/10.1016/j.scitotenv.2020.140979.

[25] Z. Wang, H. Dong, Y. Wang, R. Ren, X. Qin, S. Wang, Effects of microplastics and their adsorption of cadmium as vectors on the cladoceran Moina monogolica Daday: implications for plastic-ingesting organisms, J. Hazard. Mater. 400 (2020), https://doi.org/10.1016/j.jhazmat.2020.123239.

[26] W.P. de Haan, A. Sanchez-Vidal, M. Canals, Floating microplastics and aggregate formation in the Western Mediterranean Sea, Mar. Pollut. Bull. 140 (2019), https://doi.org/10.1016/j.marpolbul.2019.01.053.

[27] K. Kato, S. Nomura, H. Uematsu, Development of waste plastics recycling process using coke ovens, in: Proceedings of the 61st Ironmaking Conference Proceedings 61, 2002.

[28] J. Aguado, D.P. Serrano, J.M. Escola, Fuels from waste plastics by thermal and catalytic processes: a review, Ind. Eng. Chem. Res. 47 (2008), https://doi.org/10.1021/ie800393w.

[29] J. Raquez, A. Bourgeois, H. Jacobs, P. Degee, M. Alexandre, P. Dubois, Oxidative degradations of oxodegradable LDPE enhanced with thermoplastic pea starch: thermo-mechanical properties, morphology, and UV-ageing studies, J. Appl. Polym. Sci. 122 (2011), https://doi.org/10.1002/app.34190.

[30] S.M. Mintenig, I. Int-Veen, M.G.J. Löder, S. Primpke, G. Gerdts, Identification of microplastic in effluents of waste water treatment plants using focal plane array-based micro-Fourier-transform infrared imaging, Water Res. 108 (2017), https://doi.org/10.1016/j.watres.2016.11.015.

[31] C. Mihut, D.K. Captain, F. Gadala-Maria, M.D. Amiridis, Review: recycling of nylon from carpet waste, Polym. Eng. Sci. 41 (2001), https://doi.org/10.1002/pen.10845.

[32] L.B. Brennan, D.H. Isaac, J.C. Arnold, Recycling of acrylonitrile-butadiene-styrene and high-impact polystyrene from waste computer equipment, J. Appl. Polym. Sci. 86 (2002), https://doi.org/10.1002/app.10833.

[33] M.C. Jeon, H.G. Ahn, J.G. Kim, H.M. Jung, S.H. Jeong, B.J Park, Method Of Recycling Acrylic Resin, Composition For Acrylcartificial Stone, And Article Of Artificial Stone, 2011. US 8,048,934 B2.

[34] D.S. Achilias, Chemical recycling of poly(methyl methacrylate) by pyrolysis. Potential use of the liquid fraction as a raw material for the reproduction of the polymer, Eur. Polym. J. 43 (2007), https://doi.org/10.1016/j.eurpolymj.2007.02.044.

[35] F. Quadrini, D. Bellisario, L. Santo, Recycling of thermoset polyurethane foams, Polym. Eng. Sci. 53 (2013), https://doi.org/10.1002/pen.23393.

[36] M.J. Melo, S. Bracci, M. Camaiti, O. Chiantore, F. Piacenti, Photodegradation of acrylic resins used in the conservation of stone, Polym. Degrad. Stab. 66 (1999), https://doi.org/10.1016/S0141-3910(99)00048-8.

[37] A.K. Bhowmick, J. Heslop, J.R. White, Effect of stabilizers in photodegradation of thermoplastic elastomeric rubber–polyethylene blends—a preliminary study, Polym. Degrad. Stab. 74 (2001), https://doi.org/10.1016/S0141-3910(01)00188-4.

[38] D. Oldak, H. Kaczmarek, Photo- and bio-degradation processes inpolyethylene, cellulose and their blends studiedby ATR-FTIR and Raman spectroscopies, J. Mater. Sci. 40 (2005), https://doi.org/10.1007/s10853-005-2821-y.

[39] A.M. Al-Sabagh, F.Z. Yehia, G. Eshaq, A.M. Rabie, A.E. ElMetwally, Greener routes for recycling of polyethylene terephthalate, Egypt. J. Pet. 25 (2016), https://doi.org/10.1016/j.ejpe.2015.03.001.

[40] M. Pivokonsky, L. Cermakova, K. Novotna, P. Peer, T. Cajthaml, V. Janda, Occurrence of microplastics in raw and treated drinking water, Sci. Total Environ. 643 (2018), https://doi.org/10.1016/j.scitotenv.2018.08.102.

[41] C.R. Hurley, G.J. Leggett, 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 1 (2009), https://doi.org/10.1021/am900250q.

[42] H.K. Webb, J. Arnott, R.J. Crawford, E.P. Ivanova, Plastic degradation and its environmental implications with special reference to poly(ethylene terephthalate), Polymers 5 (2013), https://doi.org/10.3390/polym5010001 (Basel).

[43] L. Yang, K. Li, S. Cui, Y. Kang, L. An, K. Lei, Removal of microplastics in municipal sewage from China's largest water reclamation plant, Water Res. 155 (2019), https://doi.org/10.1016/j.watres.2019.02.046.

[44] D.E. Winkler, Mechanism of polyvinyl chloride degradation and stabilization, J. Polym. Sci. 35 (1959), https://doi.org/10.1002/pol.1959.1203512802.

[45] L.X. Tang, Q.H. Wu, B.J. Qu, The effects of chemical structure and synthesis method on photo degradation of polypropylene, J. Appl. Polym. Sci. 95 (2005), https://doi.org/10.1002/app.21272.

[46] B. Ranby, J. Lucki, New aspects of photodegradation and photo-oxidation of polystyrene, Pure Appl. Chem. 52 (1980), https://doi.org/10.1351/pac198052020295.

[47] M.B. Phillips, T.H. Bonner, Occurrence and amount of microplastic ingested by fishes in watersheds of the Gulf of Mexico, Mar. Pollut. Bull. 100 (2015), https://doi.org/10.1016/j.marpolbul.2015.08.041.

[48] R.V. Subramanian, T.V. Talele, Photodegradation of Nylon-6, Text. Res. J. 42 (1972), https://doi.org/10.1177/004051757204200403.

[49] R. Ramani, C. Ranganathaiah, Degradation of acrylonitrile-butadiene-styrene and polycarbonate by UV irradiation, Polym. Degrad. Stab. 69 (2000), https://doi.org/10.1016/S0141-3910(00)00081-1.

[50] A. Torikai, M. Ohno, K. Fueki, Photodegradation of poly(methyl methacrylate) by monochromatic light - quantum yield, effect of wavelengths, and light-intensity, J. Appl. Polym. Sci. 41 (1990), https://doi.org/10.1002/app.1990.070410513.

[51] J. Choi, V. Fthenakis, Crystalline silicon photovoltaic recycling planning: macro and micro perspectives, J. Clean. Prod. 66 (2014), https://doi.org/10.1016/j.jclepro.2013.11.022.

[52] D. Kovalev, E. Gross, J. Diener, V.Y. Timoshenko, M. Fujii, Photodegradation of porous silicon induced by photogenerated singlet oxygen molecules, Appl. Phys. Lett. 85 (2004), https://doi.org/10.1063/1.1804241.

[53] C.E. Hoyle, K.J. Kim, Effect of crystallinity and flexibility on the photodegradation of polyurethanes, J. Polym. Sci. A Polym. Chem. 25 (1987), https://doi.org/10.1002/pola.1987.080251001.

[54] M. Padervand, E. Lichtfouse, D. Robert, C. Wang, Removal of microplastics from the environment. a review, Environ. Chem. Lett. 18 (2020), https://doi.org/10.1007/s10311-020-00983-1.

[55] R. Verma, S. Singh, M.K. Dalai, M. Saravanan, V.V. Agrawal, A.K. Srivastava, Photocatalytic degradation of polypropylene film using TiO_2-based nanomaterials under solar irradiation, Mater. Des. 133 (2017), https://doi.org/10.1016/j.matdes.2017.07.042.

[56] J.A. Conesa, N. Ortuño, Reuse of water contaminated by microplastics, the effectiveness of filtration processes: a review, Energies 15 (2022), https://doi.org/10.3390/en15072432.

[57] P. Kamalian, S.N. Khorasani, A. Abdolmaleki, M. Karevan, S. Khalili, M. Shirani, et al., Toward the development of polyethylene photocatalytic degradation, J. Polym. Eng. 40 (2020), https://doi.org/10.1515/polyeng-2019-0230.

[58] T. Uekert, M.F. Kuehnel, D.W. Wakerley, E. Reisner, Plastic waste as a feedstock for solar-driven H2 generation, Energy Environ. Sci. 11 (2018), https://doi.org/10.1039/c8ee01408f.

[59] A.K. Panda, R.K. Singh, D.K. Mishra, Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value added products—a world prospective, Renew. Sustain. Energy Rev. 14 (2010), https://doi.org/10.1016/j.rser.2009.07.005.

[60] S.S. Ali, I.A. Qazi, M. Arshad, Z. Khan, T.C. Voice, C.T. Mehmood, Photocatalytic degradation of low density polyethylene (LDPE) films using titania nanotubes, Environ. Nanotechnol. Monit. Manag. 5 (2016), https://doi.org/10.1016/j.enmm.2016.01.001.

[61] S.D.A. Sharuddin, F. Abnisa, W.M.A.W. Daud, M.K Aroua, A review on pyrolysis of plastic wastes, Energy Convers. Manag. 115 (2016), https://doi.org/10.1016/j.enconman.2016.02.037.

[62] Z.N. Mageed, H.H. Mohammed, T.M. Zayer, A.M. Noori, S.A. Farhan, R. M. Dadoosh, Study the photo degradation and biodegradation of p-cresol novolac (polyepoxy) in presence and absence of di benzoylperoxide, Mater. Sci. Eng. 571 (2019), https://doi.org/10.1088/1757-899X/571/1/012088.

[63] A. Sivan, New perspectives in plastic biodegradation, Curr. Opin. Biotechnol. 22 (2011), https://doi.org/10.1016/j.copbio.2011.01.013.

[64] R.T. Thomas, N. Sandhyarani, Enhancement in the photocatalytic degradation of low density polyethylene-TiO_2 nanocomposite films under solar irradiation, RSC Adv. 3 (2013), https://doi.org/10.1039/c3ra42226g.

[65] W. Fa, J. Wang, S. Ge, C. Chao, Performance of photo degradation and thermo degradation of polyethylene with photo catalysts and thermo oxidant additives, Polym. Bull. 77 (2020), https://doi.org/10.1007/s00289-019-02813-z.

[66] B.G. Ranby, J.F. Rabek, Photodegradation, Photo-Oxidation, and Photostabilization of Polymers, Wiley, New York, 1975.

[67] W. Li, W. Zhao, H. Zhu, Z. Li, W. Wang, State of the art in the photochemical degradation of (micro) plastics: from fundamental principles to catalysts and applications, J. Mater. Chem. A 11 (2023), https://doi.org/10.1039/d2ta09523h.

[68] A.R.A. Aziz, P. Asaithambi, W.M.A.B.W. Daud, Combination of electrocoagulation with advanced oxidation processes for the treatment of distillery industrial effluent, Process Saf. Environ. Prot. 99 (2016), https://doi.org/10.1016/j.psep.2015.11.010.

[69] H. Nakatani, T. Kyan, Y. Urakawa, Novel recycling system of polystyrene water debris with polymer photocatalyst and thermal treatment, J. Polym. Environ. (2020), https://doi.org/10.1007/s10924-020-01976-5.

[70] B.E. Llorente-Garcia, J.M. Hernandez-Lopez, A.A. Zaldivar-Cadena, C. Siligardi, E. I. Cedillo-Gonzalez, First insights into photocatalytic degradation of HDPE and LDPE microplastics by a mesoporous N-TiO(2)coating: effect of size and shape of microplastics, Coatings 10 (2020), https://doi.org/10.3390/coatings10070658.

[71] T. Uekert, H. Kasap, E. Reisner, Photoreforming of nonrecyclable plastic waste over a carbon nitride/nickel phosphide catalyst, J. Am. Chem. Soc. 141 (2019).

[72] T. Uekert, M.A. Bajada, T. Schubert, C.M. Pichler, E. Reisner, Scalable photocatalyst panels for photoreforming of plastic, biomass and mixed waste in flow, ChemSusChem 13 (2020), https://doi.org/10.1002/cssc.202002580.

[73] S. Li, S. Xu, L. He, F. Xu, Y. Wang, L. Zhang, Photocatalytic degradation of polyethylene plastic with polypyrrole/$TiO2$ nanocomposite as photocatalyst, Polym. Plast. Technol. Eng. 49 (2010), https://doi.org/10.1080/03602550903532166.

[74] J.F. Rabek, Polymer Photodegradation: Mechanisms and Experimental Methods, Chapman & Hall, Sweden, 1995, 1st ed.

[75] T.S. Tofa, F. Ye, K.L. Kunjali, J. Dutta, Enhanced visible light photodegradation of microplastic fragments with plasmonic platinum/zinc oxide nanorod photocatalysts, Catalysts 9 (2019), https://doi.org/10.3390/catal9100819.

[76] V. Najafi, E. Ahmadi, F. Ziaee, H. Omidian, H. Sedaghat, Polyaniline-modified TiO_2, a highly effective photo-catalyst for solid-phase photocatalytic degradation of PVC, J. Polym. Environ. 27 (2019), https://doi.org/10.1007/s10924-018-01363-1.

[77] J. Shang, M. Chai, Y. Zhu, Solid-phase photocatalytic degradation of polystyrene plastic with TiO_2 as photocatalyst, J. Solid State Chem. 174 (2003), https://doi.org/10.1016/S0022-4596(03)00183-X.

[78] S. Chakrabarti, B.K. Dutta, Dye-Sensitised photocatalytic degradation of PVC-ZnO composite film, Int. J. Environ. Technol. Manag. 9 (2008), https://doi.org/10.1504/IJETM.2008.017858.

[79] X.u. Zhao, Z. Li, Y. Chen, L. Shi, Y. Zhu, Solid-phase photocatalytic degradation of polyethylene plastic under UV and solar light irradiation, J. Mol. Catal. A Chem. 268 (2007), https://doi.org/10.1016/j.molcata.2006.12.012.

[80] M. Camila Ariza-Tarazona, J. Francisco Villarreal-Chiu, J. Manuel Hernandez-Lopez, J. Rivera De la Rosa, V. Barbieri, C. Siligardi, et al., Microplastic pollution reduction by a carbon and nitrogen-doped TiO_2: effect of pH and temperature in the photocatalytic degradation process, J. Hazard. Mater. 395 (2020), https://doi.org/10.1016/j.jhazmat.2020.122632.

[81] W. Fa, L. Guo, J. Wang, R. Guo, Z. Zheng, F. Yang, Solid-phase photocatalytic degradation of polystyrene with TiO_2/Fe(St)3 as catalyst, J. Appl. Polym. Sci. 128 (2013), https://doi.org/10.1002/app.37751.

[82] I. Nabi, A. Bacha, K. Li, H. Cheng, T. Wang, Y. Liu, et al., Complete photocatalytic mineralization of microplastic on TiO_2 nanoparticle film, Iscience 23 (2020), https://doi.org/10.1016/j.isci.2020.101326.

[83] S. Horikoshi, N. Serpone, Y. Hisamatsu, H. Hidaka, Photocatalyzed degradation of polymers in aqueous semiconductor suspensions. 3. Photooxidation of a solid

polymer: tiO2-blended poly(vinyl chloride) film, Environ. Sci. Technol. 32 (1998), https://doi.org/10.1021/es9710464.

[84] Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar, J. He, Visible light driven type II heterostructures and their enhanced photocatalysis properties: a review, Nanoscale 5 (2013), https://doi.org/10.1039/c3nr01577g.

[85] L. Wang, A. Kaeppler, D. Fischer, J. Simmchen, Photocatalytic TiO$_2$ micromotors for removal of microplastics and suspended matter, ACS Appl. Mater. Interfaces 11 (2019), https://doi.org/10.1021/acsami.9b06128.

[86] M. Camila Ariza-Tarazona, J. Francisco Villarreal-Chiu, V. Barbieri, C. Siligardi, E. Iveth Cedillo-Gonzalez, New strategy for microplastic degradation: green photocatalysis using a protein-based porous N-TiO$_2$ semiconductor, Ceram. Int. 45 (2019), https://doi.org/10.1016/j.ceramint.2018. 10.208.

[87] A.V. Karim, S. Krishnan, A. Shriwastav, An overview of heterogeneous photocatalysis for the degradation of organic compounds: a special emphasis on photocorrosion and reusability, J. Indian Chem. Soc. 99 (2022), https://doi.org/10.1016/j.jics.2022.100480.

[88] J. Shang, M. Chai, Y.F. Zhu, Photocatalytic degradation of polystyrene plastic under fluorescent light, Environ. Sci. Technol. 37 (2003), https://doi.org/10.1021/es0209464.

[89] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006), https://doi.org/10.1080/10643380500326564.

[90] H. Feng, J. Zheng, N. Lei, L. Yu, K.H. Kong, H. Yu, et al., Photoassisted fenton degradation of polystyrene, Environ. Sci. Technol. 45 (2011), https://doi.org/10.1021/es102182g.

[91] V. Myllari, T. Ruoko, S. Syrjala, A comparison of rheology and FTIR in the study of polypropylene and polystyrene photodegradation, J. Appl. Polym. Sci. 132 (2015), https://doi.org/10.1002/app.42246.

[92] J. Kang, L. Zhou, X. Duan, H. Sun, Z. Ao, S. Wang, Degradation of cosmetic microplastics via functionalized carbon nanosprings, Matter 1 (2019), https://doi.org/10.1016/j.matt.2019.06.004.

[93] K.E. Johnson, A.L. Pometto, L. Somasundaram, J. Coats, Microtox assay to determine the toxicity of degradation products from degradable plastics, J. Environ. Polym. Degrad. 1 (1993), https://doi.org/10.1007/BF01418204.

[94] J. Almond, P. Sugumaar, M.N. Wenzel, G. Hill, C. Wallis, Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy, E Polym. 20 (2020), https://doi.org/10.1515/epoly-2020-0041.

[95] P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, Choudhary V. Studies on the photo-oxidative degradation of LDPE films in the presence of oxidised polyethylene, Polym. Degrad. Stab. 92 (2007), https://doi.org/10.1016/j.polymdegradstab.2007.01.010.

[96] A. Rjeb, S. Letarte, L. Tajounte, M.C. El Idrissi, A. Adnot, D. Roy, et al., Polypropylene natural aging studied by X-ray photoelectron spectroscopy, J. Electron. Spectros. Relat. Phenom. 107 (2000), https://doi.org/10.1016/S0368-2048(00)00121-3.

[97] W. Donbebe, E.D. Dikio, Comparative study of polystyrene and polymethylmethacrylate waste as adsorbents for sorption of Pb^{2+} from aqueous solution, Asian J. Chem. 26 (2014), https://doi.org/10.14233/ajchem.2014.16809.

[98] R. Miandad, A.S. Nizami, M. Rehan, M.A. Barakat, M.I. Khan, A. Mustafa, et al., Influence of temperature and reaction time on the conversion of polystyrene waste to pyrolysis liquid oil, Waste Manag. 58 (2016), https://doi.org/10.1016/j.wasman.2016.09.023 (Oxford).

[99] M. Majewsky, H. Bitter, E. Eiche, H. Horn, Determination of microplastic polyethylene (PE) and polypropylene (PP) in environmental samples using thermal analysis (TGA-DSC), Sci. Total Environ. 568 (2016), https://doi.org/10.1016/j.scitotenv.2016.06.017.

[100] I. Blakey, G.A. George, Raman spectral mapping of photo-oxidised polypropylene, Polym. Degrad. Stab. 70 (2000), https://doi.org/10.1016/S0141-3910(00)00126-9.

[101] N.D. Israelsen, D. Wooley, C. Hanson, E. Vargis, Rational design of Raman-labeled nanoparticles for a dual-modality, light scattering immuno assay on a polystyrenesubstrate, J. Biol. Eng. 10 (2016), https://doi.org/10.1186/s13036-015-0023-y.