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Review

Photocatalytic Degradation of Microplastics: Parameters Affecting Degradation

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Abstract

Recently, microplastics have emerged as a major environmental pollutant and have been documented globally. Several studies have shown that microplastics can accumulate heavy metals and persistent organic pollutants as they pass through the environment due to their functional groups interacting with and complex these substances. While conventional wastewater treatment methods can reduce a significant amount of microplastics, many still make their way into rivers and oceans worldwide from their effluents. One of the promising approaches to wastewater cleaning is photocatalysis. Although it has demonstrated a great potential for microplastic degradation, most trials are still lab-based and need to be scaled up for actual use. A crucial factor in determining the technology's capital cost for practical implementation is having a solid grasp of the kinetics and rate of degradation. In order to scale up the approach, it is necessary to optimize several operational parameters, such as surface area, temperature, the impact of pH, and light. This research examines various developed photocatalysts for the breakdown of microplastics. An in-depth understanding of the best variables for future designs of photocatalytic degradation of microplastic for industrial applications will result from analyzing these variables.

Keywords
Microplastics; photocatalysis; nanoparticles; parameters; upscaling

1. Introduction

Pollutants of emerging concern (CECs) are a group of contaminants recently discovered in water at significantly high concentrations and pose a potential health risk to humans. These contaminants are not commonly monitored and include pharmaceuticals, pesticides, personal care products, flame retardants, antibiotic-resistant bacteria and genes, as well as the SARS-CoV-19 virus, artificial sweeteners, nanoparticles, and microplastics, among others [1]. Microplastics are formed from the breakdown of plastics in the environment due to exposure to sunlight, air, moisture, and heat [2]. They are known to contain harmful compounds such as bisphenol A [3, 4], which can seriously threaten human health. Moreover, studies have shown that microplastics can cause pre-concentration of contaminants, such as heavy metals and organic pollutants, due to the functional groups on their surface that interact with these substances in the environment [5]. Biota can become exposed to these pollutants when they ingest microplastics accidentally or intentionally, mistaking them for food due to their small size and varying physical appearance [6]. Once ingested, microplastics can release hazardous chemicals into the bodies of organisms, potentially leading to poisoning [7]. This highlights the potential harm that microplastics can cause aquatic and terrestrial organisms, as well as the need for effective measures to address the issue of microplastic pollution.

Microplastic occurrence in wastewater has been documented in numerous studies worldwide [8-10]. Their main sources have been identified as surface runoffs [11, 12,] and personal care products [13, 14] with fragments and fibers forming the greatest percentages of their composition [15]. While wastewater treatment reduces a significant amount of microplastics getting into the water bodies, many particles still get into the rivers and oceans worldwide from their effluents [16, 17]. The existing technologies used in wastewater treatment plants include coagulation, filtration, and advanced oxidation processes [18, 19]. And although these removal methods are not targeted at microplastics, a large percentage of these microplastics are removed mostly the fragments [20]. However, wastewater treatment plants handle large volumes of water, and many microplastic fibers find their way into the effluents and the receiving water bodies, escalating microplastic pollution [21].

Several methods have been developed for microplastic removal which includes adsorption [22], magnetic extraction [23], biofiltration [24], membrane filtration [25], chemical coagulation [26], and photocatalysis [27-29], among others. Of these technologies, photocatalysis is a promising technology in removing microplastics especially in wastewater treatment systems [30]. This is because it is a sustainable method for removing pollutants from the environment without introducing secondary pollution [31]. Photocatalysts work by harnessing light energy to activate a chemical reaction. When light energy hits the surface of a photocatalyst, it creates an electron-hole pair that generates reactive oxidizing species. These species can then break down organic contaminants into harmless byproducts, such as carbon dioxide and water [32].

Several reviews have highlighted challenges associated with the photocatalytic degradation of microplastics. Some have focused on the degradation mechanisms of the products in an attempt to

describe various studies to inform possible channels of the degradation process [29, 33-35]. However, it is notable that most of these designs remain at the laboratory level due to several challenging issues [36, 37]. One is the lengthy process times which limit the feasibility of the process for full-scale applications [38, 39]. Another challenge is using single photocatalytic systems, resulting in low photocatalytic degradation performance [29, 40]. Additionally, there is a lack of analysis on treatment costs, including the reusability and stability of the catalyst [29]. Further, the generation of many potentially toxic degradation intermediates lacks toxicity evaluation for them. And finally the difficulty of recycling the catalyst which has been pointed out as a source of secondary pollution [41].

So far, there is little information on the experimental conditions and how they affect the degradation of microplastics using photocatalysts. Creating effective, scalable, and eco-friendly remedies for microplastic pollution is anticipated to be facilitated by ongoing research and advancements in materials science, developing and applying photocatalytic processes, process optimization, and knowledge of the underlying mechanisms. It is also important to consider plastic waste management to reduce microplastic pollution. Policies geared towards reduced production and promoting recycling need to be formulated since most plastics are single-use products that end up in the environment once used. For upscaling and industrial applications, a good understanding of the degradation rate and kinetics is an important criterion to inform the capital cost of the technology [42]. Parameters influencing microplastic degradation help guide these industrial scale-level kinetics [39]. This paper looks into some developed photocatalysts for microplastic degradation with emphasis on the operational parameters, including surface area, temperature, and the effect of pH and light on their reactions. An understanding of how these factors and how they influence the photocatalytic degradation of microplastics will be useful information for the optimization of the method. This will deepen the understanding of the photocatalytic degradation process and inform future designs for upscaling and practical applications.

2. Degradation of Plastics

The term "degradation" refers to the process by which the properties of a polymer are reduced [43]. Plastics can undergo degradation through two processes: biotic degradation by living organisms in the environment, or abiotic degradation by physical environmental conditions, such as light, wind, and temperature [44]. In the case of abiotic degradation, the process begins on the surface of the plastic material that is exposed to chemical reactions. Microplastics, due to their high surface area-to-volume ratio, degrade at a faster rate compared to larger plastic materials [45]. The first visible signs of plastic degradation are surface bending and changes in color. As the degradation continues, surface cracking occurs, exposing the material to further degradation, ultimately resulting in disintegration and embrittlement [46]. Plastics that are exposed to sunlight with wavelengths of 300 nm or more and oxidizing conditions, tend to degrade more quickly than those not exposed to these conditions. Polymeric materials such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) are common materials under study due to their widespread use, particularly in the packaging industry, which contributes to microplastic pollution in the environment. Other plastic-based materials that are also studied include polyurethanes (PU), polylactic acid (PLA), nylon, polycarbonates, and several biodegradable plastics [47]. These materials

possess unique properties that make them useful in various applications and contribute to their persistence in the environment.

2.1 Mechanism of Polymer Degradation

The degradation process of polymeric plastic has got three main steps. It starts with an initiation step, followed by propagation, and finally, the termination step depending on the nature of the polymer surface [48, 49]. At the initiation step, the main polymer chain is broken down by light to form free radicals. Photoinitiation occurs when chromophoric groups on the polymer chain absorb light energy and the electrons in the polymer are excited to promote a chain-breaking reaction that forms oligomers and initial radicles [50]. Polyethylene and polypropylene do not have any chromophoric groups and thus are considered immune to photoinitiation. However, the presence of impurities or even structural abnormalities in the macromolecular structure allows for photo-initiated degradation to a small extent [51]. Sunlight delivers the activation energy needed for homolytic cleavage, and the presence of a catalyst in the reaction lowers the activation energy and promotes the formation of various byproducts [52]. The propagation step follows where the radicals react with oxygen to form peroxy radicals, leading to complex radical reactions into autoxidation. Termination of the reaction occurs when radicles react with each other leading to the coupling termination products. The photo-oxidative degradation of several plastic polymers is shown in Figure 1. Several factors affect the photo-oxidation reactions of polymers which include the intensity and wavelength of the UV light, the presence of other chemicals or contaminants within the structure of the polymer, temperature, and humidity which accelerate the photo-oxidation reactions by increasing the mobility of the polymer molecules and allowing for more efficient oxygen diffusion. Polymer structure can also influence its susceptibility to photo-oxidation.

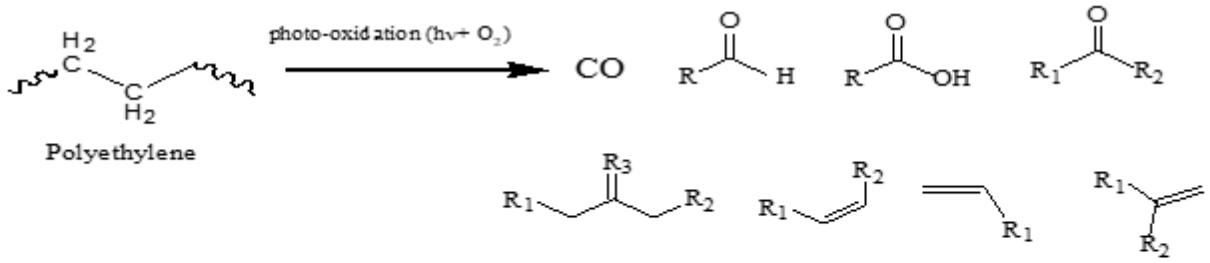

Figure 1: a) Degradation mechanism of polyethylene.

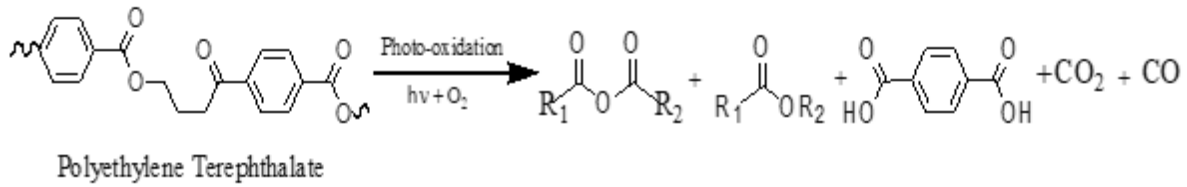

Figure 1 b) Degradation mechanism of polyethylene terephthalate.

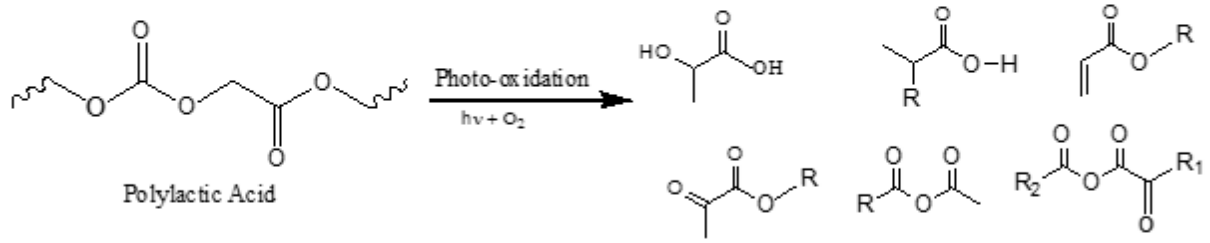

Figure 1 c) Degradation mechanism of polylactic acid.

Figure 1 a) Degradation mechanism of polyethylene. b) Degradation mechanism of polyethylene terephthalate. c) Degradation mechanism of polylactic acid.

3. Photocatalysis

Photocatalysis is a term that refers to the catalytic acceleration of a photoreaction [53]. A catalyst absorbs light energy and then drives a thermal dynamic reaction. A good photocatalyst should poseess light absorption, charge separation, and charge transfer [54]. A broad definition of a photocatalyst by IUPAC is a catalyst that can produce chemical transformations of reactants upon absorption of light [55]. Several studies have proposed using nanomaterials as catalysts sensitive to light as a promising technology for the degradation of plastics [33, 56]. Nano photocatalysts have high photocatalytic activity and therefore high efficiencies in the degradation rate of plastics. The advantage of using photocatalysts in their nano sizes is that the surface area to volume ratio increases. At the same time, new physical and chemical properties emerge due to the size of the particles [57]. Nano photocatalysts utilize light energy to increase the oxidation rate of the plastics to form lower molecular weight intermediates such as carboxylic acids, ketones, and aldehydes that are biodegradable or less toxic to the environment [56].

When a photocatalyst absorbs light energy that matches or exceeds the band gap energy, an electron moves from the valency band to the conduction band of the photocatalyst, resulting in a valence band hole [58]. Both the hole and the electrons migrate to the surface of the semiconductor

and can recombine and release heat energy. The electrons can get trapped by the unstable nature of the surface state and can oxidize or reduce molecules adsorbed on the surface of the photocatalyst. In general, water molecules are oxidized to form hydroxyl radicals while electrons reduce oxygen molecules forming superoxides and hydroxyl radicals as shown in the equations [59].

$$h^+ + H_2O \rightarrow H^+ + OH\cdot$$

$$h^+ 2H_2O \rightarrow 2H^+ + H_2O_2$$

$$H_2O_2 \rightarrow 2OH\cdot$$

$$e^- + O_2 \rightarrow O_2^-$$

$$2O_2^- + 2H_2O \rightarrow 2H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2OH\cdot$$

The generation of holes in a photocatalyst depends on its band-gap energy, E_g. A band-gap energy smaller than 3 eV extends the light absorption into the visible region for effective solar energy utilization. When a photocatalyst has a narrow band gap energy, it easily forms holes as it changes its oxidation states without it getting decomposed when it absorbs light. The generated holes oxidize adsorbed molecules like water to produce reactive oxygen species (ROS) which include the hydroxide radical ($OH^{\cdot}$), superoxide (O_2^{-}), and hydrogen peroxide (H_2O_2). The hydroxyl radical is the most effective oxidant among the ROS [60]. At very low pH, hydroxyl radicals convert to their conjugate base which is the oxide radical and is less reactive [61]. The superoxide anion is formed when an electron reduces an oxygen molecule. At low pH, it is protonated and known as the per hydroxyl radical HO_2. The protonated form of O_2^{-} is a more reactive species although present at low concentrations. The reactive oxidizing species then act on the surface of polymer plastics to oxidize them and cause polymer degradation. The mechanism of how photocatalyst work can be summarized in Figure 2.

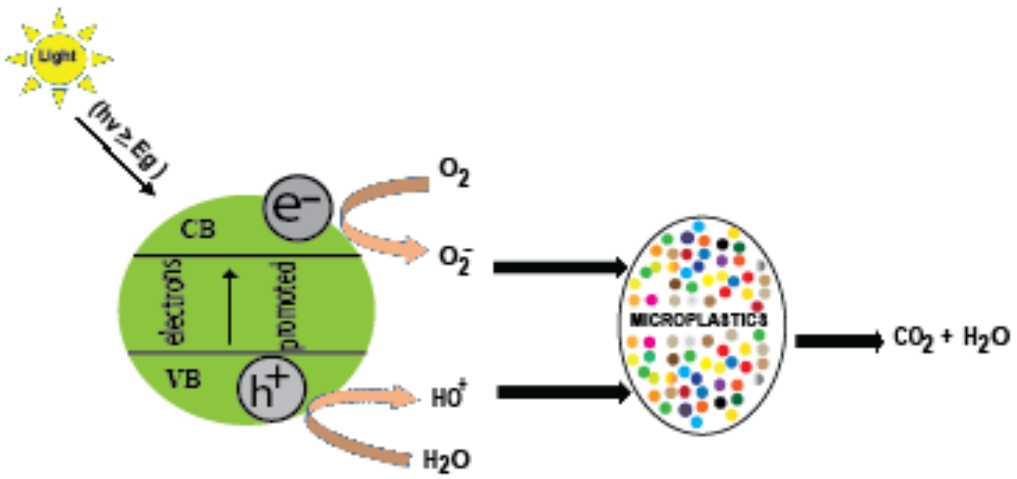

Figure 2 Mechanism of semiconductor catalysis.

During that process, the atoms are brought to a higher energy level, providing energy to the reacting substances to cause chemical reactions. Since photocatalytic reactions are light-dependent, their degradation efficiency increases when more light falls on their surface [62]. Therefore, the energy input of a photocatalyst is energy input depends on light intensity [63].

4. Synthesis and Characterization of the Photocatalysts

The synthesis and characterization of photocatalysts have been the subject of extensive research for various applications. Researchers have utilized various methods to synthesize photocatalysts, including hydrothermal synthesis, green synthesis, photo-assisted deposition, and anodization. These methods have enabled the creation of various novel materials with unique properties that can enhance their photocatalytic activity. Characterizing synthesized photocatalysts is essential to optimize their performance and understand their physicochemical properties. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and UV-Vis spectroscopy have been used to characterize synthesized photocatalysts. Characterization of photocatalysts can provide information on their morphology, crystal structure, and optical properties, which can be used to optimize their performance in various applications, including environmental remediation and renewable energy production. Some common methods of synthesizing photocatalysts for microplastic degradation from 22 articles are shown in Figure 3.

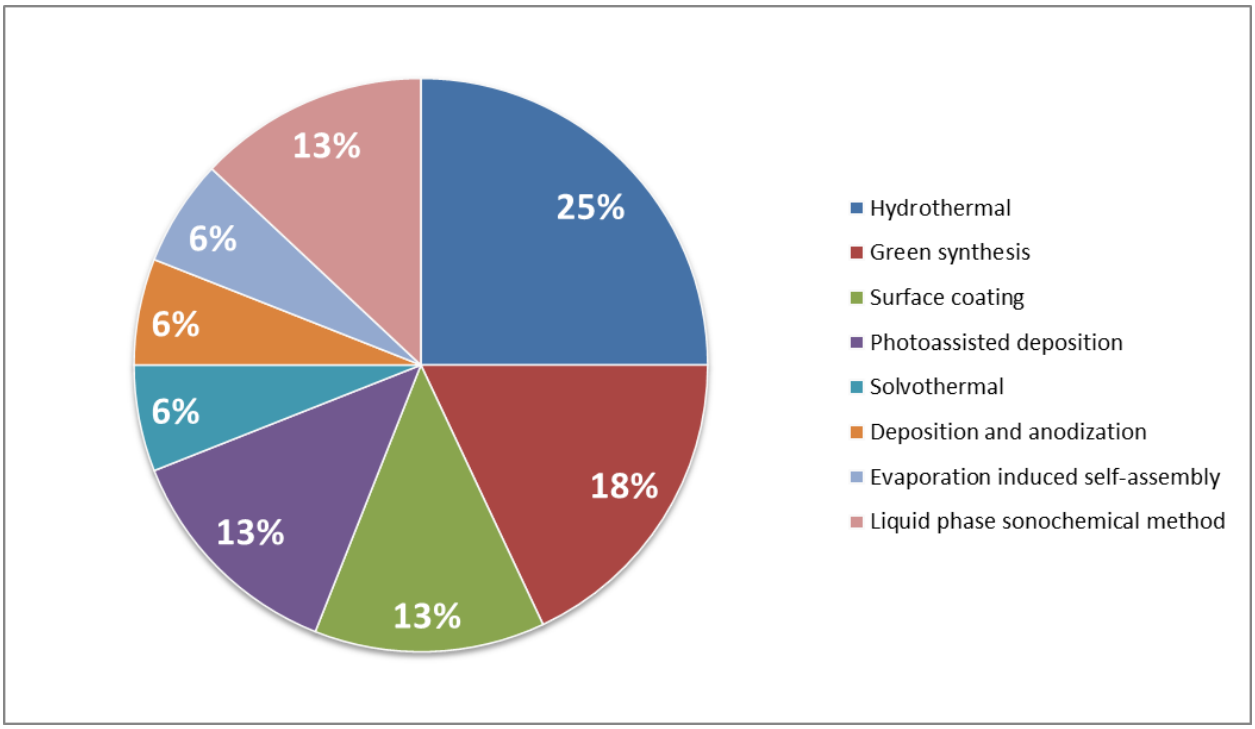

Figure 3 Common methods of synthesis photocatalysts for microplastic degradation from 22 articles.

Numerous studies [45, 64-66] have frequently employed the hydrothermal technique to create photocatalysts for the breakdown of microplastics at the nanoscale. This is due to the method's significant impact on the size, structure, and consistency of the produced crystals by introducing metal into the crystal lattice of a semiconductor. The green synthesis method, reported by [67-69],

is a simple and cost-effective way of forming stable nano photocatalysts. Additionally, the surface coating method [27, 70] and deposition [71] allow for control over the packing density of particles and thickness. The Photo-assisted deposition has been used to achieve a high percentage of Ag on Ag/TiO_2 and is considered a good method for synthesizing silver-doped photocatalysts [72, 73]. Through the anodization of titania nanotubes at high voltages (40V), researchers have achieved uniformity of the tubes. The result is highly ordered nanotube arrays on a titania plate [74].

Techniques used to confirm the nano-photocatalysts' physicochemical properties include Brunauer, Emmett, and Teller (BET), for surface area, X-ray diffraction (XRD) to determine the crystalline structure, particle size determination and aggregation using scanning electron microscopy (SEM), and transmission electron microscopy (TEM), potential measurement to tell the surface charge, as well as the measurement of transparency and contact angle (CA). SEM-EDX is commonly used to image the topographical features of the sample with higher resolving power, identify the elemental composition, and determine the percentage of elemental composition. This information is useful as it informs about the variations in chemical characterization, texture, and orientation of materials under probe. XRD determines the crystal phases to understand the nature of the materials. The nature of Bragg's peaks gives details of the morphological nature of the compounds with broad humped peaks depicting the amorphous form with short-range ordering, while sharp peaks mean that the material is crystalline. A combination of broad and sharp peaks shows that the material has semicrystalline nature [75]. Other characterization forms included XPS for surface chemistry of material where the peaks appear corresponding to the binding energy of an element, enabling their elemental identification. The intensity of the peaks quantifies the identified element. BET analysis is done to determine the surface area of the photocatalyst where the plots of the amount of gas adsorbed are drawn as a function of the relative pressure to give the BET isotherms.

Understanding the morphology, crystal structure, and optical properties of photocatalysts is crucial for optimizing photocatalysis for the degradation of microplastics. For example, photocatalysts' surface area and pore size can impact their efficiency in adsorbing and degrading microplastics. In contrast, the crystal structure of the photocatalyst can influence its catalytic activity. Optical properties, such as bandgap and absorbance spectra, determine the wavelength of light that the photocatalyst can effectively absorb, which is crucial for photoexcitation and the generation of reactive oxygen species necessary for microplastic degradation. Moreover, understanding the optical properties of photocatalysts enables the selection of an appropriate light source for the photocatalytic system. Additionally, the crystal structure of the photocatalyst can affect its stability and reusability, which are important factors for practical applications. The morphology of photocatalysts, such as their shape and size, also plays a role in the efficiency of photocatalytic degradation of microplastics. An understanding of the morphology, crystal structure, and optical properties of photocatalysts can help optimize their efficiency, selectivity, stability, and reusability for the degradation of microplastics.

5. Factors Affecting Photocatalysis

The photocatalytic degradation of microplastics is influenced by various factors that can impact the efficiency and rate of the degradation process. The physicochemical properties of the photocatalyst, as well as external factors such as temperature, pH, and light intensity, can all play a role in

determining the effectiveness of the process. Specifically, factors such as surface area, crystal structure, and the presence of dopants can affect the performance of photocatalysts. Additionally, the reaction environment's temperature and pH can influence the reaction rate. Finally, the intensity and wavelength of light directly affect photoexcitation and the generation of reactive oxidizing species, which are crucial for the degradation of microplastics. A deeper understanding of these factors is crucial for optimizing photocatalysis for practical applications.

5.1 Photocatalyst Surface Area

A photocatalyst's surface area greatly affects the pollutants' adsorption during the degradation process. This is because its activity depends on the active sites (holes and electrons) of particles generated during excitation. Reduced particle sizes translate to reduced distance traveled by electrons and holes during excitation [76]. It has been established that surface morphology is important when utilizing titania as a photocatalyst because all chemical reactions occur at the surface [77]. By employing very tiny particles that are either suspended in solvents or formed into porous films, the surface area is greatly increased for higher oxidation efficiency. Nanostructured materials with crystallite/grain sizes below 20 nm are of major scientific interest because they have novel physical characteristics and high surface area [78]. Some accomplishments involving synthesized photocatalysts point to some significant impact of surface area on microplastic breakdown. On HDPE breakdown using protein-based N-TiO_2 with a surface area of 74.7 cm^2/g saw a total mass loss of 4.6 % [79]. Titania nanotubes were prepared and used to degrade LDPE, and the results showed that the carbonyl index of LDPE increased from 0.33 to a maximum of 2.0 under UV light [80]. However, negligible weight losses were observed, concluding that surface area had little impact on decomposition. In a different study, using C,N-TiO_2 photocatalyst with a surface area of 219.42 ± 1.82 m^2 /g, it was observed that only at a very low temperature of 0°C there brittleness on the surface of HDPE [80]. In this case surface area had little impact in comparison to the temperature. Nanotubes made by anodization of titanium with surface areas of 50 cm^2 were compared with a mixture of titanium oxide structure whose surface area was 200 cm^2, in the photoelimination of polystyrene nano plastics. The results indicated that the higher surface area in the mixed structure had a higher elimination of 23.5% compared to 19.7% with the nanotube [81]. LDPE was broken down using zinc oxide nanorods prepared for their elimination. The nanorods were 34 to 65 nm wide and ranged from 250 to 1750 nm. On the LDPE surface, there were wrinkles, cracks, and cavities in addition to enhanced brittleness [82]. These studies indicated that the catalyst surface area was crucial for accelerating LDPE degradation. In general surface area of a photocatalyst in the degradation of microplastics depends on the nature of the catalyst and the type of polymer. Because microplastics in the environment exist as a mixture of polymers, a single system catalyst would not be appropriate.

5.2 Temperature

Most photocatalysts are semiconductors. Their activity depends on their charge transfer mechanism as electrons move from the conduction band to the valency band. An increase in temperature improves the generation of electron-hole pairs. The more the electron-hole pair, the higher the generation of reactive species (hydroxide radicles and oxygen species), and this enhances the photocatalytic activity [83]. Generally, for reaction temperatures above 80°C, there is a

recombination of charge carriers, which inhibits a semiconductor's activity on an adsorbed substance. But when temperature ranges between 20 to 80°C photocatalytic activity is boosted due to the available kinetic energy for the reactive species [84]. Below 0°C, the apparent activation energy increases, inhibiting the semiconductor's photoactivity [84]. Significant degradation of microplastic has been observed when the temperature is below 80°C. Since light initiates chain reactions, polyethylene in the presence of sunlight is known to undergo photo-oxidation at a temperature below 100°C [85]. Polylactic acid and polyethylene terephthalate undergo photo-oxidation above 30°C to form carboxylic acids, diketones, and anhydrides [86]. Some work carried out in the laboratory has confirmed the degradation of microplastics within the theoretical temperature range. Degradation of polyamide under UVC using TiO_2 and at a temperature of 25-38 ^{o} C recorded a 97% mass loss within 48 h [87]. Photodegradation of polypropylene plastic in aqueous samples was carried out in the air and under ultraviolet light using ZnO for 6 hours at a temperature of between 35°C - 50°C and attained the highest degradation efficiency of 7.89% [88]. Elsewhere, [89] coated TiO_2 nanoparticles with polyethylene and then monitored their aging process under visible light at 60°C. At this temperature, surface features, physical properties, and chemical compositions indicated that the film was aging with time [90].

5.3 Effect of pH

The formation of reactive oxidizing species by photocatalyst depends on the nature of the catalyst and the pH [91]. On the catalyst surface, the solution pH influences the electrical double-layer charge at the solid electrolyte interface, affecting the formation of the electron–hole pairs on the surface of the photocatalyst [92]. Changes in solution pH also alter the surface charge of photocatalyst particles and thus modifies the potentials of catalytic processes. The reaction rate changes due to the changing adsorption of organic contaminants on the surface. For instance, the surface of Titania can undergo the following reactions to become protonated or deprotonated depending on whether the environment is acidic or alkaline [93].

$$TiOH + H^+ \rightarrow TiOH_2^+$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O$$

Titania's surface will therefore continue to be positively charged in an acidic medium and negatively charged in an alkaline medium. Although extra H^+ can slow a reaction, titanium dioxide has better oxidizing activity at lower pH levels [93].

The plastic's nature also determines its stability at various pH values. High-density polyethylene is linear and crystalline and shows degradation at low pH as observed [67]. Polymethylmethacrylate and polystyrene have also shown good degradation at a pH of 6.3 and 7 [70]. This could be influenced by the interaction of the catalyst and the polymer about the catalyst's point of zero charges [94]. Both pH and temperature were monitored on high-density polyethylene and the observation indicated that the breakdown of the HDPE microplastics took place at 0°C, and pH 3, suggesting that the degradation of HDPE microplastics is dependent on the effect of pH and temperature [67, 80]. Figure 4 shows the degradation of HDPE and LDPE at pH 4 [80]. Both temperature and pH are important parameters in photocatalysis. However, few studies have reported on these parameters concerning microplastic photocatalytic degradation.

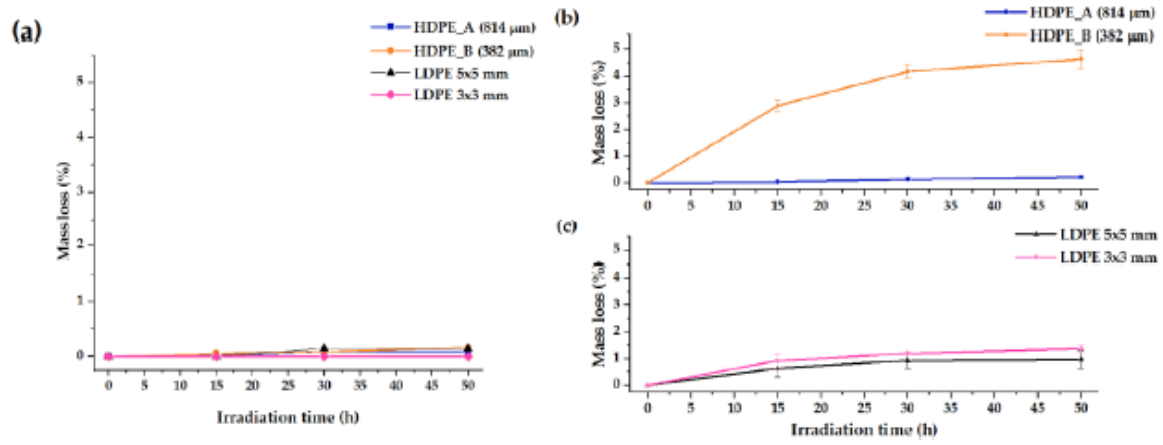

Figure 4 a) Mass loss after photolysis at pH 3. Mass loss after photocatalysis of b) high-density polyethylene (HDPE) and (c) low-density polyethylene (LDPE) microplastics at pH 3 using N–TiO_2 coating, under visible irradiation for 50 h [80].

5.4 Light

Two main sources of light are used in the study of photocatalytic degradation of microplastics. UV light and visible light. Their wavelengths and intensity affect the degradation of organic pollutants in any photocatalytic reactor [95]. UV light is stronger than visible light because its waves are shorter than those of visible light. Therefore it has higher efficiency in the degradation of microplastic [96]. Visible light has been studied to mimic natural sunlight. This is because sunlight is abundant and non-hazardous, it is also a cost-effective source of light [97]. Table 1 and Table 2 summarizes the degradation efficiencies of some photocatalyst using UV and visible light. Light intensity refers to the number of photons per unit area. It corresponds to the number of photons available for activating the catalyst surface. The lower the intensity, the lower the activation energy; hence, low degradation efficiency is observed. With an increase in intensity, more active sites are activated increasing the interactions between the catalyst and the adsorbed substrate on its surface, hence higher degradation rates are attained. However, the high intensity does not lead to higher degradation because the catalysts' activation sites remain the same, making the degradation process independent of light intensity [98]. In some of the studies that have mentioned the light intensity, it ranges between 1.76 W/m^2 and 1200 W/m^2 [64, 69, 88, 90, 99], which observed significant weight loss as shown in Figure 5, except [90] with an intensity of 1200 W/m^2 that only registered surface cracking and brittleness. However, most studies only record the light source which is an area that needs to be optimized for microplastic degradation.

Table 1 Photodegradation of microplastics using UV light.

SN	Reference	Microplastic	Concentration	Photocatalyst	Amount of photocatalyst	Duration	pH	Temperature (°C)	Intensity of light	% Weight loss
1	[88]	PP	25 mm^2& 100 mm^2	ZnO	1 g	6 hr	NA	35-50	UVC	7.89
2	[70]	PMMA & PS	300 mg/L	TiO_2-P25/β-SiC	10 g	7 h	6.3	NA	UV-A 112 W/m^2	50
3	[74]	PE	25 mg/250 mL	Metal-modified TiO_2 nanotubes	17 cm × 5 cm × 0.3 mm	90 min	NA	NA	UVC	17.33
4	[72]	PE	50 mg/100 mL	Ag/TiO_2/RGO	50 mg	4 h	NA	NA	UV	79
5	[73]	PE	10 mg/100 mL	Ag/TiO_2	50 mg	2 h	NA	NA	UV	100
6	[71]	PS PE	20 µL/20 ml 0.005 g/5 mL	TiO_2	20 µL	12 h	NA	RT	UV	98.4
7	[87]	PA66	1.3 mg/50 mL	TiO_2	100 mg	48 h	NA	25-38	UVC	97

PP; Polypropylene, PS; Polystyrene, PE; Polyethylene, PA; Polyamide, PMMA; polymethyl methacrylate.

Table 2 Photodegradation of microplastics using visible light.

SN	Reference	Microplastic	Concentration	Photocatalyst	Photocatalyst dosage	Duration	pH	Temperature (°C)	The intensity of visible light	% Weight loss
1	[64]	PS	0.05 g/L. 9	BiOI-Fe_3O_4	5 mg	120 h	pH 7	NA	3.6 W/cm^2	64
2	[65]	PE	cm^2/30 ml DMSO	$NiAl_2O_4$	30 mg	5 h			350 W	12.5
3	[90]	PP	NA	TiO_2	0.1 mg	4 h	NA	60	1200 W/m^2	NA
4	[100]	HDPE (HDPE, PP PA66, POM)	1 g/L 10 g/L	BiOCl	1 g	5 h	NA	NA	250 W	5.38
5	[66]	PLA, PCL, PET, & PP	0.64 cm^2	$BiVO_4$ microrobots	NA	7 days	NA	NA	NA	3
6	[45]	LDPE	1 cm^2	ZnO-Pt nanorods	NA	175 h	NA		Sunlight	78
7	[80]	HDPE LDPE	9 mm^2 25 mm^2	N–TiO_2	200 mg	50 h	pH 3	RT	50 W	4.65
8	[68]	HDPE	200 mg/30 mL cyclohexane	N-TiO_2	10 mg	20 h	NA	RT	27 W	1.85

9	[67]	HDPE	200 mg/50 mL	N-TiO_2	200 mg	50 h	pH 3	0	50 W	71.77
10	[69]	LDPE	200 mg	Fe-ZnO	10 mg	120 h	NA	NA	271.6 W/m^2	41.3
11	[45]	PE	1 cm^2	ZnO nanorods	NA	175 h	NA	NA	50 W	NA
12	[99]	HDPE	0.4 wt./vol %	C, N-TiO_2	200 mg	50 h	pH 3	0	(57.2 W/m^2)	71.77
13	[101]	PET	50 mL	MXene/ZnxCd 1-xS	0.10 mg	5 h	Alkaline environment	NA	300 W	NA
14	[102]	PE PVC	5% (w/v)	ZnO CeO Cu_xS TiO_2	1% (w/v)	312 h	NA	NA	11 W UV lamps 8 W fluorescent lights	85
15	[103]	PP	0.5 g	TiO2-rGO	0.2 wt%	130 h	NA	NA	Direct sunlight	NA

PP; Polypropylene, HDPE; High-density polyethylene, LDPE; Low-density polyethylene, PE; polyethylene, PLA; Polylactic acid, PCL; Polycaprolactone, PET; Polyethylene terephthalate PVC; Polyvinyl chloride, POM; Polyoxymethylene.

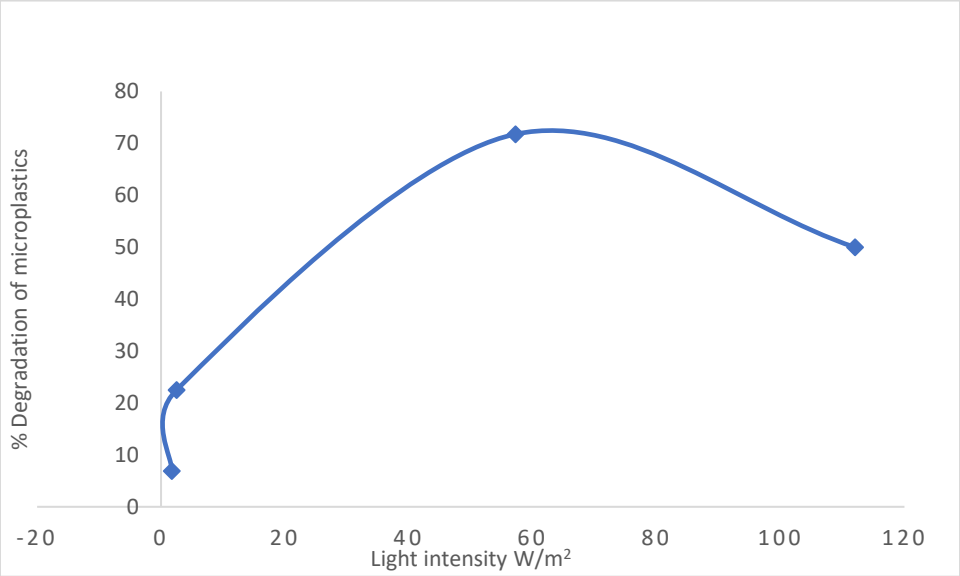

Figure 5 Degradation percentages of microplastic at different light intensities from some reviewed articles.

The ability of a photocatalyst to absorb light energy and generate electron-hole pair lies within its band gap energy which is the energy difference between the valence band and the conduction band. A material with a narrow band gap energy between 1.5-3.0 eV can easily absorb high light, especially within the solar spectrum [104]. Light intensity absorbed from 20 mW/cm^2, would result in an increased degradation rate of microplastics as observed by [69, 70, 90, 99]. A semiconductor's band gap energy is an important property for identifying a good photocatalyst for microplastic degradation [104].

Table 3 summarizes the band gap reported by some photocatalysts designed for microplastic degradation. Out of the 22 total reviewed articles, only seven reported on the band gap of the photocatalyst in use. Three articles designed photocatalysts within the UV region > 3.0 eV and four within the visible light region. Although the photocatalytic activity is not only based on the bandgap energy, a semiconductor's ability to harvest light depends on the bandgap range [105]. Materials with wider band gaps (above 3.2 eV) do not absorb light in the visible part of the spectrum. Visible light covers the range of approximately 360-800 nm with a band gap of 1.8-3.1 eV [105]. It is therefore important to tune the bandgap energy within the range where it can absorb light efficiently for either UV or visible light when designing semiconductors for microplastic degradation.

Table 3 Band gap reported from some articles.

SN	Photocatalyst	Method of synthesis	Bandgap	Reference
1	BiOI BiOI-Fe_3O_4 Fe_3O_4	Hydrothermal	1.85 eV 1.9 eV 3.2 eV	[64]
2	$NiAl_2O_4$	Hydrothermal co-precipitation	2.57 eV 2.757 eV	[65]
3	BiOCl	NA	3.39 eV	[100]

	BiOCl-1		3.29 eV	
	TNT		3.15 eV	
4	Ag-TNT	Anodization	3.0 eV	[74]
	Fe-TNT		3.06 eV	
5	C, N-TiO_2	Green synthesis	2.9 eV	[68]
6	TiO_2	Deposition	3.18, 3.32, and	[71]
	TXT, ET, & WT		3.43 eV	
	Ceria 350		1.8 eV	
	Ceria 650		1.6 eV	
	Ceria 850	Liquid phase sonochemical method	1.9 eV	
7	ZnO 100		3.4 eV	[102]
	ZnO 150		1.5 eV	
	ZnO 250		1.6 eV	
	Cu_xS		2.8 eV	
	ZnO		4.6 eV	

5.4.1 Method of Synthesis and Bandgap Energy

Two factors influence the band gap energy. The first is the synthesis method, and the second is doping. Doping narrows the band gap and extends the semiconductor's light response region, improving the light response of the material [106]. Hydrothermal method is a preferred method of synthesizing photocatalysts within the nano-range narrow bandgap. When the hydrothermal method was used to synthesize BiOI-Fe_3O_4 micro-swimmers, they could harvest visible light intensity of 3.6 W/cm^2 and were used within the visible region to reduce microplastic pollution in water [64]. A comparison of the hydrothermal method to the co-precipitation method of synthesizing $NiAl_2O_4$ spinels was carried out and it was observed that the hydrothermal method produced spinels with a narrower band gap than the co-precipitation method [65]. However, other studies have reported using the liquid phase sonochemical method to synthesize ceria and zinc oxide photocatalysts at different annealing temperatures and obtained photocatalysts with their bandgaps greatly narrowed [102].

5.4.2 Photocatalytic Degradation Using UV Light

Beyond violet in the light spectrum comes ultraviolet (UV) light. This is because the wavelength of this light is slightly beyond violet in the electromagnetic spectrum. It has short wavelengths that are invisible to the naked eye, but its effects are detected in various substances. UV light is high in energy and can alter chemical bonds resulting in chemical reactions. Different photocatalysts developed have been tested on the degradation of microplastics while utilizing UV light. Titania-based photocatalysts have been extensively carried out on various catalysts. A polyethylene degradation test was carried out using titanium oxide nanotubes that were anodized at 30V. The best degradation result, of a 17.33% reduction in weight was realized [74]. The degradation of polystyrene (PS) and polymethylmethacrylate (PMMA) nanoparticles using UV-A radiated on a composite TiO_2–P25/βSiC foams were done and it was observed that there was a higher degradation rate of approximately 50% in the carbon of nanobeads containing polymethylmethacrylate. There

is higher degradation efficiency in the composite than in the unmodified showing the increased effect of modification in the working of a photocatalyst on its ability to harness light energy [70].

An investigation of the performance of composites in degrading microplastic (polyethylene) under UV radiation was carried out for 4 hours using Ag/TiO_2/RGO catalyst which showed a significantly high degradation percentage of 76% compared to pure TiO_2 and Ag/TiO_2 with degradation percentages of 56% and 68% respectively [72]. It is observed that the degradation improved with the addition of more than one modifying agent which improves the surface area and narrows the energy bandgap, improving the ability of titania to absorb more light energy.

In a different study, the size of the microplastic particle was established to determine the interaction of the catalyst reactive species with the polymer's molecular structure. The experiment was carried out on polyethylene microplastics using Ag/TiO_2 photocatalyst under UV light for 2 hours and the optimal mass change was realized when the polyethylene particle's size was 125-150 micrometers. A 100% degradation of the polyethylene particles was achieved and hence the contact between the radical species and the microplastic was optimum at that size while using UV light [73].

It is observed that the degradation of the microplastics under UV is also dependent on the catalyst and the nature of the polymer structure. UV light is known to cause the degradation of polymers, resulting in loss of strength, discoloration, and cracking. The increased degradation effects are attributed to the coupling of the photocatalytic material [107]. Photocatalytic degradation of polystyrene (PS) microspheres and polyethylene over TiO_2 nanoparticle films under UV light irradiation was carried out and the result showed that TiO_2 nanoparticle film made with Triton X-100 had 98.40% mineralization efficiency of 400-nm PS in 12 h, and polyethylene showed a high photodegradation rate after 36 h [71].

Polyethylene shows a high degradation efficiency especially when the titania-based catalyst is used because of the ease of radical formation within the structure given the right conditions. LDPE is prepared by high-pressure ethylene polymerization, resulting in branched chains within its structure [108]. This makes LDPE chemically inert at room temperature, but it is easily attacked by strong oxidizing agents emanating from the photocatalysis process. The titania-based catalyst works well when coupled with UV light because titania is one of the highly activated UV semiconductors due to its narrow band gap energy [109]. UV light is also known to possess high energy within the solar spectrum. Therefore, a combination of titania and UV light shows the highest degradation efficiencies of up to 100% within 2 h of polyethylene polymer [73]. Degradation of polystyrene spheres under UV light is shown in Figure 6.

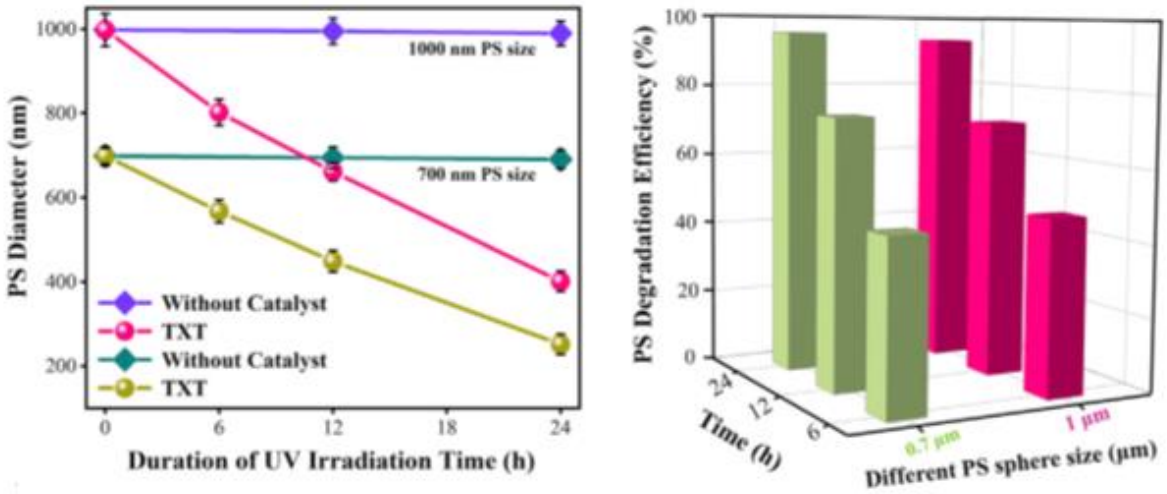

Figure 6 Diameter change of 1-mm and 700-nm PS on TXT film, and without catalyst and their degradation efficiency (%) under 365-nm UV light [110].

5.4.3 Photocatalytic Degradation Using Visible Light

Visible light lies within the visible region of the electromagnetic spectrum between the UV and infrared radiations. It has longer wavelengths than UV light, and hence it is a lower-energy form of light. Nonetheless, this light is abundant in sunlight, and therefore researchers are interested in tapping into this alternative form of green energy. Searching for a suitable catalyst for photocatalytic degradation within visible light is still ongoing. Various semiconductors have been studied although titania still is in the lead. Others like bismuthate, zinc oxide, and aluminum nickel spinels have also come up and the degradation efficiencies of these catalysts are still low in comparison to UV light-based photocatalysis. Notably, doping and preparing composites to act as photocatalysts show promising results, especially where carbon and nitrogen have been used as modifying agents for titania. Zinc oxide and ceria have also shown good photocatalytic activity in the visible region with significantly high degradation efficiencies.

The degradation of polystyrene microplastics using a flake-like BiOI-Fe_3O_4 micro swimmer using visible light in the presence of hydrogen peroxide was carried out with successful degradation of up to 64 % within 120 hours and their concentration in aqueous solution was reduced from 0.05 v/v % to 0.018 v/v % [64]. Spinels of $NiAl_2O_4$ were prepared and used to degrade polyethylene sheets using a metal halide lamp of 350 W as the visible light source. The results showed that the polyethylene sheet was degraded in 5 h with a weight loss of 12.5 % [65]. A catalyst made of BiOCl was used to degrade Polyethylene using visible light from a 250 W Xe lamp. The result showed a 5.38% mass loss. Photocatalytic degradation of HDPE plastic blocks, polypropylene, polyoxymethylene, and polyamide plastic microspheres were also studied and the results indicated that stable properties and poor light absorption greatly reduced the degradation effect of the photocatalyst [104]. The findings suggest that the photocatalyst's ability to harvest light with enough activation energy is important in the activity of the catalyst on microplastics. Although researchers have embarked on developing several photocatalysts sensitive to visible light, their degradation efficiencies are still low compared to when UV light is used due to their low ability to harness light with enough photons.

The presence of plasmonic material as modifying agent enhances the ability of a catalyst to absorb light energy within the visible region. The degradation of low-density polyethylene film in water, through visible light-induced plasmonic photocatalysts comprising platinum nanoparticles deposited on zinc oxide nanorods (ZnO-Pt), illustrated that the presence of platinum in the structure of ZnO improved the absorption of visible light. The photocatalyst was able to degrade the low-density polyethylene to a considerable change in chemical structure with the formation of several functional groups from FTIR results obtained [111].

Other photocatalysts with enhanced ability to harness visible light prepared include ceria oxide, copper sulfide, and zinc oxide nanoparticles. They were used for photocatalytic degradation of polyethylene and polyvinyl chloride in UV and visible light and sunlight, and it was observed that a degradation efficiency of up to 85% under visible light was achieved. This degradation rate is compared to the degradation efficiency of TiO_2 and therefore ceria, zinc oxide, and copper sulfide photocatalysts are active within the visible spectrum, and their band gap energy is sufficient to carry out photocatalysis of microplastics [71]. A photocatalyst composite of TiO_2-rGO was synthesized to degrade polypropylene under sunlight for 130 h. It was observed that the synthesized photocatalyst enhanced the degradation of polypropylene due to its ability to utilize the solar spectrum's energy [106].

The degradation of polylactic acid and polycaprolactone using intelligent visible-light-driven microrobots was evaluated by measuring the weight loss of microplastics after 1, 3, and 7 days. The microplastics gradually lost weight during the 7 days in the order with a maximum weight loss of ∼3% in PLA [66]. This means that the nature of the polymer affects the degradation process. Chromophore functional groups within the polymeric material increases its ability to absorb light energy for the photodegradation process.

The microplastic size is not to be ignored during visible light photocatalysis. Visible light photocatalysis under low-density polyethylene (LDPE) and high-density polyethylene (HDPE) microplastics in an aqueous solution using a coating of mesoporous N–TiO2 observed that small-sized microplastics have high degradation. In contrast, film-shaped microplastics have low degradation [80]. Because surface area affects the adsorption of plastics on the surface of the catalyst, the smaller the surface area the higher the percentage degradation. However, low efficiency was recorded and associated with poor illumination and oxygenated reaction medium.

The degradation of LDPE on a prepared LDPE/Fe-ZnO film was performed in a Petri dish under exposure to direct sunlight irradiation with the measured light intensity of 271.6 W/m^2 using a digital solar power meter and operated in the ambient and open-air conditions. It was established that in the presence of sunlight, pure LDPE film exhibited insignificant changes in weight loss (6.1%), with only a minor degradation under direct sunlight conditions. However, high weight loss efficiency was achieved on the film with a gradual increase in irradiation time between 0 and 36 h achieving a total weight loss of 41.3% after 120 h meaning that the amount of light absorbed is directly related to the degradation process [69]. Time, therefore, time is an important factor when photocatalysis is carried out using visible light because visible light is less energy than UV light.

Degradation efficiencies reported under visible light sources are lower than those of UV light. However, quite some remarkable results have been observed especially with the degradation of polyethylene. The doped titania photocatalyst and Zinc oxide have registered significantly high degradation percentages. The composite catalysts have higher efficiencies than the unmodified material due to the doping and modification effect that narrows the band gap energy, and this

influences the general trend of designing photocatalyst shifts in utilizing visible light and solar light. Visible light makes up a high percentage of the solar spectrum and therefore it is an abundant resource that can be tapped as an alternative clean form of energy. It is also inexpensive unlike UV light and hence the way to go for future technologies.

It is notable that among the most commonly studied microplastic polymers is polyethylene as shown in Figure 7. This could be because polyethylene is abundant, versatile, and has favorable physical properties [112]. In the photocatalytic degradation of microplastic materials, it is worth noting that factors like temperature, pH, and time significantly influence the process. However, due to the absence of standardized conditions, it becomes challenging to attribute the lower degradation efficiencies solely to the type of light used. Nevertheless, the results are highly promising and show that in the future suitable semiconductors, utilizing solar energy will be able to degrade microplastics.

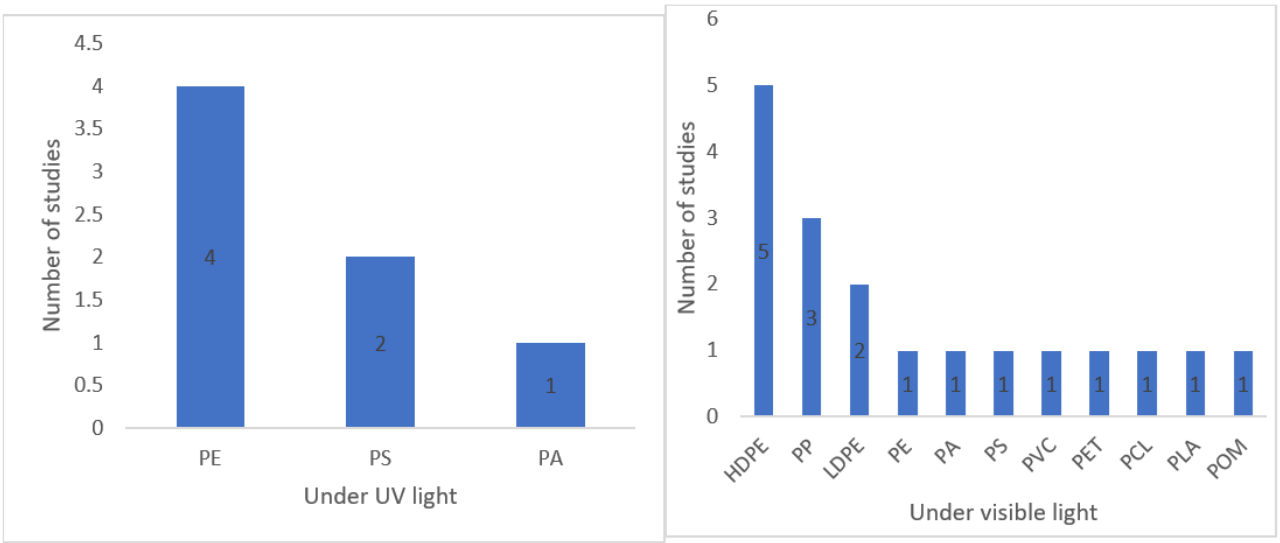

Figure 7 Common polymers under study.

6. Conclusion and Future Trends

In conclusion, the photocatalytic degradation of microplastics is a complex process influenced by various factors, including the type of photocatalyst used, the surface area of the catalyst, the pH and temperature of the reaction environment, and the intensity and wavelength of light used. The surface area of a photocatalyst depends on the type of catalyst and the structure of the polymer. Because microplastics in the environment exist as a mixture of polymers, a single system catalyst would not be appropriate. Low pH is favorable for polyethylene degradation, rampant in the environment, and the formation of hydroxyl radicals necessary for photocatalysis. A temperature of below 100°C and above 20°C promotes the photodegradation of most plastic polymers. The type of photocatalyst guides the choice of light; whether it is a simple single compound or a mixed composite system, the type of the photocatalyst as well as dopant improves on the optical properties of the catalyst. These factors should be optimized in developing novel photocatalysts with enhanced efficiency and selectivity for microplastic degradation.

To make photocatalytic degradation processes more sustainable, future research should focus on the stability and reusability of photocatalyst materials. Assessing the toxicity of both degradation

intermediates and photocatalyst materials in the environment is also necessary. Additionally, evaluating the economic viability of these techniques is crucial if they are to be adopted on a larger scale. Overall, there is a need for continued research and development to optimize photocatalytic degradation processes for practical applications and mitigate the environmental impact of microplastics.

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Author Contributions

Esther Kinyua and George Nyakairu conceived the concept, and Esther compiled the data and drafted the manuscript. Emmanuel Tebandeke and Nelson Odume revised the manuscript.

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Competing Interests

The authors declare that there is no known conflict of interest.

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