CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106163

Recent Advances in Zinc Oxide-based Photocatalytic Degradation of Microplastics in Solid- and Aqueous-Phase

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Microplastics have aroused global concern due to their widespread environmental distribution and the possible danger they pose to humans, animals, and microbes. In response to this concern, photocatalytic degradation, a technique that utilizes semiconductor nanomaterials as the photocatalyst, is being explored to reduce microplastics into less harmful compounds, making it a game-changing strategy for addressing this environmental problem. Besides the superiority of titanium dioxide (TiO_2) as a photocatalyst, zinc oxide (ZnO) nanoparticles are also one of the semiconductors that have been widely explored to date. Studies have proven its potential to degrade microplastics in either solid- or aqueous phases. In the photocatalytic degradation of microplastics, the reactive oxygen species (ROS), including hydroxyl (•OH) and superoxide ions ($O_2•^-$), play an essential role in the process, resulting in the breakdown of the polymeric chain and the generation of reaction intermediates. Therein, the primary focus of this review is limited to the photocatalytic degradation of microplastics using a ZnO-based photocatalyst and its mechanisms. The exploration and comparison of microplastic's solid- and aqueous-phase photocatalytic processes in terms of their experimental setup and performance were also discussed further. Furthermore, an insight into future research prospects is also suggested here, based on the restrictions of present photocatalytic degradation systems.

1. Introduction

Most of the consumed plastics have been discharged into the environment rather than efficiently recycled and inducing the fragmentation of plastic macro litter into smaller debris. (Razali et al., 2020). Thompson et al. (2004) were the first to use the term 'microplastics' to describe tiny plastic waste. Although other definitions of microplastics based on their size have been put forth, the scientific community typically uses the term to refer to plastic particles with a maximum length of 5mm (Pham et al., 2021). Recently, microplastics have attracted worldwide attention due to their widespread distribution in the environment and their potential for harm to human and animal health. Nonetheless, sufficient evidence shows that immediate and extensive action must be taken to reduce environmental plastic pollution and prevent future damage.

The advanced oxidation process (AOPs) is among the recent technologies explored as a remediation method for microplastic pollution. Utilizing the catalyst that works under irradiation of lights (visible, ultraviolet (UV), or solar), photocatalytic degradation is one of the AOPs that is a feasible, comparatively inexpensive, and energy-efficient process to mitigate microplastic pollution. This process degrades the polymer chains of plastics to form lower molecular weight intermediates, which are useful for organic synthesis and further mineralized into carbon dioxide (CO_2) and water (H_2O) (Ariza-Tarazona et al., 2020). The photodegradation degree of microplastics can be determined from all changes that occur in both physical (including mass loss, morphological changes, colour

Paper Received: 09 March 2023; Revised: 15 July 2023; Accepted: 30 September 2023
Please cite this article as: Noor S.F.M., Paiman S.H., Ngadi N., Malek N.A.N.N., Hamed N.K.A., Nordin A.H., 2023, Recent Advances in Zinc Oxide-based Photocatalytic Degradation of Microplastics in Solid- and Aqueous-Phase, Chemical Engineering Transactions, 106, 973-978 DOI:10.3303/CET23106163

changes, pitting or cracking, embrittlement, and roughness on the microplastic surface) and chemical (including molecular weight changes) properties of the plastics.
Zinc oxide (ZnO) has been one of the photocatalysts widely studied for photocatalytic degradation of microplastics either in the solid- or liquid phase. The experimental designs for both systems differ in ease of use, practicality, and evaluated parameters. Thus, an effort has been made herein to review the current photocatalytic degradation system of microplastics, in terms of their experimental setup and performance, either in solid- or aqueous-phase that utilizes the ZnO-based photocatalyst. Furthermore, the ZnO-based microplastic degradation response mechanism was addressed before clarifying the process.

2. Zinc oxide-based nanomaterials: Photocatalysis

The fundamentals of photocatalysis involve the absorption of appropriate light energy by a semiconductor known as a photocatalyst. Despite the popularity of TiO_2 as a photocatalyst, ZnO-based nanoparticles are extensively studied because of their outstanding photocatalytic performance against a broad variety of contaminants, good stability, nontoxicity, and inexpensive cost (Zhu and Zhou, 2019). This n-type semiconductor has a similar bandgap energy to TiO_2 of about 3.37 eV, but it has much higher binding energy (60 meV), which results in exceptional illuminating and photovoltaic properties (Hussain et al., 2013). ZnO may be employed for UV and visible irradiation due to its exceptional absorptivity throughout a significant portion of the solar area (Chakrabarti et al., 2020). ZnO also has good mechanical, optical, and electrical capabilities as well as antifouling and antibacterial features (Al-Naamani et al., 2017).

2.1 Photocatalytic degradation of microplastics: General mechanism

The mechanism of photocatalytic degradation of microplastics is similar to that of the organic polymer breakdown (Sharma et al., 2021), as shown in Figure 1. It accelerated significantly with the presence of a photocatalyst (Ge et al., 2022). A sufficient amount of photon energy higher than the bandgap energy of ~3.37 eV is required for the ZnO to generate charge carriers (electron, e^-, and holes, h^+) which are subsequently necessary to produce reactive radicals for photooxidation and photoreduction reactions. The excited e^- at the conduction band (CB) reacted with oxygen and produced superoxide radical ($O_2^{\bullet -}$), while the h^+ generated at the valence band (VB) reacted with water, forming the hydroxyl radical (•OH).
Carbon-centred radicals continuously interact with a range of ROS, breaking the chain and producing intermediates such as hydroxyl derivatives, carboxyl, and carbonyl. The produced ROS, such as •OH and O2•- radicals, will directly initiate the degradation process of microplastics by attacking the polymer backbone and causing polymeric chain scission, branching, and cross-linking. Later, the degradation process is laterally expanded into the polymer matrices via ROS propagation (Uheida et al., 2020). The •OH radicals attack the C-H bond on polymer molecules, and the hydrogen on the bond loses an electron and reacts with the radical to generate water. Due to this process, the remaining microplastic molecules are transformed to free radicals centred on the carbon atom (Ge et al., 2022).

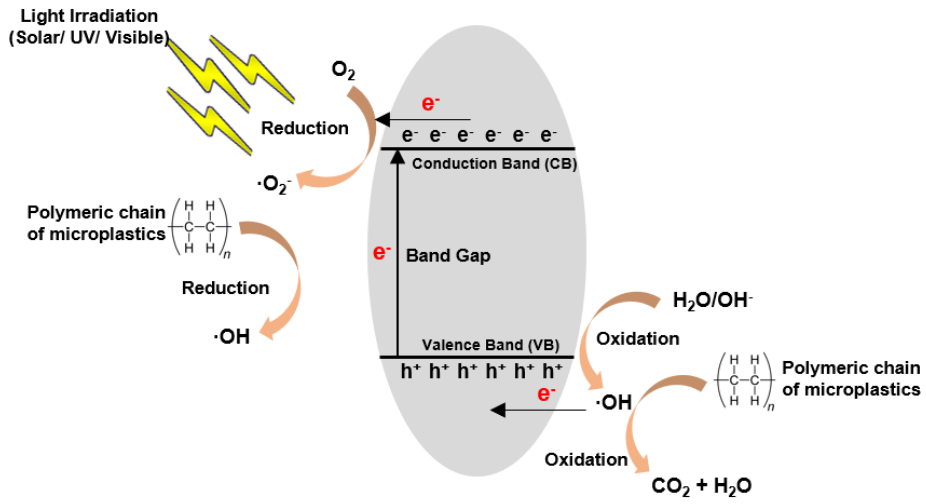

Figure 1: General mechanism of photocatalytic degradation of microplastics (Adapted from Ebrahimbabaie et al. (2022))

2.2 Solid-phase degradation of microplastics by ZnO-based photocatalyst

The degree of photocatalytic degradation of microplastics is determined by changes in their physical and chemical attributes, including mass loss, morphological and colour changes, cracking, or embrittlement, as well as changes in their surface functional groups and molecular weight. Due to the ease with which its physical and chemical properties can be monitored, solid-phase degradation is frequently chosen to experimentally develop the photocatalytic degradation system for microplastics. The synthesized catalyst is typically incorporated into the polymer matrix. Thus, separating the catalyst from the reaction system is unnecessary before the mass loss quantification step.

The solid-phase degradation of plastic film was demonstrated by Kamalian et al. (2019), where the process was accelerated by the ZnO grafted with a certain amount of polystyrene on its surface. Pure LDPE and composite LDPE films, embedded with the pristine and polystyrene-grafted ZnO nanoparticles, were fabricated by film-blowing techniques and subsequently irradiated with UV light for 200 hours. Compared to the neat LDPE film, the presence of ZnO nanoparticles increased the degradation rate after UV irradiation. A more significant mass loss was demonstrated in the ZnO-LDPE than in the pure LDPE one. Furthermore, the incorporation of 15 wt.% of polystyrene enhanced the photocatalytic performance of ZnO by improving the dispersion of nanoparticles in the polymer matrix. However, the performance of ZnO was lowered when polystyrene grafting was increased from 15 to 39 %, perhaps because of the surrounding polystyrene's blocking action, which decreased the UV absorption of the nanoparticle.

Moreover, the mechanical testing revealed that the grafting and incorporation of the nanoparticles improved the tensile strength of the prepared LDPE films. A similar trend was observed by Kamalian et al. (2020), where 10 wt.% grafting of polyacrylamide (PAM) onto the surface of ZnO nanoparticles increased its UV absorption and emission. The PAM grafting was observed to improve the dispersion of ZnO particles in the LDPE matrix. However, as the grafting extent from 10 to 39 wt.%, ZnO nanoparticles' photocatalytic performance deteriorated.

Lam et al. (2021) investigated the influence of doping on the efficiency of ZnO-based solid-phase degradation. The iron-doped ZnO (Fe-ZnO) was produced by a green approach and then employed for LDPE plastic degradation and Escherichia coli (*E. coli*) inactivation under solar irradiation. The mass loss of LDPE/Fe-ZnO film was greater than that of neat LDPE and LDPE/ZnO. As evidenced by a more pronounced deterioration of the LDPE/Fe-ZnO film, the incoprporation of 2 wt.% of iron dopant in the ZnO lattice increased the optical absorption of the photogenerated charge carriers. The occurance of carbonyl groups as the reaction by-product and the formation of surface defects at the interface of the polymer matrix further validate the findings. Furthermore, LDPE/Fe-ZnO showed a more explicit antibacterial action towards *E. coli* compared to LDPE/ZnO film.

Another work by Lam and colleagues (2022) utilized ZnO-modified polyvinylpyrrolidone (ZnO-PVP) to effectively degrade polyethylene (PE) and polystyrene (PS) under solar irradiation. The addition of PVP reduced the size of the ZnO particles while extending their range of optical responsiveness in the solar region. The ZnO-PVP outperformed the unmodified ZnO and virgin films due to their large surface area, which enhances their interaction with plastic film texture and leads to increased charge mobility for the photodegradation of polymeric materials. These findings were further supported by detecting carbonyl, peroxides, and unsaturated vinyl groups using an infrared spectrometer. Furthermore, the composite films' tensile performance and thermal stability were substantially limited when subjected to sunlight. Table 1 summarizes the solid-phase photocatalytic degradation of microplastics by ZnO-based nanoparticles.

Table 1: Solid-phase degradation of microplastics by ZnO-based nanoparticles

Photocatalyst	Type	Light Source & Intensity	Reaction Duration	Weight loss (%)	Comment	Reference
Polystyrene-grafted ZnO	LDPE	UV-A lamps (30 W × 5), 50 cm to sample	200 h	13	-	Kamalian et al. (2019)
PAM-grafted ZnO	LDPE	UV-A lamps (30 W × 5), 50 cm to sample	200 h	25	-	Kamalian et al. (2020)
Fe-ZnO	LDPE	Sunlight (271.6 W/m^2) Visible light (57 W/m^2)	120 h	41.3	Fe-ZnO have better antibacterial activity against E. coli	Lam et al. (2021)
ZnO-PVP	PE & PS	Sunlight (7.92 × 104 lux)	200 h	45	-	Lam et al. (2022)

2.3 Aqueous-phase degradation of microplastics

Aqueous-phase degradation of microplastics is typically carried out under wet conditions, with excessive moisture in the surrounding reaction matrix. The aqueous-phase degradation reflects the condition where the process is meant to diminish the microplastic pollution in the water stream, such as in the water or wastewater treatment plant, before being discharged to the water bodies. The photocatalyst and the microplastic particles are usually suspended in water. The mixture will be stirred for the batch reaction system to aid the contact between the photocatalyst and microplastic particles. The dark adsorption will be conducted before light irradiation to allow the system to achieve equilibrium.

The UV-assisted thermo-photocatalytic process was employed by Razali et al. (2020) to degrade polypropylene (PP) using commercial ZnO nanoparticles as the photocatalyst. The effect of catalyst dosage (1–3 g/L), the reaction temperature (35–50°C) and the size of PP plastic and towards the weight loss of macro/micro-plastics was investigated. The highest weight loss of PP plastic (7.8 %) was attained at 50 °C with 1 g/L of ZnO under 6 h of UV irradiation. Hence, this study suggested that the reaction temperature and microplastic size contribute significantly. Thus, those factors must be considered while designing the aqueous-phase degradation of microplastics.

In a flow-through system, Uheida et al. (2020) immobilized ZnO nanorods onto glass fibre substrates for an efficient visible-light system of microplastic degradation. The glass fibre supports the photocatalyst material and traps the polypropylene (PP) microplastic particles. The average particle volume of PP microplastics was reduced by 65% after two weeks of visible light irradiation. Gas chromatography/ mass spectroscopy (GC/MS) was used to identify the principal photodegradation by-products, which were discovered to be primarily harmless compounds in the literature.

Another sight for the photocatalytic setup in the aqueous-phase degradation of microplastics was presented by Tofa et al. (2019a) and Tofa et al. (2019b). The photocatalysis of LDPE film was carried out in a Petri dish containing the produced catalysts and deionized water for 175 hours without stirring, with the visible light source situated 10 cm distant. The performance of ZnO nanorods was compared to the platinum-doped ZnO (Pt-ZnO). Due to the plasmonic effect of the Pt on the ZnO surfaces, the Pt-ZnO nanorods indicated around 13% higher potential of LDPE film oxidation than the as-grown ZnO nanorods.Furthermore, catalyst surface area was discovered to be crucial in promoting LDPE degradation. Table 2 summarizes the recent aqueous-phase photocatalytic degradation of microplastics by ZnO-based nanoparticles.

Table 2: Aqueous-phase photocatalytic degradation of microplastics by ZnO-based nanoparticles

Photocatalyst	Type	Light Source & Intensity	Catalytic Time	Weight loss (%)	Comment	Reference
ZnO nanorods on glass substrate	PP	Visible, 120 W, 60 mW/cm^2, 20 cm distance from the light, Flow rate: 300 mL/min	200 h	65	>65 % reduction in particle volume, 14 days	Uheida et al. (2020)
Commercial ZnO	PP	11 W of UVC irradiation, 1 or 3 g/L of ~50 nm ZnO, T = 35 °C or 50 °C	6 h	7.8	-	Razali et al. (2020)
ZnO nanorods on glass substrate	LDPE	Visible, 50 W dichroic halogen lamp, ~60–70 Klux	175 h	Increment in carbonyl index (CI) value	CI value: increment by 0.8	Tofa et al. (2019a)
Pt-ZnO nanorods	LDPE	Visible, 50W dichroic halogen lamp, ~60–70 Klux	175 h	-	78 % better visible light adsorption than pure ZnO	Tofa et al. (2019b)

Based on the above discussions, it is revealed that the studies related to the ZnO-based photocatalytic degradation of microplastics have made tremendous progress recently. However, most systems investigated to date could not achieve the complete mineralization of microplastics. In addition, the significant mass loss of microplastics could only be obtained at a highly long reaction time, up to 200 h, and some are up to weeks. Most of the conducted microplastic photocatalysis systems focused on the solid phase degradation due to the separation and recovery issue. The mass loss quantification of residual microplastics in the solid phase system would be much more straightforward without separating the embedded catalyst from the reaction medium (the polymer matrix). The solid phase degradation somehow gives a good proof-of-concept on the catalyst's

efficiency in boosting the polymeric breakdown process that might be beneficial in manufacturing photodegradable plastics. Yet, for the photocatalysis system to be implemented as the remediation strategy for microplastic issues in wastewater or water treatment plant, the aqueous phase degradation system would be more suitable to simulate the actual condition, with the presence of liquid or water as the reaction medium. Table 3 summarizes the comparison between solid and aqueous phase degradation systems of microplastics.

Table 3: Comparison of solid-phase and aqueous-phase degradation of microplastics

Characteristics	Solid phase	Aqueous phase
Practicality	The photocatalyst is usually incorporated into the polymer matrix. Hence, it suggests new principles for the design of degradable plastics through solid-phase photocatalysis	Mimic the actual system of microplastic remediation in water or wastewater treatment
Production of Intermediates	Photocatalysts were adjacent and embedded in the polymer matrix, which accelerated the collapse of the plastic framework. It avoids the release of possible toxic intermediates into water bodies	Harmful intermediates (if any) may diffuse into the aqueous matrix, contaminating the water bodies
Mass loss quantification	Mass loss can be easily measured, no catalyst separation is required, and microplastic sampling for monitoring physical and chemical changes is more straightforward	Separation of catalysts and microplastics from the water matrix is needed before the quantification of mass loss
Photocatalyst Reusability	Photocatalysts are almost impossible to be reused because they are embedded into the polymer matrix	The immobilization of photocatalysts can solve the issue of recycling and reusability

3. Prospects

Despite many advantages as a solar photocatalyst, ZnO-based nanomaterials might have intrinsic toxicity owing to their nano size. Thus, it is recommended that these particles should not be discharged into the environment. Because the catalyst is suspended in water during aqueous-phase degradation, recycling it is challenging, resulting in some secondary contamination. These issues can be avoided if the catalyst is immobilized on the surface of the substrate to facilitate photocatalyst separation from the reaction matrix.

Most systems for photocatalytic degradation of microplastics that have been published only showed partial degradation. They did not use liquid chromatography-mass spectrometry (LC-MS) or other detection methods to look for the final degradation products. These processes might also release volatile organic compounds (VOC)s. Thus, identifying microplastic degradation products is crucial to understanding the mineralization mechanism and its environmental consequences, including their toxicity level.

The intrinsic properties of the microplastics, which are often hydrophobic and insoluble in the reaction medium, were not taken into account in the earlier investigations. These circumstances may be to responsible for the low mass loss of microplastics, according to earlier studies. The relative size difference that limits the adsorption equilibrium between microplastics and the photocatalyst was also seldom addressed. Therefore, a competent photocatalyst that can solve the adsorption problem of the hydrophobic and relatively large microplastics should be offered in order to increase the degradation efficiency of microplastics.

4. Conclusion

The ZnO-based nanoparticles have been proven to potentially enhance the degradation of plastic/microplastics in solid and liquid phases. However, there is still room to explore possible modifications to boost the performance of the photocatalytic system of microplastics. Yet, it is a long way off for the system to be implemented in the actual process to remediate the plastics issue in the environment. The role of reactive species, the reaction mechanism and pathways of different types and sizes of microplastics in the environment should be elucidated to facilitate the process design. Based on the limitations of the previous studies related to ZnO-based photocatalytic systems of microplastics, the suggested prospects for further research should be considered.

Acknowledgements

The authors acknowledge Universiti Teknologi Malaysia (UTM) for providing monetary funding under the UTM Fundamental Research (UTMFR) Research University Grant (RUG) (Vot No 22H62).

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