ISSN: 2710-0588

Photodegradation of Microplastics: Mechanism, Influencing Factors and Research Progress

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Abstract

Microplastics, as pollutants that are difficult to biodegrade in the environment, are widely distributed in soil, water bodies, and the atmosphere. They form complex pollution by adsorbing heavy metals and hydrophobic organic pollutants. Photodegradation, as an environmentally friendly degradation method, has attracted much attention. Photodegradation of microplastics includes direct photodegradation and indirect photodegradation. In direct photodegradation, photons directly act on the microplastic substrate, such as PE and PP, which absorb energy in the 270-300nm ultraviolet band, causing carbon-carbon bonds to break and form free radicals, which then transform into small molecules. Indirect photodegradation, on the other hand, relies on photosensitizers such as humic acid to produce active species that trigger degradation. The degradation rate of PS in water rich in DOM can increase by 2-3 times.

Keywords

Microplastics, Photodegradation, substrate.

1. Introduction

Plastic has been widely used in various fields since its invention, thanks to its low cost, durability and versatility, from everyday food packaging, clothing to personal care products, almost everywhere. However, plastic is difficult to biodegrade in the environment, making it a persistent contaminant after use. Over time, large chunks of plastic gradually break down into tiny particles, known as microplastics (less than 5 millimeters in size), which are widely distributed in environmental media such as soil, water, and the atmosphere, posing a potential threat to ecosystems and human health.

Water bodies, which are the main gathering places for microplastics, have received extensive attention from researchers. At present, research on microplastics in the environment is mainly focused on collection and detection techniques[1], while systematic studies on their existence, environmental behavior and removal pathways are still insufficient, especially in water bodies, where the treatment of microplastic pollution has not been carried out on a large scale. In addition, the degradation or decomposition of microplastics may also release potentially hazardous chemicals or substances such as copolymers (dimers or monomers), additives (dyes), and plasticizers. Nonylphenol (NP), bisphenol A (BPA), polybrominated diphenyl ethers (PBDEs), phthalates (PAEs), and organotin compounds (OTCs) have been found to be filtered out from plastic products or microplastic materials, for example.

Microplastics not only cause pollution when they decompose themselves, but their good adsorption properties enable them to act as carriers[2] to adsorb heavy metals, hydrophobic organic pollutants (such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, dioxins, etc.) in the environment, creating a complex pollution effect that further exacerbates environmental risks. Therefore, an in-depth study of the degradation pathways of microplastics is of great significance for alleviating the problem of

ISSN: 2710-0588

microplastic pollution. Among the many degradation methods, photodegradation, as an environmentally friendly degradation approach, has received increasing attention in recent years.

2. The Photodegradation Mechanism of Microplastics

2.1. The fundamentals of photodegradation

Photodegradation refers to the process in which microplastics undergo chemical structural changes under ultraviolet (UV) light, causing molecular chain breaks and polymer degradation. When microplastics absorb photon energy, the electrons in their molecules transition from the ground state to the excited state. Molecules in the excited state have higher energy, are unstable[3], and may release energy back to the ground state through multiple pathways, one of which is to trigger the breaking of chemical bonds, leading to the degradation of the microplastic molecular chain. For example, in common microplastics such as polyethylene (PE) and polypropylene (PP), under ultraviolet light, the carbon-carbon bonds (C-C) in the molecules can absorb photon energy and break, forming free radicals. These free radicals are highly reactive and can trigger a series of chain reactions to further degrade the microplastic molecules.

2.2. Direct photodegradation

Direct photodegradation refers to the direct action of photon energy on microplastic substrates, causing chemical bond breaks and molecular structure changes. Different types of microplastics have different light absorption properties due to differences in their molecular structure and chemical composition. The chemical structure of PE and PP is mainly composed of long-chain alkanes, lacking unsaturated bonds and polar functional groups, and their absorption peaks are in the ultraviolet band of 270-300 nanometers. When ultraviolet light with wavelengths in this range is exposed to PE and PP microplastics, the photon energy is absorbed by the molecules, causing the carbon-carbon bonds in the molecules to break and form short-chain free radicals. For example, PE breaks the main carbon chain under light excitation to form · PE radicals, which further transform into small molecule compounds such as ethylene, ethane, and propylene through disproportionation or coupling reactions. At the same time, physical changes occur on the surface of the microplastics during degradation, such as yellowing and brittleness, due to the formation of polar functional groups such as carbonyl (C = O) in the polymer, which absorb visible light.

The photodegradation mechanism of PP is similar to that of PE, but due to the presence of a small amount of methyl ($-CH_3$) side groups in the PP molecule, its photodegradation rate is usually slightly faster than that of PE. Under ultraviolet light, PP molecules can form tertiary carbon radicals ($\cdot C(CH_3)_3$), which eventually convert into smaller molecules such as propylene and propane through chain transfer and chain breaking reactions. The photodegradation rate of PE and PP is significantly more affected by UV-B (wavelength 275-315 nanometers) than by UV-A (wavelength 315-400 nanometers). In natural water bodies, UV-B accounts for about 5-10%

of total solar radiation, but it can trigger the degradation of most plastics. Under UV-B irradiation, the degradation half-life (t1/2) of PE and PP can be several years under indoor simulated conditions and several decades under outdoor natural conditions.

3. Indirect Photodegradation

Indirect photodegradation involves the involvement of photosensitizers or other photoactive substances. When photosensitizers are present, they can absorb light of specific wavelengths to produce active intermediates that trigger the degradation of microplastics. In the natural

ISSN: 2710-0588

environment, certain natural organic substances (NOMs) in water bodies, such as humic acid, fulvic acid, etc., can act as photosensitizers. When exposed to light, these natural organic substances produce active species such as singlet oxygen (1O2), hydroxyl radicals (OH), superoxide anion radicals (·O2-) through energy transfer or electron transfer processes. For example, humic acid, after absorbing photon energy, can transfer the energy to the surrounding oxygen molecules, transforming them into singlet oxygen (1O2), which has a strong oxidizing capacity and can attack microplastic molecules, causing their chemical bonds to break and thus triggering the degradation of microplastics.

In addition, some artificially added chemicals can also act as photosensitizers to promote the degradation of microplastics. For example, certain transition metal complexes, organic dyes, etc. can produce free radicals under light conditions. These free radicals react with microplastic molecules and promote the degradation of microplastics. Studies have shown that in systems containing photosensitizers, the degradation rate of microplastics under light conditions can be significantly increased. For example, in water bodies rich in DOM (dissolved organic matter), the degradation rate of polystyrene (PS) microplastics is 2-3 times higher than that under UV-A alone, thanks to the synergistic effect of DOM and UV-A.

3.1. Factors affecting photodegradation of microplastics

Light intensity: Light intensity is one of the important factors affecting the photodegradation of microplastics. Higher light intensity means an increase in the number of photons absorbed by the microplastics per unit time, thereby promoting the photodegradation reaction. In laboratory simulations, it was found that the degradation rate of PE and PP microplastics increased significantly with the increase of light intensity. For example, when the light intensity increased from 1000 lux to 3000 lux, the mass loss rate of PE microplastics increased significantly over the same period of time. This is because the increase in light intensity enables the microplastic molecules to absorb more energy, generate more excited-state molecules and free radicals, and accelerate the breaking of molecular chains and degradation reactions.

1. Wavelength and light quality: Different wavelengths of light have different effects on the degradation of microplastics. As mentioned earlier, UV-B degrades microplastics such as PE and PP more significantly, and its degradation efficiency is higher than that of UV-A. However, due to the absorption effect of the Earth's atmosphere, the amount of UV-B reaching the Earth's surface is lower. In contrast, UV-A is more abundant on the Earth's surface, but has a relatively weaker ability to degrade certain microplastics. In addition, light quality also affects the photodegradation process. For example, light sources with more blue light components may promote the degradation of certain microplastics because the energy of blue light is relatively high, which can trigger specific photochemical reactions in the microplastic molecules. Different microplastics also respond differently to light. PS microplastics degrade about 40% less in the UV-A band than in UV-B, but in DOM-rich water bodies, their degradation rate can be significantly increased due to the synergistic effect of DOM and UV-A.

3.2. Environmental factors

Temperature: Temperature has a certain influence on the photodegradation process of microplastics. On the one hand, an increase in temperature can enhance the thermal motion of molecules, making the microplastic molecular chains more active and facilitating the generation and diffusion of free radicals, thereby accelerating the photodegradation reaction. Studies have shown that within a certain temperature range (such as 20-40 ° C), the rate of photodegradation of PE microplastics gradually increases as the temperature rises. On the other hand, temperature may also affect the activity of the photocatalyst (if present) as well as the reactivity of the photosensitizer. For some photodegradation systems that require the participation of photocatalysts, an appropriate temperature can enhance the activity of the

ISSN: 2710-0588

catalyst, facilitate the separation and migration of photogenerated carriers, and thereby improve the degradation efficiency of microplastics.

1. Humidity and moisture: Humidity and moisture play important roles in the photodegradation of microplastics. In the natural environment, the surface of microplastics usually adsorbs a certain amount of moisture. The presence of moisture may affect the penetration depth of UV, which in turn indirectly affects the photodegradation efficiency. For example, in a high humidity environment, the water film on the surface of the microplastic may scatter or absorb some of the ultraviolet light, reducing the effective light energy reaching the interior of the microplastic and thus lowering the rate of photodegradation. However, in some cases, moisture may also be involved in the photodegradation reaction. For example, in photocatalytic degradation systems, water can act as a reactant to react with photogenerated holes to produce hydroxyl radicals (OH), which have strong oxidizing power and can promote the degradation of microplastics. In addition, for some microplastics containing hydrophilic groups, water may also affect their

4. Conclusion

The impact of microplastics on the photodegradation of pollutants needs to be comprehensively evaluated by considering specific environmental conditions and the characteristics of microplastics. On one hand, microplastics can participate in the transformation of pollutants through direct or indirect photodegradation mechanisms: In direct photodegradation, microplastics themselves absorb specific wavelengths of ultraviolet light (such as PE and PP absorb the 270-300nm wavelength band of light) to trigger molecular chain breaks, and the free radicals generated during this process may react with environmental pollutants, promoting the degradation of some pollutants; In indirect photodegradation, the photosensitizers such as humic acids adsorbed on the surface of microplastics, or substances released by microplastics themselves, can produce reactive species (such as singlet oxygen, hydroxyl radicals), providing reaction conditions for the photodegradation of pollutants. For example, the presence of PS microplastics in water bodies rich in DOM can indirectly enhance the degradation efficiency of related pollutants.

Acknowledgements

Natural Science Foundation.

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