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2. Photodegradation Processes of Microplastics in Aquatic Medium

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2.1 Introduction:

Micro Plastic (Mps) pollution in the environment has attracted growing concerns because of its nature of being difficult to degrade, small in size. Currently, plastic wastes have been widely spread over various environmental mediums such as water, soils and atmosphere. The presence of MPs in various water bodies, like oceans and urban waters (e.g., lakes, river, wastewater and drinking water) has caused scientific and public concern because of their adverse effect on aquatic organisms. MPs consumed by aquatic life are likely to enter the human body through the food chain. Their potential risk to humans' health is a rising concern due to this. As such, it is needed to remove MPs from the urban waters. Many techniques and methods like coagulation, adsorption, filtration, magnetic extraction, supporting ionic liquids, microbial degradation, and advanced oxidation processes (AOPs) such as Fenton/Fenton-like reaction and photodegradation have been used to remove MPs from the urban waters. Photodegradation is one of these techniques which has become the research hotspot in recent years due to their simple operation and lower cost. It is considered as a promising and advantageous method for the complete removal of MPs in water because the generated strong oxidizing free radicals such as hydroxyl radical ($^{\bullet}OH$) and superoxide radical ($O_2^{\bullet-}$) can convert MPs into simple non-toxic molecules (e.g., H_2O and CO_2). In this chapter we have discussed about the photodegradation activity of wide band gap semiconductor on the degradation of microplastic from the urban waters.

2.2 Microplastic:

Micro plastic has become a major problem due its adverse effect on environment specifically because of its low degrading characteristics and wide spread over the nature. Plastic pollution is primarily caused by large-scale improper use of plastic products. This is a growing concern because of the continuous accumulation and low biodegradability of plastics wastes. Currently, plastic wastes have been widely found in various environmental mediums such as water, soils and atmosphere. Plastic wastes while being in these mediums can be broken down into small particles by the natural effects like sunlight, weathering, erosion etc. Such particles with a size between 0.1 μm and 5 mm are generally known as micro plastics (MPs). Additionally the manufactured plastic products commonly known as personal care products (PCPs) and detergents are also considered as main sources of MPs. The presence of MPs in various water bodies (for example oceans and lakes, river, waste water and drinking water etc.) is imminent in the current scenario and this has raised the concern because of their adverse effect not only on aquatic organism but also human body through the food chain. Evidences are there ingestion of MPs consumed by aquatic organisms can cause chronic poisoning such as reproductive damage, malnutrition, internal abrasion etc. Apart from that potentially toxic additives used to improve plastic properties can further intensify the problem. Although report related to MP's adverse effect is not that significant so far but there are always possibilities that the scenario gets changed anytime because urban waters are among the essentials of people's daily life. As such, it is extremely necessary to remove MPs from the urban waters. Many techniques like coagulation, adsorption, filtration, magnetic extraction, supporting ionic liquids, microbial degradation have been evolved to remove MPs from the urban waters. Advanced oxidation processes (AOPs) such as photo degradation are also being practiced and it is in fact the research hotspots in recent years due to their simple and cost effective operations. The physico-chemical properties of the polymers and environmental conditions like weathering, temperature, irradiation as well as pH affect the degrading of plastics however.

A wide variety of organic pollutants can be mineralized into H_2O and CO_2 by visible light photo degradation which is an effective and low cost solution. In this process sunlight is used as a clean energy source and at the same time no generation of harmless by-products is occurred. Wide band gap metal oxide semiconductor materials such as Titania (TiO_2) or zinc oxide (ZnO) are used. These Semiconductors while interacting with light give rise to the formation of different reactive species. The MPs in water can be complete removed by photo degradation because the generation of strong oxidizing free radicals such as hydroxyl radical (•OH) and superoxide radical ($O_2^{\bullet -}$) can convert MPs into simple non-toxic molecules (e.g., H_2O and CO_2).

The Research community is very much interested on ZnO@TiO_2 photo catalyst materials as an environmental solution for removal of pollutants because of its ability form hetero junction with different band gap energy. The photo catalytic hetero junction can be classified into four types namely (1) semiconductor- semiconductor materials (S-S) hetero junction; (2) semiconductor- metal (S–M) hetero junction; (3) semiconductor- carbon materials including activated carbon, carbon nano tubes (CNT) and graphne (S-C) hetero junction and (4) multi component hetero junction. The formation of hetero junction can enhance photo generation process and cause electron transfer from ZnO CB to TiO_2 CB and thus whole transfer from TiO_2 VB to ZnO VB improves higher electron-hole transfer separation and lifetime. However, photodegraded materials in a fiber-like structure with aligned morphology showed high photodegradation properties.

The objective of this chapter is to highlight the ways in which microplastics degrade in the environment by photo degradation technologies under simulated environmental conditions.

2.2.1 Hotspots for the Accumulation of Plastics:

Increasing rate of atmospheric micro plastics has been found to be around 4% per year as per the related studies i.e. very alarming. The study has also discovered that the hotspots for terrestrial micro plastic sources and accumulation are primarily Europe, Eastern Asia, the Middle East, and the United States. Most of the atmospheric micro plastics are present above the oceans. Once the plastics enter the ocean or any water body its fate is determined by many factors including oceanographic processes, degradation (fragmentation, photo oxidation, and biodegradation) and the characteristics of plastics (e.g., size, density, and surface area). Around 74% of global plastic production is contributed by Buoyant polymers (e.g., polyethylene and low-density polystyrene). Buoyant plastics could be transported for long periods by wind and water currents until they are beached, trapped in different coastal habitats, sink due to loss of buoyancy. But these plastics (e.g., polystyrene and polyamide) are likely to sink to the seafloor also. Plastic shapes vary from elongated shapes (fibers and ropes) to a lower surface to volume ratio fragments and spheroids. A small-size plastic accumulates in the open ocean because of low buoyancy, while large plastics can be found in coastal waters. Fishing debris, including discarded and abandoned fishing gear in commercial fishing zones, constitute a high percentage of total litter of large plastics and have a wide range of ecological and economic impacts. While smaller plastics in the deep-sea sediment suggesting that this vast ecosystem is a hotspot for plastic accumulation and accounts for some of the “missing” plastics.

2.3 Degradation mechanisms of plastics:

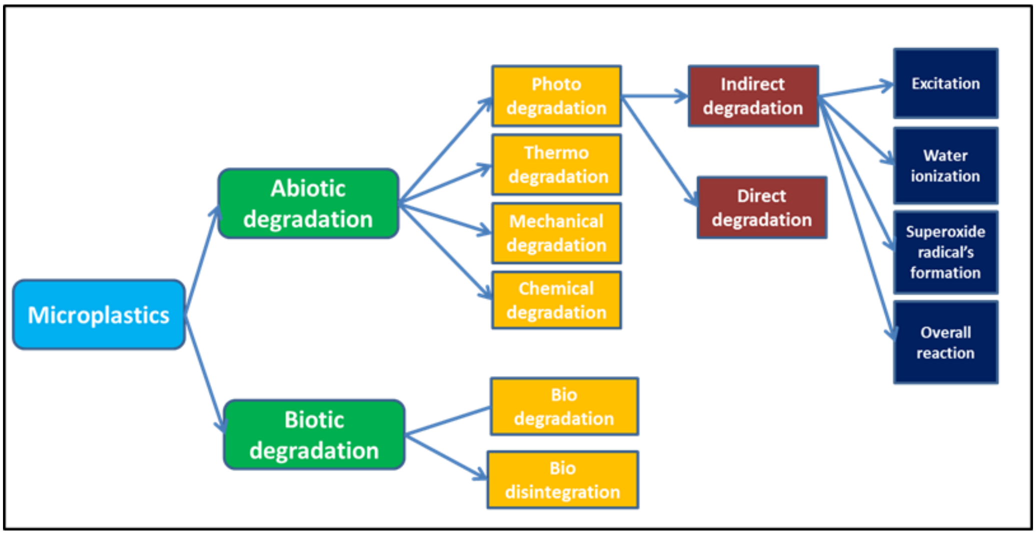

Figure 2.1: Schematic Diagram of Different Degradation Processes of Microplastics

2.2.1 Abiotic Degradation of Plastics:

Plastics are degraded by some physical factor like light, temperature, chemical, mechanical forces that changes its physical and chemical properties. In addition to these, the polymer characteristics such as its mobility, crystalline feature, molecular weight, the type of functional groups, substituent present in its structure and plasticizers added to the polymer all play an important role in its degradation as well. Initially the polymer gets converted to its monomers, after that these monomers are mineralized. In mineralization the end products are CO_2, H_2O. Abiotic hydrolysis is a vital reaction for initiating the environmental degradation of synthetic polymers like polycarboxylates, poly (ethylene terephthalate), polylactic acid, poly (α-glutamic) acids, and polydimethylsiloxanes, or silicones. Abiotic degradation technologies can be of four types: photo degradation, thermo degradation, mechanical degradation and Chemical degradation. In this chapter we will be discussing about photo degradation technology in detail.

2.2.2 Photodegradation of plastics:

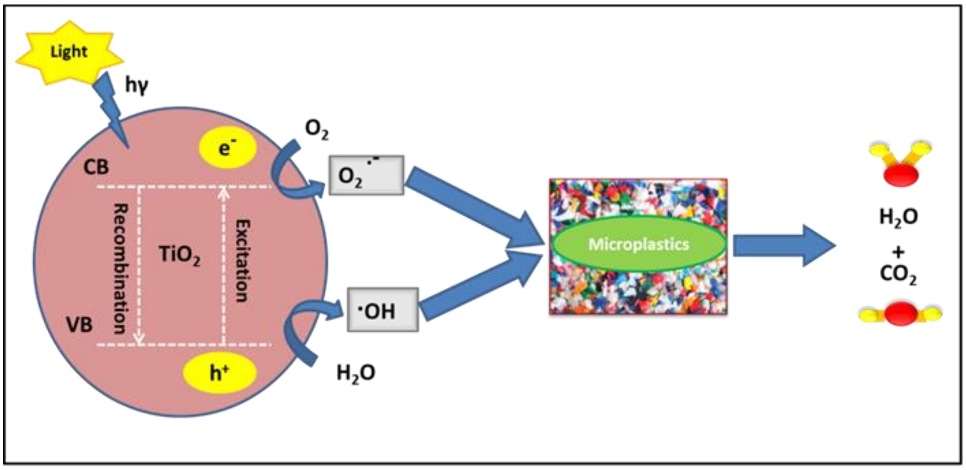

Figure 2.2: General Photo Degradation Mechanism of TiO_2 under Light Irradiation

a. Indirect degradation:

Indirect photo catalytic degradation of plastics can be explained with the following steps:

- **Excitation:**

The photodegradation begins when the electron from the Valance Band move toward the empty Conduction Band upon light irradiation. The incident photon need to have either equal or greater energy than the band gap of TiO_2.This leaves only the holes (h^+) in the VB and the reaction upon light irradiation is summarized in Eq. (1):

$$TiO_2 \xrightarrow{h\gamma} h^+_{VB} + e^-_{CB} \qquad (1)$$

- **Water ionization:**

A hole in the VB reacts with a water molecule & produces a strong oxidizing agent called hydroxyl radical (•OH). This is shown in the following Eq. (2). This radical plays an important role in photo oxidation. It leads mineralization by attacking adsorbed contaminant none selectively that is attached or near to the photo catalyst interface surface. TiO2 is useful for the photo degradation of organic pollutants under UV and visible light.

$$h^{+}_{VB} + H_2O \longrightarrow {}^{\cdot}OH + H^{+} \quad (2)$$

- **Superoxide radical's formation:**

Electron in the CB, now reacts with oxygen molecule & creates of superoxide radical

($O_2^{\cdot-}$) as given in equation Eq. (3).

This $O_2^{\cdot-}$ radical take part in oxidation and this also restrict the recombination of photo generated electron-hole pairs. In this way hence electrons sustain neutrality with semiconductor.

$$O_2 + e^{-}_{CB} \longrightarrow O_2^{\cdot-} \quad (3)$$

- **Overall reaction:**

The overall reaction for plastics degradation process can be summarized in the given form

$$h^{+}_{VB} + \text{Plastic} \longrightarrow \text{Oxidize Product} \quad (7)$$

$$^{\cdot}OH + \text{Plastic} \longrightarrow CO_2 + H_2O \quad (8)$$

$$e^{-} + \text{Plastic} \longrightarrow \text{Reduced Product} \quad (9)$$

b. Direct degradation:

TiO2 can directly degrade the pollutants also takes place to some extent under visible light by exciting of plastics from the ground state to the excited state upon photon incident.

This excited state of plastics forms semi-oxidized cation radicals through e-injection in CB of catalyst.

Trapped electrons react with dissolved oxygen and form O2•- which subsequently forms •OH. This is responsible for target pollutant decomposition.

$$h^{+}_{VB} + \text{Plastic} \longrightarrow \text{Plastic}^{*} \quad (10)$$

$$TiO_2 + \text{Plastic}^{*} \longrightarrow \text{Plastic}^{+} + TiO_2^{-} \quad (11)$$

The indirect mechanism of plastics degradation is more effective than the direct mechanism, in term of the plastic decomposition and also in term of speed.

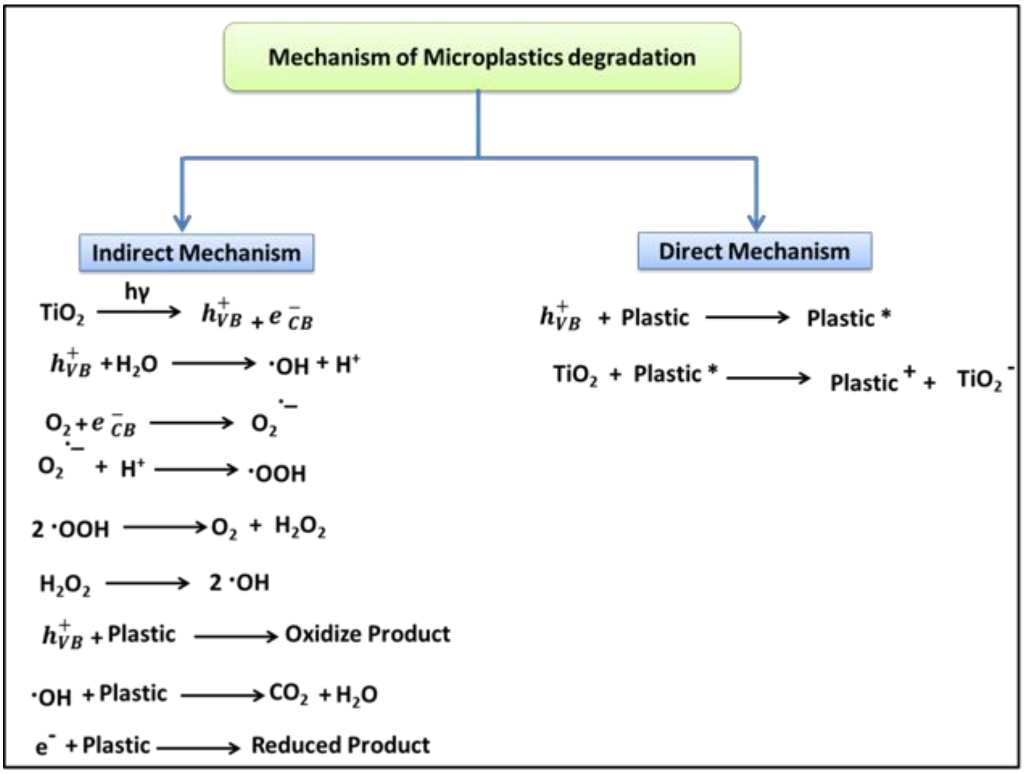

Figure 2.3: Overall Photodegradation Mechanism of TiO2 for Microplastics Decomposition under Light Irradiation

2.2.3 Biotic Degradation of Plastics:

If the deterioration of plastics is due to organisms, then it is known as biotic degradation. Organisms can degrade plastics either physically (by biting, chewing) or by digestive fragmentation or by biochemical processes.

Microorganisms, including bacteria, fungi, and insects are primarily responsible for the biological degradation of plastics. These processes have been discussed & presented in several research papers. Biodegradation can occur aerobically and produce CO_2 and H_2O, or anaerobically and produce CH_4 in addition.

Extracellular enzymes (like sterase, lipase, lignin peroxides, lactase, and manganese peroxides) of microbes are very important because they can increase the hydro-philicity of the plastics polymers by converting to a functional group such as carbonyl or alcohol that can enhance microbial attachment and further biodegradation. Hydrolases (such as lipases, esterase, poly (3-hydroxybutyrate) are extracellular enzymes and have the ability to break plastics elements into smaller molecules. These enzymes might attach to specific sensitive bonds in the side chain of polymers or chemical groups on the polymer chain (to enhance the chain cleavage) during biodegradation process. However, considering their size, the possibility to diffuse into the polymer structure is low. Therefore the degradation might occur on the surface, resulting in cracks.

2.4 Summary:

Micro plastics (Mps) have become a global problem due its adverse effect on environment and living organisms. Currently, plastic wastes have been widely found in various environmental mediums such as water, soils and atmosphere. As such, it is extremely necessary to remove MPs from the environment. We have discussed different degradation technologies to remove microplastics from environment especially TiO_2 based photodegradation which is an effective and low-cost solution.

2.5 References:

1. Mousa H.M., Alenezi J.F., Mohamed I.M.A., Yasin A.S., Hashem A.F.M., Hay A.A. (2021), Synthesis of TiO_2@ZnO heterojunction for dye photodegradation and wastewater treatment. *Journal of Alloys and Compounds*, 886, 161169
2. Olajire A.A., Mohammed A.A. (2021). Bio-diected synthesis of gold nanoparticles using Ananas comosus aqueous leaf extract and their photocatalytic activity for LDPE degradation, *Advanced Powder Technology*, 32, 606-610.
3. Uheida A., Mejíaa H.G., Rehima M.A., Hamd W., Dutta J. (2021). Visible light photocatalytic degradation of polypropylene microplastics in a continuous water flow system. *Journal of Hazardous Materials*, 406, 124299
4. Xu Q., Huang Q.S., Luo T.Y., Wu R.L., Wei W., Ni B.J. (2021) Coagulation removal and photocatalytic degradation of microplastics in urban waters. *Chemical Engineering Journal*, 416, 129123