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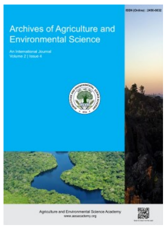

REVIEW ARTICLE

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A review of microplastics pollution and its remediation methods: Current scenario and future aspects

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ABSTRACT

Global plastic production and its use have been omnipresent since the early 19th century. The disposal of plastics undergoes breakdown due to various physicochemical and biological factors that trigger the formation of microplastics (MPs). Due to their hydrophobic properties, structural stability, and functional groups, it is difficult to degrade in natural habitat. The presence of their large surface area also helps to resist the decay of MPs. This review summarizes the recent trends and development of MPs degradation. The method includes biodegradation, various types of advanced oxidation processes (AOPs) such as photocatalytic oxidation, photo -degradation, and electrochemical oxidation, and also discussed the potential health risk factors of MPs and their degradation products. Most of the methods achieved nearly satisfactory performance that degraded the MPs into CO_2, H_20, and also secondary microplastic particles with persistent organic pollutants (POPs) under laboratory conditions, which have been studied by various researchers. It is also evident that the degradation of MPs has many challenges, therefore finding a sustainable approach is an urgent need to deal with the issue of global microplastic pollution. Some suggestions have been highlighted such as toxicity detection of remaining MPs particles after degradation, and analysis of secondary metabolites of microbes secreted during bioremediation that may have a negative impact on the environment. The selective and specific implementation of microbes and photo-catalyst that degrade MPs into useful and nontoxic components.

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INTRODUCTION

In our daily life, plastics play a key role in giving great comfort because of its properties such as light weight, low cost, durability, etc. (Gu *et al*., 2020). However, plastics are considered a highly persistent pollutant for the environment as they cannot be degraded naturally, thus known as a non- biodegradable pollutant. As per the report by (2019) Plastics Europe, global production of plastics has crossed 350 million tons, so scientists warn that it may cross 500 million tons by 2025 if we cannot take any immediate steps for its mitigation (Geyer *et al*., 2017). Due to various physicochemical and biological activities, plastic products decomposed into small particle sizes in the form of nano plastics (<1 μm), micro-plastics (≥1 μm to <5 mm), meso-plastics (≥5 mm to 5 cm), macroplastics (>5 to 50 cm), and mega-plastics (>50 cm) (Lebreton *et al*., 2018) that can be present anywhere in the environment such as air, soil, water and any other environmental media (Jiang *et al*., 2020). They can even move long distances under air and water currents. Among all, microplastics (MPs) can readily penetrate the human body via food chains. Therefore, is a great threat to human beings (Gaylarde *et al*., 2020). Their toxicity is related to their complex and diverse properties such as their composition, shape, and size. It has been reported that very small and fiber-shaped microplastics are more toxic in nature (Pirsaheb *et al*., 2020).

Basically, there are two main aspects of microplastics and plastics toxicity to organisms: 1) the intake or accumulation of plastics inhibits the normal metabolism of animals and human beings, which triggers their intestinal functions, neurological activities, and reproductive health and can be lethal in serious cases. Thus, it has self-toxic effects (Zhu *et al*., 2019). Apart from their normal compositions, plastics may contain several additives such as UV stabilizers, biocides, color pigments, flame retardants, etc. Under stress conditions, such as strong air and water pressure, strong irradiation of UV light, natural weathering, etc. releases these components into environments and cause damage to the natural biota (Lambert *et al*., 2014). 2) microplastics have a very small size and large surface area. It has a strong ability of adsorption and thus adsorbs various substances such as persistent organic pollutants (POPs), heavy metals (Zn, Cu, As), etc. These adsorb substances can travel via the food chain. Since these are persistent and toxic in nature, they can disrupt the natural food web, thus having a load toxicity effect on the environment (Wang *et al*., 2021a**)**. The destruction of plastics and microplastics is very important for determining the fate of the environment. However, the knowledge of plastic degradation and the development of microplastics is still limited and requires a better understanding (Andrady *et al*., 2017). Currently, there is undergoing various research and developments for the degradation of microplastics based on the intervention of biotic components such as (fungi, bacteria, and algae) and also various types of advanced oxidation processes (AOPs) such as (photocatalytic degradation, photodegradation, and electrochemical degradation) which help for their structural destruction via depolymerization into oligomers, dimers, and monomers. Under biodegradation, the main factors responsible for the destruction of plastic polymers are enzymatic actions, temperature, and specificity (Ganesh *et al*., 2019). AOPs are currently one of the most studied and hot trends used for the degradation of microplastics (Du *et al*., 2021). To maintain the sustainability of the environment, control over plastic pollution is a must. Since, it is persistent in nature so conventional approaches such as coagulation, flocculation, sedimentation, incineration, etc. may restrain the formation of microplastics (Zhang *et al*., 2020a). Incineration is the process of burning wastes at high temperatures to convert them into ashes. However, due to the release of dioxins, it is difficult to decompose, as dioxins are one of the most highly toxic chemicals. Once it enters the human and animal body via the food chain, it will disrupt the normal metabolism and triggers reproductive and endocrine functions. It is lethal due to cytotoxic and neurotoxic in nature (Yang *et al*., 2012). There is always a chance that MPs escaped with final effluents released into municipal water and water bodies such as rivers, lakes, and the sea directly. Presently the reliable and the most promising approach for the fate of MPs in recycling and utilizing is the chemical recycling approach that transforms the wastes into useful products which can be used as fuel (Miao *et al*., 2020). This review aims to summarize various MPs degradation methods such as biodegradation, different types of advanced oxidation processes (AOPs) i.e. (photocatalytic degradation, photodegradation and electrochemical degradation), and also discussed potential risks factors for human beings and also highlighted some suggestions such as toxicity detection of microplastics degraded products, the effect of secondary metabolites secreted during biodegradation, implementation of specific microbes based on proteomics and genomics and also the specific selection of photocatalyst which degrades the MPs into useful and nontoxic components.

METHODOLOGY

The process of review was carried out by specific internet searches using Pub Med, Science Direct, Scopus, and Web of Science databases. The articles, most of the last 10 years were studied thoroughly to understand the challenges and possible future perspectives related to microplastic pollution and control mechanisms. The keywords (plastics or microplastics); (ecosystem, or habitat); (remediation or degradation); (advanced oxidation process or biodegradation) were used. This process helped allow and sort recent advances in microplastic pollution and control strategies. The published articles on macroplastics were excluded and articles from predatory journals were not taken into consideration. Finally, the searched data were analyzed and presented in a proper manner to understand the background of this article.

METHODS OF MPs DEGRADATION

This review focused on the biodegradation and different types of advanced oxidation processes (AOPs) such as photocatalytic oxidation, photo-degradation, and electro-oxidation which work significantly for the remediation of microplastics (MPs) pollution.

Bioremediation of MPs

It is the process of the mineralization of plastics with the intervention of biotic components such as (fungi, bacteria, and algae). It involves the formation of biofilms on the surface of plastics that results in the destruction of the structural integrity of plastics through depolymerization under the action of specific enzymes. The products may involve oligomers, dimers, and monomers along with carbon dioxide, water, and depolymerization by-products (Zhang *et al*., 2020a). Biotransformation may occur resulting in the formation of persistent organic pollutants (POPs) which is toxic to the environment. Under aerobic conditions, the end products of biodegraded plastics involve water and carbon dioxide; carbon dioxide and methane under anaerobic conditions (Giacomucci *et al*., 2020). Marine animals range from zooplanktons to top predators and decomposers ingest MPs (Alomar *et al*., 2017). Although it is harmful to them. Their toxic effects in the wild environment are still unknown because most experiments are conducted ex-situ so further study is needed for proper validation (Lenz *et al*., 2016). Figure 1 is showing the pathway of MPs biodegradation.

Algae are the oxygenic photo-autotrophic organisms that take plastics as a source of carbon and thus degrade the polymers.

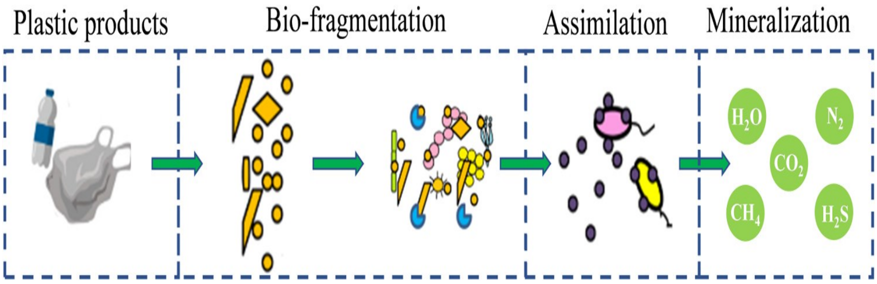

Figure 1. *MPs biodegradation pathways (Source: Hao et al., 2021).*

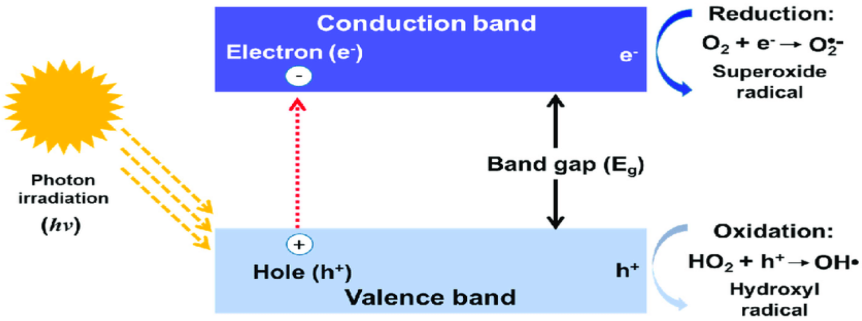

Figure 2. *Mechanism of photo-catalytic process (Source: Park et al., 2019)*

Algae, specifically microalgae have been tested for bioremediation of MPs over years and has found the promising potential microorganisms (Roccuzzo *et al*., 2021). Very limited work and research have been done up till now and only a few strains of algal species are known to have the ability for the degradation of microplastics and plastic particles. Algae produce lignin and extracellular polysaccharides on the surface to degrade the plastic wastes (Sarmah and Rout, 2018). It has been observed that some sources of algae (*Scenedesmus dimorphus, Anabena spiroides*) colonized over the surface of plastics and degrade the polymer. The same phenomena were observed using diatom, *Navicula pupula* (Ramachandran *et al*., 2017). Degradation can be specified with reference to the type of microplastic polymer and the candidate species because a higher degradation rate of polyethylene terepthalate (PET) was found followed by polyethylene (PE) in a study (Khoironi *et al*., 2019). Using the biotechnological approach, algae can be used as a source of engineered PETase (Zurier *et al*., 2020). For the duration of 60 days *Bacillus sp.* and *Paenibacillus sp* effectively reduced the size of polypropylene (PP) (Park and Kim *et al*., 2019).

Similarly, *Bacillus cereus and Bacillus gottheilii* reduced the size of various components of MPs such as polyethylene (PE), polyethylene terepthalate (PET), polypropylene (PP) and polystyrene (PS) within 40 days under lab conditions signifies the reduction of MPs weight and quantity (Auta *et al*., 2017). Fungus, *Aspergillus flavus* also played a significant role for the degradation of plastics (Zhang *et al*., 2020b). Biodegradation has gained worldwide acceptance due to its eco-friendly and affordable nature. However, there are several drawbacks such as time-consuming, difficulty in on-site implementations, species-specific gaps, etc. So, these issues need to be considered for the degradation of MPs in terms of a sustainable approach to gain microplastic pollution under control without harming the natural environment.

Photo-catalytic oxidation of MPs

It is regarded as a green technology that can degrade organic pollutants into water, carbon dioxide, and inorganic acids (Ariza-Tarazona *et al*., 2020). The method for the degradation of microplastics is mainly based on semiconductor materials such as (TiO_2, ZnO, etc.) which act as a photocatalyst and the source of the photon which influence the process of degradation of MPs (Nabi *et al*., 2020; Uheida *et al*., 2020). Figure 2 is showing the process of photo-catalysis. The very first step in the photo-catalytic process is the excitation of photo-generated electron (e^-) and hole (h^+) pair when a sufficient form of energy must be equal to or higher than the band gap energy (E_g) falls. The narrow band gap is more favorable for the process. In simple terms, the electrons (e^-) in the valence band (VB) transfer to the conduction band (CB), and thus the positive holes (h^+) are produced in the VB (Nakata *et al*., 2012). These charged particles can come to rest from the excited condition on the surface. The excited electrons will react with dissolved oxygen in the water and produce superoxide radicals ($.O_2^-$) and further decomposed into hydroxyl radicals (.OH). The separated holes react with a water molecule and produce hydroxyl radicals (.OH). These radicals are highly reactive oxygen species (ROS) that involves in the degradation of organic pollutants and plastic products (Tofa *et al*., 2019a).

(Ariza-Tarazona *et al*., 2020) found that using C, N-TiO_2 as photo -catalyst works better for the degradation of MPs. Under the exposure to direct sunlight for 50 hours, the degradation efficacy of HDPE was 70%. (Uheida *et al*., 2020) used ZnO-NRs (zinc oxide-nanorods) as a photo-catalyst and the degradation rate was > 65% when PP was exposed to 500 hours of incubation time. Nabi *et al*. (2020) found more than 98% of complete mineralization of MPs polystyrene, polyethylene, polyether sulfone (PS, PE, and PES) to CO_2 and H_20 when exposed to UV light for 12-14 hours using TiO_2 nanoparticles as photo-catalyst.

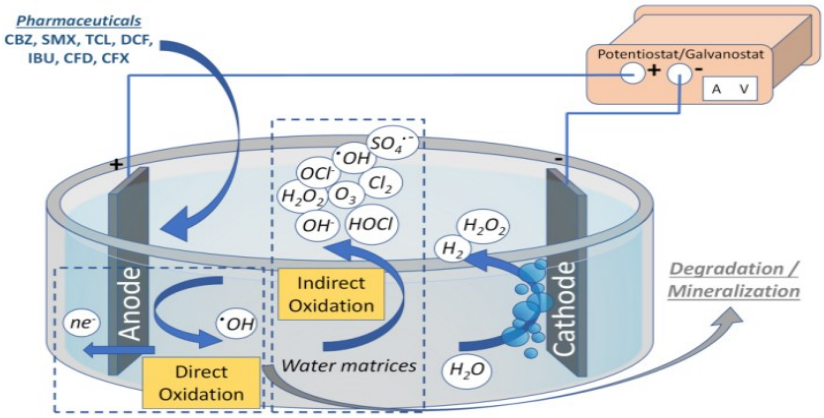

Figure 3. *Mechanism of electro-oxidation process (Source: Bampos et al., 2021).*

Photodegradation of MPs

The irradiation of UV light can break the molecular structure of plastic polymers and can cause cross-linking reactions to form new polymer structures, oxidation of polymers, and other by-products such as gases (Gewert *et al.*, 2015). Different wavelengths of UV light and depending on the type of chemical bonds present in the plastic polymers can determine the destruction of microplastics. In the natural environment, the degradation of MPs under the exposure of light energy is the common mode and is often called oxidative decomposition as plastics activated their electrons in order to achieve higher reactivity (Singh and Wahid, 2015). Under xenon light treatment, it has been found that the hydroxyl content and surface area of MPs increased; thus, disrupting their structural integrity (Luo *et al.*, 2020). There have been found significant changes in the morphological and mechanical properties of microplastics when it was exposed to UV light. It was confirmed using scanning electron microscopy (SEM) which proves the reduction of plastic properties (Ainali *et al.*, 2021).

Electro-chemical oxidation of MPs

It is an electrochemical technology that has gained a lot of importance in the last two decades because of its significant results for wastewater treatment. It is composed of two electrodes i.e., anode and cathode that are connected to a power source which works when a sufficient source of energy along with supporting electrolyte is applied to the system, then strong oxidizing species are formed that degrade the contaminants and form CO_2, H_2O, and intermediates or may completely mineralized (Anglada *et al.*, 2010). Electrochemical oxidation is divided into indirect cathode oxidation and anodic oxidation. Among both, the most common and generally suggested method is anodic oxidation (AO). It involves the direct oxidation of organic pollutants on the surface of an anode via the transfer of charges. Indirect oxidation of pollutants involves hydroxyl radical or reagents (such as hydrogen peroxide, ozone, peroxy-monosulfate, etc.) in an aqueous solution as shown in Figure 3. Indirect cathode oxidation is also known as the Electro-Fenton process (EF). The hydroxyl radical or other reactive oxygen species (ROS) forms through the decomposition of hydrogen peroxide via the catalytic reaction of Fe^{2+}. Free radicals are responsible for the degradation of organic pollutants by generating a redox reaction. (Miao *et al.*, 2020) studied the decomposition of PVC microplastics using the EF system, which is based on TiO_2 / graphite cathode.

The result showed successful degradation of PVC MPs with more than 55% weight removal and 75% dechlorination ability at 0.7 V vs Ag/AgCl at 100°C for 6 hours. Sulfate and hydroxyl radical are proved to be very effective in the elimination of persistent organic pollutants in water (Moreira *et al.*, 2015). Sulfate-based free radical exhibits great ability for catalytic degradation of cosmetics microplastics that consists mainly of polyethylene (Kang *et al.*, 2019). Easy operation, less secondary or tertiary pollution, and strong controllability make the EF process sustainable with the assistance of efficient heterogeneous catalysts that generated free radicals for the degradation and elimination of organic contaminants and MPs (Chen *et al.*, 2020).

INFLUENCE OF MPs ON ENVIRONMENT

The presence of microplastics is ubiquitous to the environment which is interconnected via diverse networks, which triggers the integrity of both biotic and abiotic components (Chunzhao *et al.*, 2019). It adsorbed various toxic chemicals in the environment and transported them within different habitats and consumed by diverse groups of aquatic organisms. It resists the growth of microorganisms such as algae, bacteria, and yeast, thus affecting their fundamental positions in the environment, and finds various ways to affect terrestrial organisms through respiratory pathways, especially humans. It triggers normal metabolic performance, can accumulate inside cells and shows cytotoxic effects (Hu *et al.*, 2020). The degradation of microplastics sometimes releases harmful and potentially hazardous substances such as organic contaminants, co-polymers, etc (Chunzhao *et al.*, 2019). Photodegradation of PE microplastics inhibits the growth and liver functioning in juvenile grouper, *Epinephelus moara*, mainly due to their accumulation in their bodies and secretion of endogenous contaminants (Wang *et al.*, 2020b). The presence of microplastics and their toxic degradation products affects soil fertility by disrupting soil microbe's structure, nutrient uptake capacity by plants, and soil physicochemical properties (Sintim *et al.*, 2021).

Challenges and suggestions

The degradation of microplastic releases some intermediate products that may be toxic to the environment. So it is important to find out a way to segregate the toxic products thus they cannot be sustained in the environment. Toxicity detection of the products after degradation is necessary to figure out their impact on the environment. Selective use of microbes and specific photocatalyst helps for the degradation of MPs into useful and non-toxic components. The application of proteomics and genomics can help in the isolation and selection of specific microbes for the degradation of MPs. The use of biotechnological tools can be implemented for the production of engineered microbial enzymes that degrade plastics.

Conclusion

Microplastics (MPs) are persistent organic pollutants that have gained serious concern over the last couple of decades because of their drastic impact on the environment. This comprehensive review summarized the possible current microplastics remediation technologies, their mechanisms, current developments, and challenges with suggestions. The technologies so far discussed here include advanced oxidation processes such as photocatalytic oxidation, photodegradation, electro-oxidation, and also focused on bioremediation technology. Traditional methods such as incineration and landfills are challenging due to their small size. There are few studies based on the environmental impact of microplastic degradation products and found to have potential risks. So, further optimization of the process of degradation, extraction, and identification of the products needs to be done. In near future, we can implement in-situ management of microplastic degradation if we overcome the knowledge gaps through proper research and developments to achieve fruitful results in a sustainable manner.

Conflicts of interest

The author declares no conflict of interests regarding the publication of this manuscript.

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