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Micro Plastics as Critical Micro Pollutants in Green Chemistry for Sustainable Environmental Protection

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The advent and utilization of plastics can be traced from the late nineteenth century when the first man-made plastic, termed Parkesine was developed by Alexander Parkes. Lesser did he know, despite the global and widespread longing for a plastic-free economy, plastics would become an inseparable component of almost every industry today. At this stage, we have brought to light the minute subsets of plastics, known as microplastics. As the term implies, microplastics are the tiny particles, or more appropriately, small fragments of plastic that originated from the disintegration of larger plastic objects, so tiny that they cannot even exceed the threshold of 5 millimetres. Sometimes, we deliberately produce small plastics such as abrasive powders deployed in industrial cleaning and call them primary microplastics while the secondary ones are a consequence of breakdown of larger plastic items due to various factors. Primarily contaminating soil, water bodies and the other components of the environment, microplastics are more of a hazard than an asset. Their non-biodegradable nature contributes to their adverse effects both on the surroundings and the living beings. They keep on accumulating in the environment, incorporating themselves into the food chain, soil and water leading to detrimental outcomes. Through this chapter, we would be uncovering what these microplastics really mean and the significance they hold around the globe. Additionally, we will be examining the dire and unfortunate results of the accumulation of these plastics in the ecosystem.

Keywords: Plastics, Microplastics, effects, environment, non-biodegradable

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Right from the beginning, it has been ingrained in us that despite their usefulness, plastics pose extreme threat to our environment, leaving behind a permanent imprint on the planet. It is not hidden from any of us that plastics do not degrade or vanish completely from the ecosystem, even after hundreds of years of their creation. Bio-degradable substances get decomposed by micro-organisms with the passage of time and the process is aided by physical factors too, leading to them being dissolving in the environment. On the contrary, plastics being non-biodegradable substances, never completely breakdown and keep on accumulating in the environment, entering our surroundings and the resources we consume, leading to poisoning of habitats. Professor Richard Thompson from the University of Plymouth in the UK, specializing in marine biology, was once surveying and examining the sea shores when he noticed something unusual.

Every day, he saw a heap of plastic debris on the shore, no matter how much he cleaned the litter. But what was really astonishing for him were not the large plastics objects like bottles, wrappers or fishing nets, but tiny, coloured plastic particles mixed with sand. These micro particles were never included in plastic pollution surveys, leading to a huge neglect in studying the various sources of pollution. This was when his students had been assigned the work of looking for these tiny plastic particles everywhere near the beach. What they discovered were blue and red coloured particles and some of them were even not visible to the naked eye. It was confirmed that it wasn't natural debris but synthetic polymers when they were scanned through electron microscopy. In 2004, Thompson published his breakthrough paper on microplastics, "Lost at Sea: Where Is All the Plastic?", in which the term microplastics was coined for the first time. He reported them as tiny fragments or particles of plastic, smaller than 5mm. through his publication, he asked some crucial questions- Do these plastics release injurious chemicals? Are they entering the marine life? How widespread is this pollution? These questions of Professor Thompson sparked a debate around the globe, leading to widespread research and recognizing microplastics as a major concern, both for the environment and the health of the living beings.

The first and the foremost thing that stuck people's minds was how are these microplastics formed? It would be surprising to know that not all

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microplastics in the environment form on their own. Some are intentionally created and are known as primary microplastics while the others are formed as a result of degradation of larger plastic objects [10]. Plastic are a part and parcel of the modern world. They exist everywhere, from our toothbrush that is the very first thing we use in the day, the lunchboxes we carry our food in, packaging materials to the electronic devices we use, healthcare, transportation and the construction sector. The list is endless and so are the forms of plastic. But it is a shocking reality that plastics can't truly be destroyed. They can only be converted from one form to another. It more logical than shocking. It is in accordance with the principle of conservation of matter, which states that matter can neither be created nor be destroyed but only be transformed from one form to another. In the case of biodegradable substances, they get decomposed by microorganisms and break down into simpler substances like carbon dioxide, water and other gases. All of these products are clean and do not harm the environment. On the other hand, plastics cannot be acted upon by microbes. They are non-biodegradable and never converted into a form that does not possess harm to the environment and the living beings. They keep on breaking into smaller fragments, leading to formation of microplastics and nano plastics. Even if they are burned, they release toxic gases and fumes, and leave behind ash. As a result, plastics, in any form, cannot be considered environmentally clean and safe.

The most intriguing question that now arises is that can these minute plastic fragments be more insidious than the larger plastic objects we use every day? Large plastic items have been known for their visible consequences on the environment since a long time but microplastics have stayed away from the limelight for an extended period of time. These small plastics are found in soil, water, air and even inside living beings. They are possible more dangerous than their larger counterparts, owing to their size, mobility and other factors. The very first concern regarding them is their size. Unlike macro-plastics, they are not easy to detect. Some are even invisible to the naked eye and often require microscopic instruments. They are harder to track and regulate as compared to larger plastic objects. Adding to this, they can be ingested by marine organisms and even birds and mammals. They cause both immediate and long-term effects. They accumulate in the bodies of living beings and can even become a part of the food chain. Moreover, they can carry heavy metals and disease-causing organisms with them due to their high surface-area-to-volume ratio.

EXPERIMENTAL

This paper aims at theoretically and conceptually analysing and examining the ongoing issue of microplastic pollution. The chapter throws light on the following key themes:

- Conceptualizing microplastics and origin-oriented categorization of microplastics
- The worldwide relevance of microplastics
- The deleterious role of microplastics in the ecosystem

In addition to this, we will be illustrating the journey of a microplastic from its source to the adverse effects it presents through the example of cosmetic microbeads. The idea of anything is best conveyed by something familiar and used in day-to-day life.

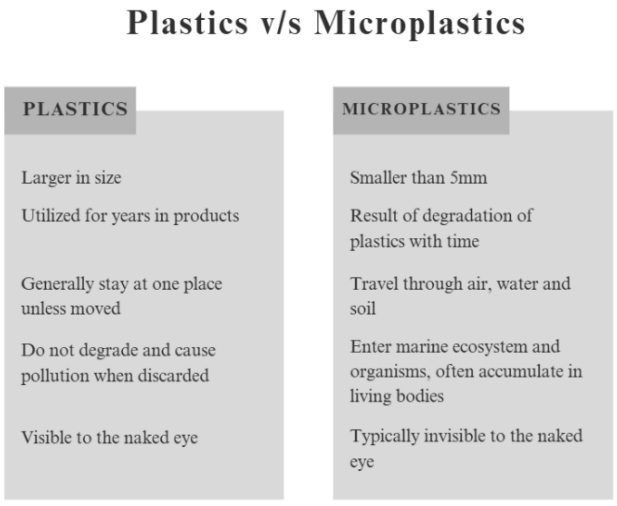

Figure 1. Difference between plastics and microplastics.

Understanding Microplastics and their Classifications

Definition and Terminology

Microplastics are minute particles or fragments of plastics, having a diameter less than 5mm. Typically, microplastics are larger than 1 micrometre and smaller than 5 millimetres. Plastics smaller than 1micrometre in size are termed as nano plastics, another member of the pollution causing plastic family. Generally, microplastics are indiscernible to the human eye and can only be viewed under a microscope. The shape and texture of microplastics isn't standard and varies from spherical, fibrous, irregular to films, foams and pellets, depending upon the origin and the degradation process responsible for their formation. Plastics are non-biodegradable materials which persist in environment for an extended duration with detrimental effects. Unlike the biodegradable ones, they do not decompose by the action of microorganisms and enzymes but keep on breaking into smaller fragments. Plastics are synthetic polymers, composed of a large number of repeating molecular units termed as monomers. Microplastics and nano plastics are no different but merely smaller fractions of plastics. According to the principle of conservation of matter, matter cannot be created or destroyed but only be changed from one form to another. Biodegradable materials breakdown on the action of microbes and get converted into non-poisonous products like carbon dioxide, water and other gases. Plastics, conversely, cannot be degraded into non-injurious products, owing to their structure and composition. They just breakdown into smaller plastic fragments.

Plastics are renowned for their durability, flexibility and resistance to the environmental stress or damage. Plastic products do not rust, break or get damaged by biological factors which makes plastics a widely chosen choice for manufacturing. But the same advantages which make plastics suitable for most applications make them responsible for harming the environment. Remember, plastics are not found in nature but engineered by human beings. Nature has the solution for everything it produces but mere consequences for something that harms it. The primary structure of microplastics relies on the carbon-carbon backbone. C-C and C-H are strong covalent bonds and possess high bond dissociation energies. This implies they require a huge amount of energy to be broken, making them resistant to processes like enzymatic action, oxidation and hydrolysis. In addition to this, microplastics are resistant to water. Metals like iron and steel are susceptible to corrosion by water but plastics are hydrophobic. This means they repel water and protected from the breakdown that can occur due to aqueous biological actions. Opposing natural polymers like cellulose, microplastics lack reactive sites (sites that contain functional groups) which makes them inert to the action of enzymes or microorganisms. The long list doesn't end here. Plastics are also added with some chemicals to further enhance their life time and strength. They contain UV stabilizers which make them impervious to photodegradation as these chemicals absorb the harmful UV radiations. Antioxidants prevent oxidation some other chemicals enhance flexibility and make them resistant to flame. These chemicals get integrated in the structure of plastics and provide them an extra shield against the environmental stress. All these factors are together responsible for the never degrading nature of plastics.

Classification of Microplastics

Plastics are not found in nature but created synthetically. When these plastics break into smaller particles, they give rise to microplastics and nano plastics. Are microplastics solely created by breakdown of larger plastic items? No. Some microplastics are manufactured intentionally while others are the result of breakdown of larger plastics. Microplastics are called primary or secondary on basis of their origin and how they were created.

Primary microplastics are manufactured intentionally. They are not smaller fragments of some larger plastics but manufactured for utilizing them in practical applications. Some of the examples of primary microplastics include:

Microbeads - These are spherical microplastics, typically less than 1 mm in size. They are commonly used in cosmetic and self-care products like scrubs, body washes, face washes, toothpastes, creams, etc, to name a few. These are also deployed in industrial applications as abrasives for cleaning. Their smooth texture and spherical shape are credited for their ability to act as exfoliants in cosmetics. They are buoyant which means they can float in water and inert to chemical reactions. All these characteristics make them a great choice in cosmetic products. But certain things serve great utility yet carry injurious consequences. Being plastics, they are non-biodegradable and tend to persist in the environment. They cannot be treated in wastewater treatment plants due to their size and buoyancy which lets them pass through the screens and other filtration devices designated for larger particles. As a result, they can enter water bodies with ease [1]. They enter the food chain and food web as they can be ingested by marine organisms like fishes and plankton, and can enter human bodies through sea food. Not only they persist and accumulate inside systems but they can additionally absorb and carry harmful chemicals, including pesticides and heavy metals, and transfer these to the bodies of living organisms. They can also cause physical harm to marine species by blocking their digestive tracts. Many nations are heading

towards the complete abrogation of microbeads in cosmetics to mitigate the havoc wrecked by these.

Nurdles or Preliminary Stage Pellets - These are very small plastic particles, or more appropriately granules, ranging from 2 to 5 mm in diameter, which are used as raw materials for the manufacturing of larger plastic products and items. These are raw plastic resin, which are the building units of every plastic product. It is a startling fact to note that their primary source of production is petroleum and natural gas. Components of crude oil are processed to form the polymers required to create the plastic resin. These pellets are shaped and created into different sized plastic items. Firstly, they are easy to manage. They are light weight, can be transported easily and can be converted into plastic products of any size. Owing to these features, the transportation is also economical. But everything has its pros and cons and these are no exception. They can escape during transportation as they are light weight and lentil sized. Due to this spillage, they are generally found near coasts and ports causing pollution. Like microbeads, they too can enter food chain and living systems and carry toxic chemicals with them. Most significant step while manufacturing plastics is handling these nurdles and prevent their spillage as much as possible.

Secondary, as the name suggests, these microplastics are not manufactured directly. They are a result of breakdown of larger plastic products, already existing in the environment. The breakdown of plastics occurs as a consequence some degradation process, which can be either physical, chemical or biological. Various mechanisms that lead to their formation are listed as follows:

Photo-degradation - 'Photo' signifies light. Photo-degradation refers to the breakdown of materials due to action of sun's ultraviolet radiation. The UV light has sufficient amount of energy to break the high energy C-C and C-H bonds in plastics. This process consists of various steps. In the beginning, the plastic absorbs electrons due to which the electrons present in the polymer bond get agitated and this energy is enough to break the bonds and the polymer chains, leading to formation of free radicals, an important step in photo-degradation. To prolong their lifetime, these plastics are added with stabilizers and UV blockers to slow down the degradation process. This is a chemical process which weakens the plastics chemically and causes them to become brittle.

Mechanical Abrasion - The term 'mechanical' clearly indicates that this is a physical process. Microplastics are formed when larger plastic items disintegrate into smaller fragments due to mechanical factors such as friction, collision with surfaces, wave action, wind action and scaping. The steps are different than photo-degradation as this is a process which follows the initial degradation process. It fragments already weakened plastics. Plastics that become brittle and chemically weak as a result of one of the chemical processes like thermal or photo degradation, are further disintegrated due to mechanical factors to form microplastics.

Thermal Stress - 'Thermal' means related to heat. Thermal stress is a result of repeated heating and cooling or sudden exposure to very high or very low temperatures, which takes a toll on a plastic's molecular bonds. We already know that plastics expand on heating and contract on cooling. When they are exposed to such extreme temperatures continuously, an internal stress is created which weakens the plastic material over time. There are various pathways for breakdown of plastics due to thermal stress.

Degradation of Polymer Chain - In this mechanism, heat causes breaking of polymer chains which leads to reduced molecular weight of plastic and making it brittle.

Speeding up the Oxidation Process - Sometimes, heat doesn't directly harm the plastics but aids other processes which can result in its degradation, as in this case. Oxygen reacts with plastics with more ease at high temperatures. This oxidation, aided by heat, is called thermal oxidation. This oxidation of plastic causes roughness of the surface and induces cracks in the material.

Rupturing due to Fatigue/Stress - When the material is continuously heated and cooled, even small cracks in it can enlarge which can lead to disintegration of the plastic.

Synergistic Effects - Combination of UV rays, mechanical abrasion and other factors with thermal stress multiplies the breakdown rate several times.

It is important to note that plastics are non-biodegradable materials and cannot be converted into some other form with the action of microorganisms.

Some real-world examples to illustrate secondary microplastics are as follows:

Bags Made of Plastic - The pair of UV radiations and thermal stress from the heat of sunlight leads to the scission of polymer chain of polyethylene which causes the plastic to become weak and develop cracks over time.

Ropes and Nets - Fishing nets and ropes are subjected to repeated action of waves and rocks which results in mechanical abrasion [4]. When the UV rays mix with the seawater, the rate of polymer disintegration increases dramatically. This triggers the fibres in these materials to detach and leads to the formation of threads of microplastics.

Clothing Items Made of Synthetic Materials - Clothes made of synthetic fibres such as nylon, polyester, when washed, undergo various damages due to friction (mechanical stress), detergent (chemical exposure) and heat (thermal stress) which causes embrittlement of fibres and even their breakdown into microfibers. It would be interesting to note that a single clothing item made of these materials can give rise to 1 lakh+ fibres in a single wash. Just think of the cumulative release of microfibers from merely these garments.

Significance and Relevance of Microplastics Around the Globe

The global significance of microplastics is not limited but spans over multiple facets such as innovation, convenience, ease, degradation of environment and heated debates centred around its use. Knowing the widespread use of plastics, it is not astounding to discover that microplastics are found in all kinds of environments, whether the it's the blue-green oceans, the soil cover, the air around us or our own bodies. According to Ocean Conservancy organisation, microplastics are found in all marine habitats [2]. The synthetic clothes we wear have a share of 34.8% in the microplastics present in oceans. This implies that every time we wash our clothes, they shred millions of tiny fibres, which pass through the wastewater treatment plants. These numbers also highlight the fashion trends around the world. In the fast-pacing era, people are also heading towards fast fashion. Not only for the products we use, but we are relying on cheap, synthetic fibres even for the clothes we wear. These synthetic fibres are non-breathable, contrary to natural fibres like cotton and linen. They trap heat and moisture inducing skin irritation, rashes, allergies and bacterial growth, especially in humid conditions. But it is unusual to note that the friction of tyres accounts for a significant 28.3% share. Tyres worn out due to friction and produce tiny, synthetic particles which get washed away with surface runoff into water bodies and ground water. There is an urgent need for better runoff management rather than letting it simply wash away into water bodies and developing filtration systems to trap microplastics. Steps like imposing ban on plastic items, say, bags and cutlery miss the bigger picture. The wearing out of tyres is rarely discussed or addressed as a cause of microplastic production. We need to fill the policy gaps to combat these seldom discussed issues. Indirectly, it hints at rethinking about vehicle design and tyre composition, along with its durability.

Studies have shown that synthetic paint is one of the most dominant sources of microplastics in the aquatic environments [8]. Most paints nowadays are composed of synthetic polymers like acrylics and epoxies. When paints wear down, chip or flake, they produce small particles of these synthetic polymers which are microplastics. Ship paints majorly contribute to the ocean pollution caused by microplastics [3]. Ships are layered with anti-fouling paints to prevent the growth of algae. Ships are always in contact with ocean water and at the risk of barnacle and algae growth. To prevent them from this damage, the paints containing synthetic polymers are used. The ship along with the paint is exposed to UV rays, saltwater and mechanical stress like winds, ocean waves, etc, regularly. with the passage of time, the breakdown of the synthetic polymer containing paint occurs and releases small particles of this paint. These particles, essentially, microplastics enter the ocean. Alarmingly, marine paints are projected to release approximately 2 million tons of microplastics directly into the ocean, rendering them the title of one of the major contributors of microplastics present in oceans. Other than the tyre itself, road markings also wear down due to the friction caused by tyres of moving vehicles. These road markings are also paints containing synthetic polymers. Inappropriate disposal of paint wastes and cleaning tools used for painting can also result in release of microplastics. Microplastics are generally associated with plastic products like bags and straws but we do not care to understand that most of the major contributors of microplastics are always overlooked. Marine paints are not only synthetic polymers but also contain harmful chemicals to prevent the action of sunlight and algae growth. These chemicals are heavy metals and biocides which are extremely harmful for marine organisms. The fight against plastics is much beyond the scope of banning of plastic bags. Some better alternatives need to be found for ship paints and ports need better regulation. Most countries are heading towards a plastic free economy but lack regulations for the release of microplastics from marine paints. Have you ever heard a 'say no to plastic' campaign listing marine paint as a source of microplastic pollution? Lack of awareness is what wages lack of standards. These often-neglected causes of microplastic emissions need to be paid attention to.

The long list of sources of microplastics do not end here. Microfibers are not only the ones released by the synthetic fibre garments we wash every day but also entail cigarette butts [3]. There are some elements that prove to be detrimental across all dimensions and cigarettes are one of them. Everybody knows what serious damage cigarette causes to our bodies. Not only through active and passive smoking, but even after being used they possess harm to the environment. The filter of cigarettes is made of cellulose acetate, a plastic that takes 10 years to break down. It is inculcated in the cigarette to trap toxins from the tobacco smoke. After being used, the filter contains harmful chemicals like heavy metals such as lead and arsenic, carcinogenic compounds, tar and nicotine. When thrown away, these filters gradually break down into microplastics due to UV radiation and mechanical stress. They get

washed into water bodies due to rain water, storms and winds. It has been observed that a single cigarette butt can defile 1000 litres of water with harmful chemicals. Toxins from them can poison aquatic animals and can alter water quality. More than 5.7 trillion cigarettes are smoked in a year worldwide and around 3 lakh tonnes of microfibres are released from them. Fines need to be imposed on those who litter cigarette butts. There are regulations on smoking in some places but nobody cares about the after effects of the improperly disposed cigarettes. In addition to this, mandate producer accountability for cigarette filter waste under EPR (Extended Producer Responsibility) regulations. This implies that tobacco companies would be legitimately responsible for the entire lifestyle of cigarette filters, even after they have been used and produce waste. Companies would be required to fund and manage the waste collection of cigarette butts. People need to be made aware about the adverse effect of cigarettes not only on their bodies but also on the environment.

Devastating Effects of Microplastics on the Environment and Health of Living Beings

Human beings embody the nature to be drawn towards convenience. Convenience is what we yearn for, work for and look for, even at the expense of long-term well-being. Plastic is a material that provides convenience along with flexibility and durability. These traits of plastic have made it a popular choice for every single product we use. From the bags we carry daily to the paints that sit on the walls of our homes, plastics have transformed industries and our daily lives by being affordable, convenient and versatile. But what is making us choose them over and over again even when we are aware of their consequences. Plastics, being non-biodegradable materials, do not breakdown into non-poisonous products by the action of microorganisms. They are synthetic polymers that either need to be burned or they themselves breakdown into microplastics and nano plastics. But these microplastics pose a grave threat, both to the environment and living beings.

Adverse Effects on the Aquatic Ecosystem

The most visible and threatening effects of microplastics are on the oceans and the marine life. Oceans are the ones that get preyed upon by microplastics directly. Tiny fragments of plastics breaking from ship paints, particles of worn-out tyres from the roads that get washed away into oceans, fishing nets, ropes and many more to name, directly enter the oceans [5]. Approximately 8 million tons of plastic waste enters the oceans annually.

Microplastics are mistaken as food from aquatic organisms like fishes, turtles and plankton. Once they enter the bodies of these organisms, they can cause severe consequences such as blocking of the digestive tract, improper nutrient absorption and even death [9].

Plastics are added with chemicals to improve their durability and prevent their breakdown form UV radiations, thermal and mechanical stress. They can also absorb toxic substances from the environment such as heavy metals and pesticides. Microplastics, too, carry these insidious substances. These materials get accumulated in the bodies of these organisms and pose long-term harm. They enter the food chain and can even reach human beings.

Microplastics in the oceans can also lead to habitat disruption. They settle on the ocean floor and alter the sediment composition which adversely affects benthic organisms and coral reefs.

Contamination of Soil

The primary source of microplastics found in soil[4] is plastic mulching. The use of thin plastic films to cover soil results in its breaking into small particles and entering the soil. Agriculture also involves practices like spreading the collected sludge from wastewater treatment onto the fields as fertilizers. But microplastics are minute enough to pass filters and is collected with sludge. Due to this, the soil cover in the fields gets exposed to microplastic pollution. Improper waste disposal, escaping of microplastics from landfills, plastic pellets lost during production or transportation and degradation of larger plastics like bags, bottles and straws over time, all contribute to the increasing amount of microplastics in the soil. Microplastics negatively impact plant growth and microbial activity in the soil by affecting the composition, porosity and water retention of soil. The toxic chemicals present in microplastics can leach into soil causing toxicity and affecting soil health.

Detrimental Effects on Biodiversity

Microplastics possess great threat to various species present in the ecosystem [6]. Through seafood and plants, they can enter human bodies and can enter the bodies of animals through their prey. Microplastics get incorporated into the bodies of foundational species like plankton and worms due to which the entire food chain and web can collapse. Prolonged and continuous exposure to microplastics is known to cause fertility issues in various species, resulting in reproductive problems.

Challenges Linked to Waste Management

As already discussed, plastics do not breakdown in a clean manner [7]. They release toxic substances when burned or just break into smaller particles with the passage of time. A very small share of plastics, around 9%, is recycled worldwide. Rest stays in the

environment or subjected to incineration and put into landfills. Plastics fragment even during recycling. Managing plastic waste is a challenge to clean and circular economies.

RESULTS AND DISCUSSION

It can be deduced from the above- mentioned findings that microplastics are structurally identical to plastics, just smaller in size. As plastics are non-biodegradable materials, they are immune to the action of microorganisms and cannot be broken down into simpler substances by clean methods, nor they disintegrate into non-toxic products. Plastics are a popular choice in all the industries due to their durability and convenience but not a favourite of the environment. Furthermore, the investigations indicate that microplastics come from both primary and secondary sources. The plastics that are manufactured intentionally in minute sizes for some practical applications are called primary microplastics. On the other hand, when large plastic products fragment into smaller particles due to action of sunlight, heat and mechanical factors, they are referred to as secondary microplastics. In conjunction with this, the chapter has drawn attention towards the significance of plastics throughout the world. Microplastics are found in all kinds of environments, whether they are oceans, soil, air or the bodies of living organisms. A startling fact has been revealed by the studies. The least discussed factors contribute to the major amount of microplastics found in the environment. For common people, microplastics are synonymous to plastics bags and bottles. But what has been observed is that marine paints, particles produced due to the friction between the tyres of vehicles and the roads, and cigarette butts are the hidden elements responsible for the ever-increasing volume of microplastics in the ecosystem. The last section of the chapter discussed about the ill effects of the microplastics on the environment and the living beings. Microplastics affect all the organisms, from the aquatic species such as fishes and plankton to the plants in the soil and even the bodies of organisms living on ground. Through these organisms, they enter food chain and food web, ultimately reaching the bodies of human beings. The use of plastics and their breakage into microplastics is causing an imbalance in the ecosystem. Alternatives need to be found and plastics need to eliminated from the lives of the organisms living on the planet.

CONCLUSION

The modern world may has relied on plastic for its needs and convenience, but what needs to be kept in mind is their blind use which is causing significant harm to the nature and its creations. Better and clean alternatives need to be found urgently. We are sitting on a ticking time bomb that would bring irreversible destruction when it explodes. Development and economy have to come in harmony with the nature, not at its cost. Immediate attention is needed and strict actions have to be taken to halt the skyrocketing damage caused by plastics.

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