Detection of microplastic and poly-perfluoroalkyl substances in treated sewage water: Review

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***Abstract-* The article, "Detection and Remediation of Microplastic and Poly-Perfluoroalkyl Substances (PFAS) in Treated Sewage Water," reviews environmental concerns surrounding microplastics and PFAS. Microplastics, minute polymer particles measuring less than 5 mm, have infiltrated aquatic ecosystems, posing threats to marine life and entering the human food chain, potentially causing health problems. Conversely, PFAS, industrial chemicals, are linked to human carcinogenicity and are released from submerged microplastics. Despite sewage treatment efforts, both microplastics and PFAS persist in treated water, posing a persistent challenge. The review employs advanced techniques such as Fourier Transform Infrared Spectroscopy (FTIR) to precisely detect microplastics and PFAS in treated sewage water. Additionally, the article investigates the role of Lactic acid bacteria producing exopolysaccharides, substances that adhere to microplastics and PFAS, leading to their sedimentation and facilitating removal through filtration processes. Understanding these biological processes enhances wastewater treatment methods and fosters the development of effective remediation techniques. Remediating water sources for microplastics can lower the hazards of exposure to humans and health problems. We can reduce the possible effects on the ecology and public health by carrying out this activity.**

***Index Terms*: Microplastics, poly-perfluoroalkyl substances, exopolysaccharides, FTIR.**

I. INTRODUCTION

Plastic pollution is regarded as one of the most serious dangers to the world ecology, affecting both biotic and abiotic components. It is widely used in various industries because of its lightweight nature and durability of the material and the low cost [1]. In last few years, the growth of plastic production has drastically increased reaching 230 million tons in 2009. Although the plastics were considered as harmless and inert, however after many years of plastic disposal there is a report exhibiting that the chemicals present in the plastics leach out into environment causing the various human health issues and environmental pollution [1]. There are 20 types of prime plastics used worldwide. Approximately 50 percent of plastics are used for single-use disposable applications, such as packaging, agricultural films and disposable consumer items, between 20 and 25 percent for long-term infrastructure [2]. According to the WHO the present plastic production is increased to 158 million tons and 43% of global plastic waste are mismanaged resulting in the 68million tons of plastic in the nature and it is estimated to triple by the year 2050 [3]. The global average consumption of plastic per person is 20.9kgs. Asia is the biggest maker and producer of plastics in the world. Among worldwide plastic producers, China is the largest producer by 32%, followed by North America (18%), rest of Asia (17%), Europe (15%), middle east and Africa (8%), Latin America (4%), Japan (3%), CIS (3%). Various plastic waste management is done to reduce the plastic pollution, like landfills, discarding into oceans, burning, and reusing. Each of these methods itself has the disadvantages like the usage of land to dump the garbage which can lead to land pollution, and the limitation of the natural resources. Research released by Geyer et al., 2017a, Geyer et al., 2017b claimed that from 1951 to 2015 just 9% of the plastic manufactured was recycled, 12% was properly burnt, and the other 79% was either publicly discarded, landfilled, or strewn in the environment, which is disturbing [4].

The plastics under the influence of Ultraviolet radiation, erosion, weathering and temperature process resulting in fragmentation of the larger plastic debris into smaller, micro range plastics. These fragmented plastics are of varying sizes, including microplastic (>25mm), mesoplastic (5-25mm), microplastic (0.001-5mm) and nanoplastic (<1μm) [5, 6]. The microplastics are classified as primary and secondary microplastics based on its origin. Primary microplastics are the polymers that are designed for commercial use. Typically, these minuscule particles are included into industrial and personal hygiene goods, such as scrubbing agents in toiletries and cosmetics (e.g. shower gels), toothpaste, oil, gas, and medicinal agents, as well as industrial and medical applications. Secondary microplastics are the larger plastic debris which are fragmented through photodegradation and other weathering processes of mismanaged waste [7]. Microplastics can be swallowed by a wide range of creatures, including marine life, birds, and terrestrial animals, causing physical injury, impaired feeding efficiency, and harmful chemical bioaccumulation [8]. Additionally, it has been shown that microplastics serve as carriers of pollutants, such as heavy metals and persistent organic pollutants

(POPs), hence endangering the health of ecosystems and species [9]. Concerns about microplastics extend beyond their environmental effect, with rising research pointing to possible hazards to human health. Microplastics have been found in a variety of foods, drinking water sources [10, 11]. Although the health effects of ingesting microplastics are still unclear and need further research, there are worries about the possible spread of diseases and hazardous substances linked to these particles [11, 12]. Addressing the challenge requires the indisciplinary research.
The remarkable stability and water- and grease-resistant properties of PFAS has led to their extensive use in the various applications, including manufacturing of non-stick cookware's, waterproof fabrics, and firefighting foam. Poly- and perfluoroalkyl substances (PFAS) are the class of synthetic chemicals manufactured and have strong covalent C-F bond and are thermally stable [13]. PFAS's broad usage and persistence have resulted in its prevalence in the environment, including air, water, soil, animals, and human tissue. This has raised worries about their possible negative impacts on the environment and public health. PFAS have been found in human blood, breast milk, and organs, as well as in populations of fish, birds, and mammals in the wild [14]. In the present-day, PFAS is a predominant concern for the cancer to spawn [15].

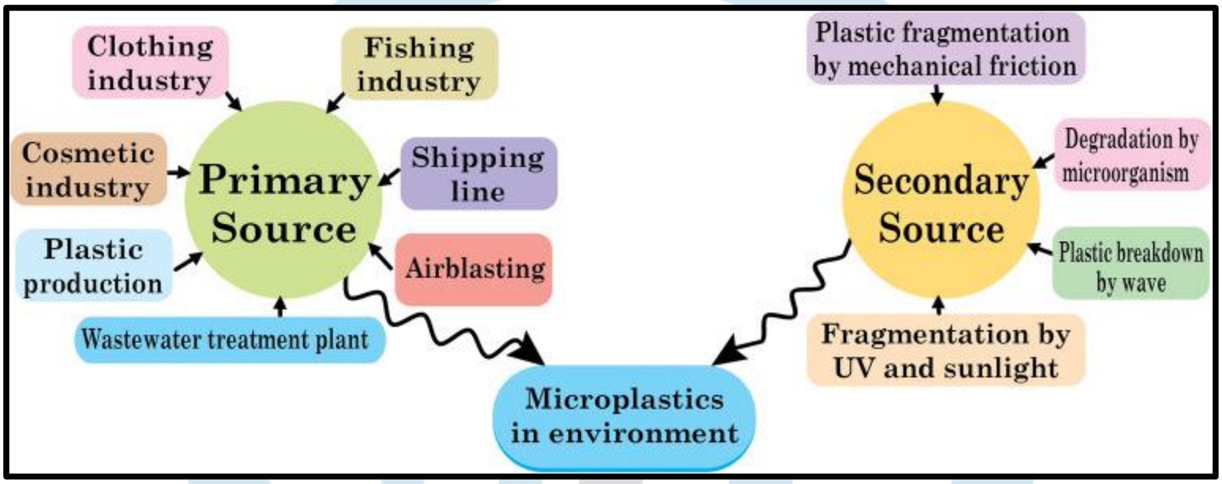

Fig 1: Origin and Classification of Microplastics [3].

II. METHODOLOGY

1. Collection and Sampling of Treated Sewage Water

The collection of water sample is the basic step in the microplastics detection. The microplastics are easily affected by the chemicals used in sampling methods. Therefore, the sampling of microplastics is the important basis for the analysis. The selection of water sample is done depending on the availability of the equipment and the objective of the work employed [16]. The sewage plants receive the public domestic waste products and pollutants from the public which leads to high microplastic concentration. A total of 5L of sample was collected from which 100ml was used for the total detection. Each sampling batch of 10ml of water was collected in 2×5ml in PET water bottles.

Table 1: Methods of sample collection with Advantages and Limitations [16, 17]

Methods	LOD	Advantages	Limitations
Nets	Particle collection ranging in size from 16 cm to 80 μm.	Easy to use. Simple and rapid method for sample collection.	Time consuming. Potential contamination by tow ropes. May become clogged or break.
Sieving	Achievable purification for particles larger than 100 μm [18]. Depends on the sieve mesh size chosen.	Simple method, does not require specialized equipment.	Laborious and time consuming; Samples medium volumes; Manual transfer of water with buckets

Filtration	It is feasible to purify particles larger than 10 nm [19]. Dependent upon filter pore size selected.	Potential for usage with particles in the submicron and nanoscale range Relatively easy, quick, and inexpensive procedure.	Risk of clogging if sample containing more amount of materials, time consuming depending on the mesh size,

2. Detection of Microplastics

Microplastics are distributed in the water based on their size, density, adsorption of chemicals and biofouling. Consequently, the depth and position of the sample have a significant impact on the amount and quality of microplastics retrieved [16]. Several approaches are used to detect microplastics. After a water sample is collected, the samples are mostly inspected visually for particles that are between one and five millimeters in size or under a microscope [6]. The glassware was washed three times before and after use. The greatest impediment to measuring microplastics in environmental samples is the removal of organic and biological contaminants. Since organic matter aggregates on the surface of many plastics, which are hydrophobic by nature, the organic matter must be eliminated before the microplastics can be spectroscopically identified.

The plastics in the water samples are filtered or sieved based on the size and rinsing it with ethanol before drying. These methods are most frequent method for separation of microplastics from the buoyant polymers present [20]. The filteration or sieving is done using the Whatmann filter paper of pore size 11μm, the filtrate is collected and kept in the hot air oven for the removal of excessive water for 20 minutes. Following the addition of 30%(W/V) Hydrogen Peroxide (H_2O_2) as the main pretreatment chemical which subjects the water sample to the oxidative digestion for removing organic matter [21]. Incubation of the same is done in room temperature for 3 days for effective degradation of organic substances. Subsequently put through density based separation, where difference in density can be used to separate plastics, usually by carefully mixing the sediment with salt solution and collecting the supernatant containing microplastics [16]. The salt solution used is 10%(W/V) Potassium Hydroxide (KOH). Incubation of the same at 60ºC for 24 hours for effective separation of microplastics based on their size. Further analysed by various spectroscopical and microscopical analytical techniques like Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, SEM, TEM, Fluoresence microscopy, Dark Field Microscopy [17].

Table 2: Methods of Digestion process for organic matter digestion [16, 17]

Methods	Advantages	Limitation	Adaptaion
Acidic Digestion			
HCl	Polymer Recycling-in process hydrolysis, it breaks down the polymers into monomeric forms allowing these monomeric for recovery and reuse [22]. Has 100% digestion efficiency for fish tissue samples. Ease to handling.	It is highly corrosive causing safety hazards to equipment and personnel [23]. It is shown to melt or destroy PET and PA microplastic fragments [24]. The treatment of HCl showed lesser efficiency in digestion as compared to enzymatic digestion like Proteinase-K [25].	Can be used in varying temperatures ranging from 25ºC to 60ºC having maximum digestion efficiency [24].
HNO_3	It whitens the PVC, degradation of PA [26]. It has higher degradation efficiency than other chemicals [24]. Rapid degradation process. Effective for degradation of wide range of polymers.	Melts PE and PP microplastics. 5% solution had a 52% digestion efficiency of fish tissue. Displayed	Higher temperature can have maximum degradation process [28]. The temperature

		aggregation of suspended plastic particles [27].	ranges between 20°C to 100°C, optimum efficiency is between 25°C to 60°C [24].
Basic Digestion			
KOH	It is strong base making it highly reactive with various polymers [29]. Gives 98% digestion efficiency for fish tissue at 50°C [24]. Rapid degradation of polymers. When used at room temperature, there is minimal effect on plastic particles of any kind [30].	It is highly corrosive in nature. Above 50 °C, there has been found to be a minor browning of PA particles and a small corrosiveness to PVC microparticles.	Optimum digestion efficiency ranging between 25°C to 60°C. Some reactions may require higher temperatures, reaching up to 150-200°C for efficient degradation.

Table 3: Summary on Analytical Techniques of Microplastic Detection. [17, 31, 32]

Methods	LOD	Advantages	Limitations
Spectroscopic method			
FTIR	Viable for particles as tiny as 10µm in size .	Non-destructive analysis. Provides information on the chemical bonds, functional groups. Relatively fast and minimum sample preparation.	Influenced by other organic matters. It is relatively small in size. Not suitable for submicron and nanoplastic particles
Raman spectroscopy	Viable for particles with sizes between 100µm-2µm	Non-destructive analysis. Has ability to potentially speciate particle size distribution within mixture. Target identification	Time consuming. Does not provide full chemical composition analysis. Signals are altered by presence of fluorescent molucules.
Thermal based analysis			
Differential scanning calorimetry	Restricted to a minimum sample mass of >0.2 mg. Measuring device dependent technique.	Ability to use small sample sizes. Can analyse both solids and liquids. Allows mass quantification of particle present in the sample.	Sample destruction. No direct structural information. Not suitable for analysis of particles composed of polymers with broad thermal transition temperature range.

Microscopy Techniques			
SEM	Spatial resolution limit of >5 nm	Non-destructive. High resolution images. Gives detailed 3D topographical images.	Expensive technique. Chemical information can only be obtained via the use of complimentary techniques Charging effects
TEM	Spatial resolution limit of >0.1 nm	Provides better special resolution. Provides	Requires high vacuum condition, thin sample section. Time consuming sample preparation.
Fluorescence microscopy	Spatial resolution limit of >120 nm × 120 nm. Highly dependent upon microscope used for measurements.	Revolutionizing cell biology by allowing imaging of fluorescent molecules in the live cells. Non-destructive.	Potential for mistakes. Requires attention to detail and expertise. Only suitable for particles which are fluorescently tagged. Risk of photo bleaching.
Dark field microscopy	Spatial resolution is diffraction limited, limiting detection to particles >250 nm	Offers high degree of contrast, making it easy to see samples on difficult background. Non-destructive. Reliant on light scattering, so no particle tags are necessary.	Encountering of background problems and the signal does not last very long. The intensity of light for Dark field microscopy leads to glare and distortion leading to difficulty in specimen measurement.

Spectroscopic techniques are most commonly used techniques for detection of microplastics as the spectroscopic technique like Raman and FTIR combining with microscopy provide information on both sample's chemical fingerprint and its physical properties like size and shape. The primary benefit of using FTIR for microplastic detection is that it is a non-invasive technique that causes less damage to environmental samples [33, 34]. One of the drawbacks of employing FTIR is that its unique resolution of 10–20µm means that it can only detect microplastics with particle sizes larger than 20µm [16, 35]. FTIR is a vibrational spectroscopy method that generates infrared spectra by measuring variations in the material's dipole moment [16]. The obtained spectrum is then utilized to analyze the compositions of plastic particles and ascertain the chemical makeup of the microplastics by comparing it with known polymer standard spectra from spectral libraries [36].

3. Detection of Per- and Polyfluoralkyl Substances

The sample collection and sampling is done by the above procedure as done for microplastic detection. The US Environmental Protection Agency (EPA) indicates a drinking water heath guidance for PFAS. The measurement of these components are at ng/L levels is quite challenging [37]. In 2009, US EPA established EPA Method 537 for quantification of 14 PFAS using Solid-phase extraction (SPE) and Liquid Chromatography (LC) coupled with tandem mass spectroscopy (MS/MS). An SPE cartridge containing polystyrenedivinylbenzene (SDVB) is used to extract method analytes and surrogates from a 250 mL water sample that has been fortified with surrogates. The compounds are eluted from the solid phase sorbent with the small amount of methanol. The extract is heated to a dryness using nitrogen in a water bath, and the internal standards are added after the extract is adjusted to a 1-mL volume using 96:4% (V/V) methanol: water. A 10-µL injection is conducted into an LC with a C18 column, which is connected to an MS/MS. By comparing the obtained mass spectra and retention durations to reference spectra and retention durations for calibration standards obtained under the same LC/MS/MS conditions, the analytes are distinguished and identified. By applying the internal standard approach, the concentration of every analyte is found. To keep track of the method analytes' extraction efficiency, surrogate analytes are introduced to all field and QC samples [38].

III. CONCLUSION

Microplastics are tiny plastic particles, often less than 5 millimeters in size, that originate from the breakdown of larger plastic items or are intentionally manufactured for various purposes such as microbeads in personal care products or microfibers from synthetic textiles. These particles pose a significant threat to the environment due to their widespread presence and persistence. FTIR is a powerful analytical technique used to identify the chemical composition of materials by measuring the absorption of infrared radiation. By employing FTIR, researchers can accurately detect and characterize microplastics in treated sewage water, providing valuable insights into their types, concentrations, and sources. This step is crucial for understanding the extent of microplastic pollution and devising effective mitigation strategies. Microplastics can have detrimental effects on aquatic life and ecosystems. Marine organisms may ingest microplastics, leading to physical harm, blockage of digestive tracts, and the bioaccumulation of toxic substances. Additionally, microplastics can serve as vectors for transporting harmful pollutants and invasive species, further exacerbating ecological degradation. PFAS are a group of synthetic chemicals widely used in industrial and consumer products for their water and grease-resistant properties. Due to their persistence in the environment and potential adverse health effects, PFAS have emerged as a significant concern in water pollution. PFAS are highly resistant to degradation, earning them the nickname "forever chemicals." Once released into the environment, PFAS can persist for extended periods, accumulating in water bodies, soil, and biota. Their persistence poses long-term risks to environmental and human health. The inclusion of PFAS in the study emphasizes the importance of detecting and monitoring these contaminants in sewage water. Analytical techniques such as liquid chromatography-mass spectrometry (LC-MS) or gas chromatography-mass spectrometry (GC-MS) can be employed for accurate detection and quantification of PFAS compounds. Continuous monitoring is essential for identifying sources of contamination, assessing exposure risks, and implementing preventive measures to mitigate further spread. Addressing the critical issues of microplastics and PFAS in treated sewage water requires interdisciplinary efforts encompassing scientific research, technological innovation, policy interventions, and public awareness. By understanding the environmental impact and implementing proactive measures, we can strive towards safeguarding ecosystems, protecting public health, and promoting sustainable water management practices.

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