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Research Progress on Analysis Methods of Microplastics in Water

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Abstract

In the environmental water, microplastics is a new pollutant with potential risks because of its strong adsorption and migration ability and bioaccumulation. Because the water environment is complex and the microplastics particles are usually very small, the analysis and identification is the bottleneck of the current research work. Through literature collection and induction, this paper introduces the methods of sample collection, classification and extraction, component identification and analysis of microplastics in water in recent years, and systematically expounds the application and prospect of micro-FTIR in microplastics analysis. By analyzing the applicability and limitations of various methods, the whole process analysis method suitable for microplastics analysis of water environment is summarized, which provides a basis for future research on the occurrence characteristics, migration and transformation laws and potential environmental risks of microplastics in environmental waters.

Keywords

Microplastics; Water; Extraction Method; Quantitative Analysis; Micro Micro-FTIR.

1. Introduction

Plastic is a kind of high-molecular polymer, which has excellent physical and chemical characteristics such as durability, waterproofness and strong corrosion resistance. Since 1950s, plastics have been produced, used and discarded in large quantities. Under the physical, chemical and biological effects, the waste plastics in the water body are gradually degraded into micro-particles with a particle size of less than 5 mm, and become the main carrier of organic pollutants and metal pollutants. As early as 1970s, microplastics particles were first found on the sea surface [1]. In 2011, the United Nations Environment Program (UNEP) officially listed the environmental problems caused by the microplastics as an important issue, and microplastics gradually gained more attention.

As a new type of environmental pollutant, microplastics usually has strong hydrophobicity and persistence due to its own chemical properties, so most of microplastics entering the environmental water is difficult to be naturally degraded in a short time. Especially in the marine environment, microplastics can migrate over a long distance through the action of wind, rivers and ocean currents, and now it has been widely found in the global ecosystem. Because of its high specific surface area and strong lipophilicity, microplastics is easy to adsorb toxic pollutants on its surface during water movement. Aquatic organisms can't digest microplastics which carries pollutants by mistake, so microplastics enters the chain of marine organisms, and

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it is enriched in various organisms, releasing toxic by-products, and finally posing a risk to human health.

At present, scholars from all over the world have done a lot of research on microplastics pollution in water, but there are still big differences in analysis methods such as treatment methods and identification methods, which leads to the failure of mutual verification of research results. The collection and pretreatment process of microplastics is an important process to analyze microplastics, but most of the processes are easy to lose, damage microplastics or be polluted by microplastics, which directly affects the reliability of quantitative analysis in microplastics. A large number of scholars also study the quantitative and qualitative methods of microplastics, but they mainly focus on the differences of each method, lacking the description of mainstream recommended technologies. For example, Lee et al [2] comprehensively analyzed the applicability and limitations of common quantitative and qualitative analysis methods; Xu et al [3] introduced the comparison between Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) in the identification of microplastics. Peñalver et al. [4] summarized the identification methods of microplastics based on pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) and thermogravimetric analysis (TGA), but none of them proposed a whole-process analysis method suitable for detecting microplastics in water environment, and the introduction of micro-FTIR, a new mainstream method, was not detailed. On the basis of research at home and abroad, this paper summarized the methods of collection, extraction and identification of microplastics in water, and focused on the application of micro-FTIR in qualitative and quantitative analysis of microplastics, in order to provide technical support for microplastics research in environmental water.

2. Microplastics Acquisition and Extraction Method

2.1. Collection Method of Water Samples

In water bodies, at present, more collection methods are sample concentration method and large sample method. The sample concentration method is to select different plankton nets, such as Manta trawl and Neuston trawl, to collect microplastics at the sampling site in combination with the location of sampling points [5]. The key of this method is to select the plankton net with appropriate pore size. If the pore size is too small, all kinds of suspended substances will block the mesh, while if the pore size is too large, small-sized fibrous microplastics will be lost [6]. To solve the problem that small particle microplastics can't be captured due to the pore size limitation, the large sample method can be selected, that is, the water sample can be collected directly by a water pump [7] or a stainless-steel barrel [8], and the water sample can be transported back to the laboratory after being frozen and preserved, and then the microplastics can be obtained after being filtered and enriched [9].

Microplastics in water body is small in abundance and particle size, so it can't be separated by visual inspection. Liu et al. [10] compared the difference of microplastics concentration detected by sample concentration method and large sample method in the same place, and the concentration measured by large sample method was about 3 orders of magnitude higher than that by sample concentration method. From the particle size distribution, it can be seen that the particle size distribution of the sample concentration method is easily affected by the trawl aperture, and the proportion of small particle size is obviously lower than that of the large sample method, and the particle size distribution obtained by the large sample method is more complete than that obtained by the sample concentration method. Therefore, it is considered that the large sample method is more suitable for water samples [11].

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2.2. Extraction Method of Microplastics in Water Body

The water environment is complex, microplastics particles are small, and they are easy to stick to each other in the water, so it is often necessary to extract microplastics samples through pretreatment. The following focuses on three extraction methods: digestion and purification, density flotation and filtration.

2.2.1. Digestion and Purification

At present, commonly used digestion and purification solutions are 30% H_2O_2 [18-19], Fenton reagent (H_2O_2+ Fe^{2+}) [1,20], strong acid and alkali [21], biological enzyme, etc. Different digestion and purification solutions have different digestion effects on organic and biological substances, and the recovery rate of microplastics is also different. The research shows that at room temperature, it is difficult for strong acid and alkali to completely digest the surface attachments, which will damage the surface of microplastics, while 35% H_2O_2 solution can dissolve biological substances, and under the action of Fe^{2+} as catalyst, H_2O_2 can more efficiently digest the refractory organic substances. This method has the advantages of high recovery rate and little change to the shape of microplastics [22]. As the digestion solution of biological enzyme, it has the same advantages as H_2O_2, but it is difficult to keep the activity of biological enzyme, and the digestion takes a long time, which limits the application of this method.

2.2.2. Density Flotation

When there are a lot of sediment in the water sample or after digestion and purification, the microplastics cannot be effectively separated by filtration, density flotation can be used as an auxiliary method for filtration. The density of microplastics is generally 0. 8-1. 4 g/cm^3, and about 46% of microplastics will float on the water surface, while microplastics, with relatively high residual density, can be separated by flotation with high density saturated salt solution. Because NaCl is cheap, nontoxic and easy to obtain, saturated NaCl solution (ρ = 1. 2 g /cm^3) is the most commonly used salt solution in research [12,23]. For higher density microplastics, saturated $ZnCl_2$ solution (ρ = 1. 6 g /cm^3), saturated potassium formate solution (ρ = 1. 6 g /cm^3) and saturated NaI solution (ρ = 1. 8 g /cm^3) are often used for further separation.

2.2.3. Filtering Treatment

Filtration is a necessary process to extract microplastics from water. According to the size of the target microplastics, a suitable screen or membrane filter is selected, and the target microplastics particles are retained on the membrane by classification, so as to obtain the particle size distribution characteristics of microplastics in water. Many researches use stacked screens with different hole diameters for particle size screening [15,20]. The screening treatment is simple and will not affect the surface structure or other physical characteristics of microplastics. However, the main disadvantage is that microplastics is easily stuck in the pores of the filter membrane, which leads to the low concentration of microplastics. Moreover, the pore sizes selected by scholars are not consistent, which makes the concentration data of microplastics in different regions not comparable. Therefore, a unified particle size division is urgently needed to standardize the selection of filter pore sizes. A variety of extraction methods can obtain clean microplastics, which provides a good foundation for qualitative analysis, but it can't avoid the loss in the transfer process. Therefore, it is necessary to choose the pretreatment steps according to the water quality of water samples and the occurrence of microplastics [24].

3. Analysis Method of Microplastics

The composition, particle size and surface structure of microplastics in water will determine its environmental behavior. The degradation rate of plastics in water can be obtained by analyzing the particle size distribution and surface texture of microplastics, and micro-plastics with

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different particle sizes have different reaction mechanisms and toxic effects on aquatic ecosystems. Different polarity microplastics is easy to carry different pollutants, and the composition analysis of microplastics can provide effective information for traceability, degradation and transformation. Therefore, the composition, particle size and surface structure of microplastics should be studied at this stage.

3.1. Physical Morphology Characterization Analysis

The particle size characteristics and structural characterization of microplastics can be judged by microscope, but due to the limitation of resolution, optical microscope is only suitable for identifying microplastics particles with particle size larger than 1 mm. In order to realize the efficient detection of microplastics, scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) can not only obtain the surface characteristics and particle size of microplastics, but also the chemical composition of the sample, and can identify microplastics [18].

3.2. Quantitative Analysis

3.2.1. Counting Method

At present, the abundance of microplastics is often expressed by numerical measurement. At present, the most commonly used quantitative method is the traditional manual counting, that is, grouping microplastics particles under a microscope, counting subjectively, and calculating the abundance of microplastics. The manual counting method is simple to operate and low in cost, but it is easily influenced by factors such as naked eye recognition and background interference, and the human error increases significantly with the decrease of the particle size of micro-plastics. The combination with microscope FTIR can effectively improve the accuracy of microplastics identification. Li Shan et al. [26] used micro-FTIR in attenuated total reflection (ATR) imaging mode to quantitatively detect microplastics in drinking water. ATR-Micro-FTIR based on focal plane array (FPA) detector can scan the target microplastics in multiple areas at the same time, independently analyze and count the infrared images, effectively reduce human error and detection time, and efficiently obtain microplastics abundance [27].

3.2.2. Mass Concentration Method

In recent years, thermal analysis is often used to quantify the mass concentration of microplastics. Py-GC-MS uses thermal analyzer to break the chemical bond of microplastics in the absence of oxygen, and generates volatile substances with low molecular weight. Quantitative analysis by gas chromatography/mass spectrometry shows that the LOD is in pg ~ mg [2,4], and the interference of organic additives can be avoided. Scherer et al. [21] quantitatively analyzed microplastics in water by Py-GC-MS, and calculated the polymer abundance by comparing the peak intensity of characteristic pyrolysis products with the results of calibration standard curve. Thermoanalysis-Differential Scanning Calorimetry (TGA-DSC) combines the advantages of these two thermal technologies. When the sample is endothermic or exothermic, the peak generated in DSC system is the basis of quantitative analysis. For PE with high endothermic absorption rate, its LOD can reach 1mg [28]. Compared with counting method, thermal analysis method can avoid the high error rate of subjective counting. At the same time, the thermal analysis instrument has high adaptability to samples, and the attachments on the surface of microplastics have little influence on the results, which can reduce the sample pretreatment steps. The main disadvantage of this method is that it is destructive, can't realize the pre-enrichment of microplastics, and has a small amount of detection each time, so it is not suitable for batch detection.

To sum up, micro-FTIR, which has independent analysis ability and intuitive expression unit, is more recommended for quantitative analysis. Under the conditions, Py-GC-MS can be used for supplementary detection of the mass concentration of microplastics.

3.3. Component Identification and Analysis

Organic compounds constituting microplastics have different functional groups, and the chemical composition of microplastics is often identified by analyzing the characteristic spectra generated by samples. FTIR [8] and Raman spectra [23] are the most commonly used methods. Polymer has a highly specific infrared spectrum and unique band pattern, which makes FTIR one of the preferred technologies of many scholars. In FTIR, samples absorb infrared light with different frequencies, and then generate infrared spectra according to the changes of molecular dipole moments to identify the components of microplastics, which is more suitable for the detection of microplastics with polar functional groups, such as PVC and PA. In order to meet the detection requirements of small particle size microplastics, micro-FTIR has been gradually developed. Micro-FTIR has three testing modes: transmission, reflection and ATR. Transmission mode is suitable for microplastics with good light transmission, but it can't detect thicker microplastics samples. The quality of the reflected spectrum mainly depends on the surface roughness of the sample. When detecting the water micro-plastic sample with rough and irregular surface, the analysis result may be affected by the refraction error [29]. ATR mode information is directly collected on the sample surface, and is not interfered by the sample thickness, surface roughness, background noise, etc., but it takes a long time and has low time benefit [27]. Micro-FTIR based on FPA can perform high-throughput analysis on microplastics samples on the stage, shorten the detection time, reduce the detection limit of particle size, and detect particles over 10μ m. Xu et al [3] pointed out that FPA detector can collect the spatial and spectral information of heterogeneous microplastics particles, which overcomes the disadvantage that FTIR can't detect thicker microplastics. Micro-FTIR combines the qualitative analysis technology of FTIR with the microscopic visualization technology of microscope [30], which can obtain the characteristic chemical composition on the basis of obtaining the spatial structure of microplastics, and avoid the loss caused by the transfer of samples between instruments. Löeder et al. [29] used FPA-based micro- FTIR to analyze microplastics in the samples, and only 1. 4% of the particles were plastic particles after spectrum comparison. It can be seen that the purification treatment still can't prevent impurities with similar appearance from being mixed into the sample, and the simultaneous observation of surface characteristics and component identification can reduce repetitive work and save a lot of time for microplastics identification. At the same time, because of its advantages of simple operation, low cost, no damage to samples, more direct, accurate and high efficiency, micro-FTIR based on FPA is considered as an ideal method to detect microplastics at present.

Raman spectra method can obtain the information of the molecular structure of the sample according to the change of the polarizability of the molecule in the vibration mode, so it can identify the molecules with nonpolar functional groups, such as PP, PE, PS, etc. more accurately. Compared with infrared spectroscopy, Raman spectroscopy has a wider spectral range and higher resolution, which effectively expands the types of detectable components and particle size range, and can identify microplastics particles with particle size less than 1 μm or even smaller. Xu et al. [31] found that surface-enhanced Raman spectra can detect and identify (single) micro-nano plastics, and the detection size is as low as 360 nm. However, microorganisms and pollutants on the surface of the sample will produce fluorescence interference, which puts forward higher requirements for sample pretreatment.

Thermal analysis is a technology based on the decomposition of polymer structure at the temperature above 500℃. The chemical composition information of microplastics can be obtained by characterizing the pyrolysis gas. Py-GC-MS, TGA- DSC and other methods can determine the mass concentration and identify the components of microplastics, but this method is destructive and the results are easily affected by inorganic pollutants on the surface. To sum up, the analysis methods are complementary, so it is still recommended to use micro-FTIR and Raman spectra to identify the components of microplastics.

4. Conclusion

(1) Inappropriate microplastics sampling method is easy to lose microplastics or introduce microplastics pollution, and different microplastics extraction methods will cause irreversible damage to microplastics in different degrees. Collecting microplastics in water by large sample method can better retain the particle size distribution in water. In the process of extracting microplastics from water, it is recommended to select the pretreatment methods of screening and filtering, digestion and purification and flotation according to the water quality and microplastics concentration of water samples, and optimize and adjust them to meet the requirements of different analytical instruments. However, in the process of analysis, it is still necessary to formulate a unified standard for dividing the particle size of microplastics, and establish a concentration unit related to the particle size, so as to show the comparability of microplastics concentrations around the world.
(2) In quantitative analysis of microplastics, manual counting error is large; Py-GC-MS has high accuracy, but the expression units are not uniform; ATR-Micro-FTIR based on FPA can realize multi-area scanning counting and obtain microplastics abundance quickly and accurately, which is an ideal method for quantitative analysis of microplastics. Electron microscope, micro-FTIR and Raman spectra are recommended for qualitative analysis. The electron microscope can intuitively obtain the physical characteristics of sample particles for preliminary judgment; Micro-FTIR has less interference factors and good spectrum quality, and Raman spectra method is complementary to it, which can detect microplastics with smaller particle size and further identify the target microplastics.
(3) At present, the analytical techniques are still confined to the identification of single-component and μm-grade microplastics, while it is still difficult to identify multi-component and nm-grade microplastics. Grade nm microplastics has a large specific surface area, which makes it easier to carry more pollutants in water interaction. The application of nm technology in the detection of nm-grade microplastics should be developed, and the detection particle size range should be widened. The morphology and artificial intelligence algorithm are combined to realize accurate and efficient microplastics morphology recognition and counting.

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