

Research Progress on Separation and Detection Methods of Microplastics in Soil Environment

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Abstract: As a new type of environmental pollutant, microplastics (MPs) exists in the soil environment for a long time and pollutes the ecological environment of the surface system. Separation and detection of microplastics in soil environment is the basis of controlling microplastics pollution in soil environment. The research progress of separation and detection technology in microplastics was introduced, and the existing problems of separation and detection methods were put forward. The results show that the screening-filtration method and density separation method are simple, operable and effective, but the cross-contamination rate is high in the extraction process, and the recovery rate of high-density microplastics is not high. Pressurized fluid extraction technology is convenient and easy to operate, but it may affect the particle morphology of microplastics. Visual detection, Raman and infrared spectroscopy, chromatography and mass spectrometry combined pyrolysis analysis have some problems, such as high cost, long time and loss of samples. In the future, it is necessary to further explore the analytical method of microplastics, and develop the separation and detection method without loss of microplastics.

Keywords: Soil environment, Microplastics, Separation detection.

1. Introduction

Because of its high chemical stability, strong plasticity and durability, plastics are widely used in medical treatment, agriculture, industry, catering service and other fields [1]. When plastics enter the environment, they are cracked, broken and worn by external conditions, and become small pieces, particles and other different forms. These small and different forms of plastics are called "microplastics" [2]. As a new type of environmental pollutant, microplastics has long-term stable existence in water, atmosphere and soil environment, which has a certain impact on people's production and life [3-6].

At present, the detection and separation technology of microplastics in soil ecological environment system has limitations, and the research on microplastics in air and water ecological environment is concentrated. The key to treat microplastics in soil environment is to separate and extract microplastics from soil environment, and identify and quantitatively detect it. The research of Bergmann et al. [7] shows that, compared with the marine environment, the terrestrial soil environment is both the "birthplace" of microplastics and the "gathering place" of microplastics. At present, there are few studies on the separation and detection methods of microplastics in soil environment, so it is necessary to further study the separation and detection methods of soil microplastics [8-10]. In this study, the separation method and detection method of microplastics in soil environment were expounded, and the research emphasis on soil environment microplastics was put forward. The research on microplastics in soil environment was prospected, which provided some reference for further study on soil environment microplastics.

2. Microplastics's Soil Environmental Behavior

There are many sources of microplastics in the soil, such as agricultural film, sewage, landfill leachate and so on. Microplastics is widely distributed in agricultural soils and industrial land soils. And vertical migration of lateral transfer are the main migration and transformation forms of microplastics in the soil ecological environment system. Microplastics's soil environmental behavior is very complex, which interferes with the separation and detection of microplastics in soil environment.

3. Separation Method of Microplastics in Soil

The composition of the soil is complex, containing a large number of microorganisms and abundant organic matter, and the organic matter stably exists in the soil environment, which interferes with the separation and detection of microplastics in the soil environment and increases the difficulty of the separation and detection of microplastics. At present, the separation methods of microplastics in soil environment are mainly divided into two parts: one is to extract microplastics from soil; The second is to remove impurities from the soil to separate microplastics.

3.1. Extracting microplastics from soil

3.1.1. Screening-filtration method

The filtration method is similar to the screening method, and microplastics is filtered by small holes with different particle sizes. Screening method [11] is to pass air-dried soil samples through sieves with different pore diameters, with

small holes trapping microplastics, and sort out larger particles and other impurities. The material of the mesh is usually stainless steel or copper. The material used in the filtration method is a filtration membrane with a smaller pore size than the sieve. The pretreatment of filtration is simple, but the extraction purity of the method is not high [12]. Generally, a 2 mm sieve is used for the initial screening of soil samples to screen out the basic impurities in the soil, so as to reduce the deep separation of soil microplastics to a certain extent. Then, screens with different pore diameters are used to separate microplastics with different particle diameters, and the retentate is washed to obtain the test object.

3.1.2. Density separation method

And the density difference between microplastics and microplastics soil samples is the separation essence of density separation method. The density of is generally 0.8~1.4 g/cm³[13], but the density of soil samples is generally 2.6~2.7 g/cm³[14]. Because of the adsorption effect of soil aggregates and the large specific surface area of microplastics, microplastics and soil aggregates combine in different limits, which increases the difficulty of separating microplastics in soil environment [15] and reduces the extraction efficiency of density separation method in soil environment. Therefore, the use of density separation method needs to be carried out under certain conditions.

The density separation method makes use of the density difference between impurities in soil and microplastics, and uses high concentration flotation liquid, which can collect many kinds of microplastics, but float out more impurities. The research of Liu et al. [16] shows that with the increase of extraction and ultrasonic treatment times and the extension of flotation time, plastics such as PE, PP, PS, PA, PC, ABS and PMMA can be successfully extracted with NaCl solution, but high-density polymers such as PET and PVC can't be separated. Therefore, saturated NaCl solution as the flotation solution of soil microplastics will cause high density microplastics flotation error. Compared with NaCl solution, the extraction efficiency of CaCl₂ solution is relatively high, but it will interfere with microplastics identification [17]. The research of Van Cauwenberghe et al [18] shows that the use of NaI and ZnCl₂ can meet the requirements of high density microplastics flotation.

Density flotation is widely used in the process of separating microplastics from soil, but there are still some problems in this method, such as complex extraction process and long time consumption, high cross-contamination rate in the extraction process, and low recovery rate of high density microplastics. Therefore, it is necessary to speed up the research and development of soil microplastics extraction methods with high efficiency, less pollution and low cost.

3.1.3. Pressure fluid extraction technology

Pressurized fluid extraction technology is a solvent extraction technology used under subcritical temperature and pressure conditions, which can recover organic pollutants from soil, sediment and waste [19]. Okoffo et al. [20] used dichloromethane to extract microplastics such as PS, PP and PET in one step at 180 °C, and the average extraction efficiency was not less than 80%. In the process of pressurized fluid extraction, the particle morphology of microplastics may be affected, the physical characteristics of microplastics have changed, and the judgment of the source and ecotoxicological effect of microplastics is biased. Pressurized fluid extraction technology can separate microplastics (PS, PE, PVC, etc.)

with particle size less than 30m from soil environment [21], which has the advantages of convenience, rapidness and simple operation. It is one of the potential separation technologies in microplastics at present.

3.2. Remove impurities from soil and separate microplastics.

The concentration of microplastics, impurities and organic matters in the soil leads to the high content of organic matters, so the removal effect of single density separation method is not ideal [11]. The soil environment is rich in impurity organic matters, which will easily affect the separation and detection of microplastics, and in the process of Fourier transform infrared spectroscopy and Raman spectroscopy analysis, the signal of microplastics will be distorted, which is not conducive to the appearance analysis of microplastics. Removing interfering organic impurities is an important step to accurately analyze microplastics in soil environment [16]. Alkaline method, acid method, oxidation method and enzyme digestion method are usually used to digest organic matter in soil samples.

3.2.1. Acid hydrolysis

In acidolysis, HNO₃, HCl, HNO₃+HClO₄ are beneficial to decompose organic matter and biological samples in sediments, but microplastics in soil samples is easily destroyed by decomposition. When HNO₃ is used as an acid digestion agent, polymers such as ABS, PA, PS and PET are destroyed [11]. Generally, the digestion efficiency of HCl is low, so it is usually not used as an organic acid digestion agent.

3.2.2. Alkali solution

NaOH and KOH in alkaline hydrolysis are beneficial to decompose biological samples, which is milder than acid treatment and will not damage microplastics in soil samples [22-23]. However, the decomposition of humic acid is incomplete, and the organic matter insoluble in alkali cannot be removed. The research of Dehaut et al. [24] shows that the structure of microplastics, such as PE, PET, CA and PC, is destroyed by NaOH hot alkali digestion.

3.2.3. Oxidation method and enzyme digestion method

At present, the commonly used oxidant for soil organic matter removal is hydrogen peroxide (H₂O₂). However, when 30% H₂O₂ is used to treat samples rich in organic matter, it usually produces rich foam, which hinders the filtration and further treatment of samples, resulting in a low recovery rate of microplastics [25-26]. Mintenig et al [27] combined enzymatic digestion with oxidation to pretreat wastewater samples to remove organic substances in wastewater samples, but further research is needed to separate microplastics from soil environment by this method.

The change of microplastics in the soil and the changes of various substrates and soil physical and chemical properties bring uncertainty to the removal of soil impurities by digestion. At present, there is no standard and unified method to remove impurities on the surface of microplastics in soil environment. In order to better separate and extract microplastics from soil environment, it is necessary to further improve the microplastics separation method.

4. Detection Method of Microplastics In Soil

At present, the mainstream methods of microplastics detection in soil environment include physical methods

(microscopic detection) and chemical methods (Fourier transform infrared spectroscopy, Raman spectroscopy, gas mass spectrometry or chromatography, etc.).

4.1. Physical detection method

Visual inspection and identification method belongs to physical inspection method, which is a simple and convenient microplastics analysis and identification technology with strong operability, and can intuitively and quickly obtain information such as the appearance characteristics and texture of microplastics [28]. Visual inspection and identification methods usually use naked eyes or microscope. It is generally used to detect plastic particles with a particle size of 1 ~ 5 mm. Optical microscope, stereomicroscope and field emission transmission electron microscope are important tools for direct observation, identification and classification of microplastics. Visual detection and identification have a small identification degree for particles with smaller particle size, and there are problems in identification accuracy. Therefore, it is necessary to detect the chemical composition of plastic particles in order to further verify the results of visual inspection and identification.

4.2. Chemical detection method

4.2.1. Spectral analysis method

Fourier spectrum and Raman spectrum are commonly used methods to detect and identify microplastics, and the two methods are costly, which can identify the appearance characteristics, types and abundance of microplastics [29-30], but can't detect the content of microplastics in soil environment [31]. Fourier transform infrared spectroscopy (FTIR) was used to measure the specific chemical bonds of chemical substances in microplastics. Comparing the spectrum of the target polymer with the standard spectrum, a specific microplastics could be identified, but the appearance characteristics of microplastics interfered with Fourier transform infrared spectroscopy [32]. In addition, the application effect of Fourier transform infrared spectroscopy in soil environment is also affected by organic impurities in soil environment. Raman spectroscopy is basically unaffected by the appearance characteristics of microplastics. The combination of Raman spectroscopy and microscope can improve the particle size range of microplastics detection, and can identify microplastics particles with particle size < 1 μm . Moreover, when Raman spectroscopy is used to detect and identify microplastics in soil environment, it is also interfered by organic impurities in soil environment [23].

Infrared spectroscopy and Raman spectroscopy are costly and time-consuming, both of which are interfered by organic substances in the soil environment. The two methods need to purify the sample before identifying microplastics [33].

Before identifying microplastics, it is necessary to purify the sample [33]. In the process of detecting microplastics in soil environment, it is necessary to strengthen the research on spectral technology and give full play to its advantages of stability and reliability. The combination of some emerging technologies can improve the detection efficiency of microplastics in soil environment, such as near infrared spectroscopy, visible near infrared spectroscopy and hyperspectral imaging technology, which can quickly measure microplastics in soil samples. However, the reliability of the combined use of these emerging technologies is uncertain.

4.2.2. Pyrolysis analysis method

Pyrolysis analysis mainly includes thermogravimetric analysis-mass spectrometry (TGA-MS), thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC-MS) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). At present, all three technologies can effectively identify and detect microplastics in the environment, but the three technologies cannot detect the morphological characteristics and abundance of microplastics [34]. Yu Jianping's [35] research shows that TGA-MS analysis of PET in soil samples requires no pretreatment. Compared with Py-GC-MS, TGA-MS can treat samples in batches, but it is not conducive to distinguishing compounds with similar quality and degradation temperature. Compared with Py-GC-MS, TED-GC-MS improves the analysis efficiency of samples, and the processing time is 2~3 h, but some microplastics is lost.

Reasonable combination of various technologies may improve the identification efficiency of microplastics and reduce the cost. Because of the complexity of soil environment, the detection of microplastics in soil environment is the focus of current research, and the physical and chemical detection methods need to be improved and innovated. Therefore, it is necessary to develop a new technology that can qualitatively, quantitatively, quickly and efficiently detect microplastics in soil environment rich in organic impurities.

5. Conclusion

The sources of microplastics in soil are extensive, and the components of soil environment are complex and diverse, which interferes with the separation and detection of microplastics in soil environment. At present, there is no uniform technical means and standard for the detection and separation of microplastics in soil environment, which makes it difficult to identify the abundance and type of microplastics. Therefore, it is necessary to study the identification methods with strong operability, low cost, high efficiency and convenience according to different soil environments, so as to standardize the standards of microplastics detection and identification of soil environment. Besides, we should continue to explore the migration, transformation, separation and detection methods of nano microplastics. Paying attention to the soil environmental behavior in microplastics, we should also strengthen the research and development of new technologies to prevent and control microplastics pollution in the soil environment, so as to provide scientific basis for solving microplastics pollution in the soil environment.

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