Challenges in characterization of nanoplastics in the environment

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Abstract Plastic pollution has been a legacy environment problems and more recently, the plastic particles, especially those ultrafine or small plastics particles, are widely recognized with increasing environmental and ecological impacts. Among small plastics, microplastics are intensively studied, whereas the physicochemical properties, environmental abundance, chemical states, bioavailability and toxicity toward organisms of nanoplastics are inadequately investigated. There are substantial difficulties in separation, visualization and chemical identification of nanoplastics due to their small sizes, relatively low concentrations and interferences from co-existing substances (e.g., dyes or natural organic matters). Moreover, detection of polymers at nanoscale is largely hampered by the detection limit or sensitivity for existing spectral techniques such as Transformed Infrared Spectroscopy (FTIR) or Raman Spectroscopy. This article critically examined the current state of art techniques that are exclusively reported for nanoplastic characterization in environmental samples. Based on their operation principles, potential applications and limitations of these analytical techniques are carefully analyzed.

Keywords Nanoplastics, Microplastics, Plastic characterization, Particle separation

1 Introduction

Natural weathering or biological degradation causes bulk plastics to decompose into microplastics (dimension < 5

mm) and nanoplastics (dimension < 0.1 μm). Plastic residuals of different sizes may impose different ecological or human health risks. Compared to microplastics, nanoplastics are small insoluble and colloidal plastic debris that has the size between microplastics and those soluble oligomers and monomer and is considerably difficult to detect in the environment or biological systems. Clearly, nanoplastics may have very different environmental fate and biological effects when compared to larger plastic fragments. For instance, a handful of research suggest the possible aerial transport of nanoplastics due to the low density and sizes (Bianco and Passananti, 2020; Materić et al., 2020; Materić et al., 2021). The biological impacts of nanoplastics to living organisms could be greater than that of microplastics because of the potential penetration of cell membranes and bioaccumulation. Thus, a rigorous examination of environmental nanoplastics is critical to assessing the impact of this new anthropogenic pollutant. However, separation or detection of these small plastics especially nanoplastics encounters tremendously great challenges caused by their low concentrations (low detection rates) and conjugations with interfering substances. For instance, nanoplastics are difficult to be identified in complicated matrix (e.g., proteins and exopolymers) that could interfere the analytical detection. So far, there have been very limited applications of effective instrumentation and methods for separation, detection, visualization, and chemical identification of nanoplastics as illustrated in Fig. 1.

2 Pretreatment and separation

Detection of nanoplastics is prone to the surface contamination by surrounding organic matters, minerals, or salts, which are typically removed by chemical (acid/base or organic solvents) cleaning or enzymatic digestion. However, these treatments may compromise the integrity
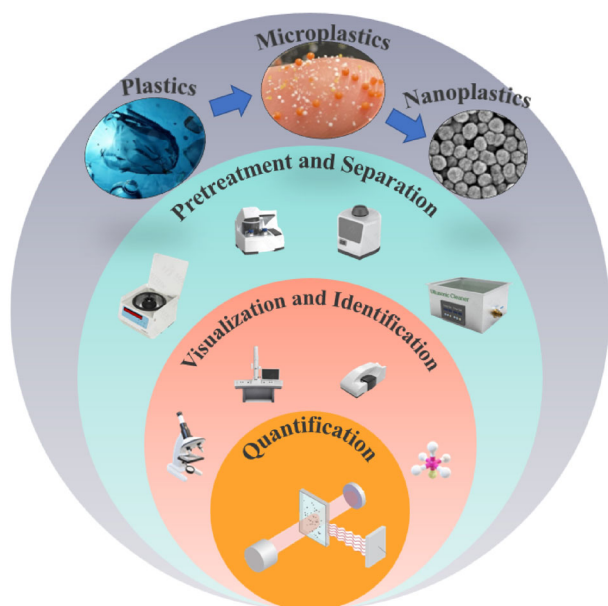
Fig. 1 Interrelationships of pretreatment/separation and characterization techniques for plastic wastes-derived microplastics and nanoplastics.

of plastics and lead to non-detectable plastic fragments (Hurley et al., 2018), which interfere with the separation and analysis of the target nanoplastics.

Ultrafiltration or nanofiltration membranes with small pore sizes (e.g., 0.02–5 μm) can potentially separate nanoplastics. Due to the low concentrations or particle numbers, further separation of nanoplastics from the polymer membranes is a problem. The polymer filter membranes will largely impede the FTIR or Raman detection of the target nanoplastics by increasing the background signals.

For nanoplastics smaller than 1 μm, active chromatographic separations, such as asymmetrical-flow field flow fractionation (AF4) combined with multiple online detectors, could successfully separate them (mostly above 200 nm) (Correia and Loeschner, 2018). However, the AF4 method has not been intensively used except for some specific types of nanoplastics (e.g., polystyrenes). Passive separations, such as hydrodynamic chromatography (HDC), employ hydrodynamic and surface forces to separate particles of 10 nm to 1000 nm in liquid based on their size differences. Though widely used to separate diverse inorganic nanoparticles (Pirok et al., 2017), the applications of HDC in the separation of nanoplastics is quite rare.

3   Visualization

Nanoplastics are difficult to visualize with conventional optical microscopes, fluorescence microscopes or even electron microscopes as they approach the optical diffraction limit. For instance, SEM-EDS detects the scattered electron (Auger electron) with the lateral resolution of commonly 1 μm and about 1–2 μm in depth. Similarly, EDS detects the X-rays created from the material surface bombarded by the electron beam, which can only resolve chemical information at a lateral resolution of over 1 μm. Though increasing the electron beam intensity (over 5 kV), SEM or TEM may be able to detect nanoplastics but still hardly distinguish the type or chemical compositions of polymers, especially in biological matrices, such as cells and tissues.

Dark field Hyperspectral Imaging (HSI) technique is shown to potentially overcome the above problems by generating images with spectral fingerprint signatures or features that are highly dependent on the chemical compositions and physical properties (e.g., shape, size and color) of the target materials. HSI detected polystyrene nanoparticles down to 100 nm in live organisms (Nigamatzyanova and Fakhrullin, 2021). However, the operation of HSI is not straightforward as HSI requires sophisticated modeling and calibration chemicals or materials to process the massive pixel information via a model transfer procedure.

4   Quantification

Dynamic light scattering (DLS) can be used to measure the hydrodynamic size and zeta potential of suspended nanoplastics in liquid. However, DLS is unable to quantify the concentrations of suspended particles. Similar to DLS, Nanoparticle Tracking Analysis (NTA) measures the particle concentrations in addition to the size or zeta potential measurement. NTA was reported to detect the formation of nanoplastics detached from a disposable PS coffee cup lid during degradation (Lambert and Wagner, 2016) which rendered polystyrene nanoparticles at a concentration of 10^7–10^9 mL^{-1}. However, the accuracy of NTA's detection is affected by the random Brownian motion that could vary with particle's size, shape, and interactions with liquid substances. Moreover, DLS and NTA require purification of the detected particles in solutions and may suffer interferences from co-existing colloids and fragments.

Atomic force microscope (AFM) is a promising technique for visualization of the morphological and chemical properties with the combinations of Raman or IR techniques (Fu and Zhang, 2017). The 1000-nm PS particles were identified in the mussel siphons by AFM/IR (Merzel et al., 2020). However, to perform sample mapping, AFM requires thin and smooth sample surfaces as the chemical mapping from AFM-IR results from the effective IR absorption on sample surfaces that causes local thermal expansion. The thermal expansion of

nanoplastics could be too small to be detected, especially when nanoplastics are surrounded by IR responsible chemicals.

5   Chemical identification

Clearly, nanoplastics are below the detection limit of FTIR or Raman even micro-FTIR (μ-FTIR) that may resolve sample chemical information down to 1–10 μm. Though commonly used to characterize plastics, Raman usually detects chemical species on sample sizes greater than about 10 μm, whereas micro-Raman can achieve a higher resolution of up to 1 μm. Hyphenated techniques such as GC-MS coupled with other techniques such as sequential pyrolysis (Pyr-GC/MS) and thermal desorption pyrolysis (TD-Pyr-GC/MS) can identify organic fragments and structural information of polymers such as chemical additives. These methods require certain sample weight or mass (e.g., 100–200 μg) to release detectable polymer vapors for identification, which could be challenging for detecting the low-concentration nanoplastics. Moreover, GC-MS may have a narrow mass range to analyze high-molecular-weight compounds in nanoplastics. For the nanoplastic analysis, other hyphenated mass spectrometry techniques were reported, including thermal desorption proton transfer-reaction mass spectrometry (TD-PTR-MS), which detected the volatile and semi-volatile dissolved organic matters with the molecular weight up to a size of ~500 m/z (Materić et al., 2020). Additionally, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) provides a solution of soft ionization (without compromising chemical structures) of polymer species from nanoplastics with the use of the vaporized matrix to assist in the laser energy absorption. The polymeric repeating unit mass, end groups, and molecular formula could be resolved by high-resolution TOF. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) characterizes the microplastic particle size and abundance by collecting the ejected secondary ions from the sputtered primary ion on the specimen surface. With the different mobility in carrier gas, ion mobility spectrometry (IMS) separates and recognizes the target molecules, nanoplastic size distribution, structural porosity and pore volume distribution could also be resolved. All of the above mass spectrometry methods have limited capabilities of quantification. By contrast, single particle-inductively coupled plasma mass spectroscopy (ICP-MS) achieved a detection limit of 8.4×10^8 nanoparticles per liter for polystyrene (PS) particle with plastic particles size ranging from 1 nm and 1 μm (Jiménez-Lamana et al., 2020).

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