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评 述

环境中纳米塑料的分离与检测*

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摘 要 微塑料作为环境中一类新兴污染物备受关注.然而对于尺寸更小的纳米塑料,尽管毒性效应被不断发现,但其在真实环境中的存在水平和检测技术还鲜有报道.本文评述了有限研究中纳米塑料分离和检测方法的优点与局限,并依据现阶段纳米污染物分析方法存在的问题,对相关方法的未来发展进行了展望.

关键词 纳米塑料,环境分布,分离,检测.

The separation and detection methods of nanoplastics in the environment

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Abstract: Microplastics are highly concerned emerging pollutants in the environment. However, for the nanoplastics with smaller size, researches of their distribution in the real environment and detection technology are still lacking, although their toxic effects have been reported. In this paper, the advantages and disadvantages of nanoplastics separation and detection methods in recent limited research are reviewed. In addition, the future development of related methods is prospected based on the problems existing in the present analysis methods of nanopllutants.

Keywords: nanoplastics, environmental distribution, separation, detection.

目前,全球每年塑料生产量已超过 3.2 亿吨,其中只有 6%—26%的塑料制品被回收,而多达 74%的塑料垃圾最终通过各种途径被排放到环境中[1].环境中的塑料因长期的物理、化学作用会分解成无数微小的塑料碎片或颗粒[2],当其直径小于 5 mm 时,即被定义为微塑料.个人护理品中的塑料微珠以及人造纺织品聚合纤维等微塑料,也会直接进入环境.环境中的微塑料理论上仍会进一步分解,形成尺寸小于 100 nm 的纳米塑料[3].由于体积小、比表面积大[4],纳米塑料更易吸附携带其它污染物[5-6].与微塑料相比,纳米塑料的尺寸极小,更容易被生物体吞食或被动摄入.已有研究证明水蚤、贻贝、浮游动物和藻类等多种水生生物可以主动地吸收或吸附纳米塑料[7-10],这些纳米塑料还可能沿着食物链传递[11-12].被摄入体内的纳米塑料,可能通过循环系统进入到不同组织和细胞中如在所有喂食纳米聚苯乙烯(PS)颗粒的鱼脑中都检测到了此类塑料颗粒,证明纳米塑料颗粒可以穿透血脑屏障进入脑组织中,从而对生物体

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产生更加深远的影响[12].此外,纳米塑料还会抑制有机污染物的降解,导致其在环境中的积累[13].

极微小的尺寸使得纳米污染物在环境介质中很难被分离和鉴定.目前环境中纳米材料的常见分离方法有膜分离、凝胶电泳、尺寸排阻色谱法和非对称流场流分离技术等.微孔滤膜的孔径通常大于0.1 μm,而超滤膜的孔径最小可以达到 1 nm,但是两种滤膜都易发生表面极化现象,导致操作耗时较长[14],从而影响浓缩分离的效率;此外,膜过滤一般需在减压条件下进行,这也导致目标物与滤膜结合过于紧密,难以洗脱分离,且粒径大小也可能改变[15].在使用凝胶电泳分离纳米颗粒时,由于凝胶具有纳米孔结构,纳米颗粒可能会嵌入孔结构中,为后续检测带来困难[16],此外,电泳分离通量较小,很难对复杂基质中的纳米塑料进行高效分离.尺寸排阻色谱法根据凝胶孔隙的孔径大小与待测组分尺寸的相对关系对纳米颗粒进行分离,但由于纳米颗粒具有高表面活性,易与色谱固定相发生相互作用[14],因此分离效果也受到限制.非对称流场流分离技术根据目标物流体动力学粒径的差异实现分离,与传统的分离技术相比,具有分离条件温和,分离流道中没有固定相,对样品无损伤等优势.目前已有研究利用非对称场流分流技术对环境水体中胶体[17]和纳米颗粒物[18]进行分离.但由于纳米颗粒易发生团聚,该方法需向流动相中加入一定量的表面活性剂;此外,在方法开发中通常需对流速、pH 值、进样量等多个参数进行细致优化[19-20].

由于空间分辨率的限制,常用的微塑料光学检测技术,如基于红外光谱和拉曼光谱的显微成像技术往往难以直接应用于纳米塑料的检测.仅在相同材质的纳米塑料颗粒经大量富集形成更大尺寸的团聚体后,才有可能采用这类技术进行成分鉴定[21-22](表 1).此外,将质谱技术用于纳米塑料的尝试近年来也逐渐开展[23-24].

目前对环境介质中纳米塑料进行分离和检测的成功技术十分有限.2018 年,Correia 等[25]提出利用非对称流场流分离与多角度光散射法联用(AF4-MALS)检测鱼体中人为添加的纳米塑料(表 1).使用 MALS 检测器可获得每个洗脱组分不同角度的光散射信号和均方根直径的详细分布.该方法被认为对于鱼肉中人为加入的 PS 塑料纳米微球具有检测能力,最低检出限为 52 $\mu g \cdot g^{-1}$;然而对粒径小于 1 μm 的聚乙烯(PE)颗粒的检测效果并不理想.非对称流场流分离法适用于分散性较好的纳米颗粒的分散液体系,而稳定性良好的分散液制备是该分离技术应用的重要前提;此外,MALS 无法提供所分离出微粒的化学结构信息,因此该技术也难以区分天然环境介质中性质复杂的纳米微粒组分.Hernandez 等[21-22]利用分级膜分离-干燥-红外光谱法对个人护理品-面部磨砂膏和便捷茶包溶出物中的纳米塑料进行分析.将样品溶于水通过不同孔径的微孔滤膜,收集的滤液干燥后利用扫描电子显微镜(SEM)进行观察,确定样品中纳米颗粒的存在;以 X 射线光电子能谱(XPS)和傅里叶变换红外光谱(FT-IR)分析粒子的化学组成.该研究证实了面部磨砂膏中聚乙烯(PE)纳米塑料和便捷茶包溶出物中大量纳米级尼龙和聚对苯二甲酸乙二醇酯塑料的存在(表 1).

最近,刘景富团队[26]提出了浊点萃取(CPE)与热裂解气相色谱质谱(Py-GC/MS)联用检测水体中聚苯乙烯(PS)和聚甲基丙烯酸甲酯(PMMA)纳米塑料的分析方法(表 1).由于塑料具有疏水性,理论上浊点萃取对纳米塑料具有较高富集效率.利用非离子表面活性剂 TX-45 对水样中的纳米塑料进行浊点萃取富集,并使用 Py-GC/MS 对其进行定量检测,方法具有灵敏度高、耐基质干扰、操作简便等优点,使环境水平的纳米塑料检测成为可能,而 CPE 处理可以保持纳米塑料原有的尺寸和形状,因此可能通过表征富集在表面活性剂相中的纳米塑料来了解其粒径分布和原始形貌.此方法对于水中 PS 和 PMMA 纳米塑料的方法检出限可达 1.1 $\mu g \cdot L^{-1}$、0.6 $\mu g \cdot L^{-1}$.然而该研究并没有在天然水样中检测到 PS 和 PMMA 纳米塑料成分,表明受检水样中的纳米塑料浓度可能低于检出限水平,或在水样前处理过程中被消耗损失.另外,Py-GC/MS 无法排除能提供相同结构碎片的天然聚合物的干扰,如甲壳素在热解后也会产生苯乙烯信号[23],这会给纳米塑料的定量带来偏差.

CPE-Py-GC/MS 在实现环境样品中纳米塑料的检测方面最具潜力,但目前仍未能提供纳米塑料环境分布的直接证据.如果降解速率高于微塑料的分解速率,纳米塑料可能无法在环境中大量富集.对于环境中痕量水平的纳米塑料,在建立温和解聚方法的基础上[28-30],采用膜分离技术提高富集倍数,并将膜上富集的纳米塑料原位解聚为功能单体化合物分子,再进行质谱定量分析(表 1),可能是环境介质中纳米塑料检测的另一个有效的技术模式.但如何避免功能单体的背景值干扰,将是此方法应用的难点.

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环境中塑料聚合物的种类繁多、形态各异,直观的显微成像和成分鉴定仍将是未来技术探索的重要方向.但对于纳米塑料的环境检测,选择性富集与净化是此类技术能否成功的先决条件.然而,样品前处理过程如分级过滤、样品消解等,不仅可能导致纳米塑料的损耗或增加,也可能改变纳米颗粒的自身性质(如聚合度、粒径、表面电荷等),这仍将是纳米塑料检测中的重要挑战.

表 1 纳米塑料的分离与检测技术比较

Table 1 Comparison of Separation and Identification Methods of Nanoplastics

方法 Methods	应用 Application	局限 Limitations	参考文献 References
分级膜分离-干燥-红外光谱检测	采用滤膜分级过滤,干燥富集、FT-IR检测的方法,证实了个人护理品和便捷茶包溶出物中已知材质纳米塑料的存在	不适用于环境浓度纳米塑料以及复杂基质下纳米塑料的检测	[21-22]
非对称流场流分离与多角度光散射法联用	对鱼肉样品中人为加入的纳米 PS 颗粒实现分离和定量检测,检出限为 52 $\mu g \cdot g^{-1}$	对纳米颗粒分散性要求高,无法区分不同成分的颗粒	[25,27]
浊点萃取与热裂解气相色谱质谱联用	有效萃取富集并检测水样中加标 PS 和 PMMA 纳米塑料,方法检出限达 1.1 $\mu g \cdot L^{-1}$ 和 0.6 $\mu g \cdot L^{-1}$	未能检出实际水体中纳米塑料的存在水平;质谱可能受到天然聚合物的干扰	[26]
膜分离-原位解聚-质谱检测	滤膜分级过滤,在滤膜上进行原位温和解聚,对解聚功能单体进行质谱定量	仅能对有限的塑料成分进行检测	

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