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污水处理厂中微塑料的分析方法研究进展

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摘要: 随着研究的深入,微塑料在世界各地的污水处理厂中的赋存特征及潜在影响已逐渐成为新的研究热点,而研发适用性强、重复性高的提取鉴定方案是重要前提。当前,污水处理厂样品的复杂性导致现有微塑料的提取及鉴定方法多种多样。本文对现有的样品采集(大样本法与浓缩样本法)、预处理(消解及分离方法)和鉴定方法(目视法、光谱法及热分析法)进行了系统梳理和对比分析,以期为今后污水处理系统中微塑料的相关研究提供帮助。
关键词: 微塑料;污水处理厂;分析方法
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Progress in the Analysis of Microplastics in Wastewater Treatment Plants

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Abstract: With profound research, the existence characteristics and potential impacts of microplastics in the wastewater treatment plants (WWTPs) have gradually become a new research hotspot. Especially, the investigation about the extraction and identification methods of microplastics with high applicability and repeatability is an important premise. Currently, due to the complexity of samples in the WWTPs, various methods can be used to extract and identify of microplastics. In this study, the analysis methods of microplastics in WWTPs, including sample collection (bulk sampling and volume-reduced sampling), pretreatment (digestion and separation), and identification (optical evaluation, spectral analysis, and thermal analysis) were systematically compared and analyzed, which would provide helpful information for future researches about microplastics in WWTPs.
Keywords: microplastics; WWTPs; analysis method

塑料因其质轻、耐腐蚀及价格低廉等优点而在日常生活及工程中广泛应用。但值得注意的是,塑料的回收率低,只有6% ~26%的塑料被回收[1]。因此,大量塑料废品积累在环境中,其中粒径<5 mm的塑料碎片、纤维或颗粒又被称为“微塑料(microplastics, MPs)[2]”。据报道,微塑料分布极其广泛,从赤道到南北极附近海域、再到人迹罕至的青藏高原都发现了微塑料;在河流、土壤和大气颗粒物等不同

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环境介质中,甚至在食盐和饮用水中也都检测出微塑料[3-6]。微塑料因其粒径小,容易被生物误食,甚至还会随着食物链富集,对生物体造成损伤。此外,微塑料的疏水性高,会从周围环境中吸附并富集痕量有机污染物及重金属(如三氯生及镉离子等)[7-8],并作为其传输的载体,进而造成更大的环境危害,成为目前研究的热点之一。

微塑料可分为 2 类:原生微塑料和次生微塑料[9]。原生微塑料指的是人为制造用于工业或日常生活的粒径<5 mm 的塑料颗粒,多用于个人护理品、工业研磨剂及油漆等产品中[10-11]。据报道,在土耳其伊斯坦布尔,每年因牙膏使用而排放的微塑料可达 8.71 亿 g[11],这类微塑料在使用后会随着生活污水一起进入污水处理厂。已有多地的污水处理厂的出水和污泥中检测到该类原生微塑料颗粒[12-13],证实了微塑料的这一迁移趋势。次生微塑料则是指塑料制品在使用或废弃的过程中因环境因素(如光照、热氧化及物理摩擦)而破碎产生的粒径<5 mm 的塑料碎片,如空气中飘浮的合成纤维和道路上磨蚀的轮胎颗粒;研究表明,塑料茶包在使用过程中会产生微米级甚至纳米级的塑料颗粒[14]。次生微塑料在风力、雨水等环境作用力的裹挟下不断迁移,其中一部分会随初期雨水汇入污水处理厂。因此,污水处理厂是微塑料重要的汇之一。此外,污水处理厂又是微塑料重要的污染源。据统计,我国每年通过污水处理厂出水排放的微塑料占进入水生环境微塑料总量的 80% 以上;通过污泥进入土壤或其他自然环境的微塑料更是高达 1.56×10^{14} 颗[15-16]。因此,微塑料在污水及污泥中的赋存特征、迁移转化和环境归趋有待深入研究。为此,亟需建立和完善污水处理厂中微塑料的分析方法。

相较于自然环境中收集的样品,污水厂中的样品更加复杂多样。既有较为洁净的样品,如二沉池出水、最终出水等水样,也有富含有机与无机杂质等复杂成分的样品,如进水与污泥等样品。这些杂质会显著影响微塑料的检测。例如,活性污泥中大量存在的胞外聚合物(extracellular polymeric substances, EPS)会降低微塑料检出率[17];而进水中的泥沙和脂类颗粒及纤维素也会干扰微塑料的检测。与此同时,现有微塑料的检测方法多种多样,缺少统一的、标准化的采集和检测方法,不利于检测结果的横向对比。因此,研究适用面广、简单高效的微塑料分析方法成为当前研究的热点之一。本文从采样、预处理和检测 3 个方面对现有污水厂中微塑料检测分析方法进行了系统梳理和对比总结,以期为未来的研究提供帮助。

1　采样及预处理方法(Sampling and pretreatment methods)

1.1　采样方法(Sampling methods)

现有研究中所涉及到污水厂中微塑料的采样方法大体上可分为两类[18]:一是指在采样现场不对样品经行预处理的大样本法[19-24],适用于收集微塑料含量较高的环境样品。该方法能最大程度上保留样品的原始信息,操作简单,但采样量相对较小,样品的代表性会有所下降。为解决这一问题,Mason 等[19]采用自动采样器进行 24 h 连续采样,降低采样的偶然性。另外一种则是在采样现场通过过滤、筛分等方法降低样品体积的浓缩样本法[25-28],更适用于水体样品的采集,尤其是较为清洁的水样。此方法采样量大,检出限较低。此外,浓缩样本法根据过滤的方式不同又分为分级过滤和表面过滤。

各类采样方法和适用范围汇总详情如表 1 所示。总的来说,采样方法的选择上应注意所取样品的代表性及充分性,同时还应考虑取样的工作量(如采样体积、运输及保存过程的便捷程度)。对于二沉池出水及最终出水样品,微塑料含量低,通常需要收集大量水样进行分析。若采用大样本法,样品需求量大,运输及保存是一大难题。而这类样品水质清澈,杂质含量少,非常适合过滤收集;该方法可大幅提高样品收集量,同时降低了后续预处理的工作量。考虑到实验结果的横向可比性,推荐在实验中使用统一孔径的筛网;该方法也适用于与此相似的水体以及河湖水及海水等天然水体[23]。污水厂进水杂质较多,容易堵塞网孔;若采用简单过滤法,收集效率低,造成样品膜的用量过多,后续分离时容易造成目标物损失。但该类样品中微塑料含量波动较大($1\sim10^4$ 颗·L^{-1})[13,20-21],同样需要大量样品,仍需考虑样品保存及运输的问题,因此推荐采用分级过滤的方法收集,逐层对杂质及目标物进行截留,在缓解堵塞的同时提高采样体积,但需要留意的是筛网层数及相应孔径的一致性。污泥中微塑料的含量最高,且生物量及无机质丰富,难以进行浓缩,因此适合采用大样本法收集;而淤泥及沙滩类样品因富含无机杂质难以浓缩,该方法同样适用[27-28]。

1.2　预处理方法(Pretreatment methods)

环境样品中微塑料的预处理方法较为简单。从

主要杂质成分上,大体上可以分为2类:一是以有机杂质为主的生物样品,如鱼体及牡蛎等[29],其预处理方法以消解为主;二是以无机杂质为主的样品,如海滩砂砾样品[30],多采用密度分离进行样品预处理。对于无机杂质和有机杂质均较为丰富的污水处理厂样品常采用的预处理方法是消解与密度分离相结合[31]。值得注意的是下列方法重点从基质中无机和有机杂质的去除进行叙述比较,因此以下方法也是适用于与之类似的环境样品(如自然水体样本及沉积物等[32-33])。

1.2.1 有机杂质消解方法(Organic matter digestion method)

1.2.1.1 过氧化氢消解法(H_2O_2 solution)

过氧化氢(H_2O_2)消解是去除基质中有机物的常用手段,多用于消解含有少量有机杂质的样品,如去除海水样品中微塑料表面附着的有机物及微生物[34]。但经研究发现,在环境温度下,H_2O_2的有机物去除率较低,且会对某些塑料材质有一定的损伤。Nuelle等[35]用35% H_2O_2处理生物有机质,7 d的去除率仅为50%,而且聚乙烯(polyethylene, PE)和聚丙烯(polypropylene, PP)长时间暴露于H_2O_2中还会发生降解。有研究在消解过程中采用更高的温度以提高效率。在70 ℃下,30% H_2O_2的反应时间能降到12 h左右,但过高的反应温度也会导致聚酰胺类(polyamide, PA)微塑料的降解。为克服这些问题,研究人员使用Fenton试剂替代单纯的H_2O_2进行样品消解。在催化剂Fe(Ⅱ)的存在下,H_2O_2的氧化能力显著上升,能更有效地去除有机杂质,如高度氯化的芳族化合物。此外,Fenton反应速率更快,通常只需不到1 h即可完成废水样品的处理,效率明显提升[36-37];接触时间的缩短也降低了该方法对微塑料颗粒的不良影响。但需要注意的是,Fenton试剂的最佳pH值在3~5之间,在使用时需调节体系pH值;而且反应放热明显,需加水浴以控制反应温度。

表1 微塑料采样方法汇总

Table 1 Summary of sampling methods for microplastics

方法 Method		采样量/L Quantity/L	筛网孔径 Mesh size	优缺点 Advantages and disadvantages	适用范围 Application	参考文献 References
大样本法 Bulk sampling		0~100	/	操作简单、保留样品原始信息,但采样量小、误差较大 The operation is simple, could retain the original information; but the sampling amount is small and the error is large	进水、污泥等 Influent, sludge, etc	[19-24]
浓缩样本法 Volume-reduced sampling	简单过滤 Simple filtration	0.1~10^6	300~500 μm为主,最大能达5 mm 300~500 μm mainly, up to 5 mm	采样量大,检出限低,纤维类有损失可能 Large sampling amount and low detection limit, but the fiber may be lost	进水、二沉池出水、最终出水等 Influent, secondary sedimentation outlet, effluent, etc	[21,25]
	分级过滤 Fractional filtration		45~400 μm	在粒径上对微塑料分级收集,但分离效果受微塑料不规则性的影响 Collect microplastics in different grades, but affected by the irregularity of microplastics		[26-28]
	表面过滤 Surface filtration		125 μm	操作简单,但相对密度较大的微塑料可能采集不到,受空气污染的可能性更大 Simple operation, but microplastics of high density may be lost and easily contaminated by air		[13]

1.2.1.2　酸消解法(Acid digestion)

酸消解法是另一种重要的样品预处理方法,采用强无机酸,如硫酸(H_2SO_4)和硝酸(HNO_3),在高温和高压下氧化并裂解杂质。此方法在有机物质消解方面非常有效,常用于处理有机质含量高的样品。Yan 等[38]利用 50 ℃水浴下的 HNO_3(65%)对粪便样品深度处理,有机质的去除率可达 97%。但 Avio 等[39]发现高温下(100 ℃),强氧化性的 HNO_3 会侵蚀微塑料颗粒,如 PA 类和聚苯乙烯(polystyrene, PS),而且还生成氮氧化物,产生二次污染。为避免微塑料的降解,有研究采用低浓度的非氧化无机酸——盐酸(HCl)进行样品处理,但有机物的去除效率较低,不到 90%;仍需进一步的改进。

1.2.1.3　碱消解法(Alkali digestion)

碱可以很有效地促进一些天然大分子有机物的水解,而且试剂廉价易得,多用于富含蛋白质的样品(如鱼肉组织)消解,并采用加热的方式提高效率。通常所用碱为氢氧化钠(NaOH)和氢氧化钾(KOH),浓度范围在 2~10 $mol \cdot L^{-1}$ 之间,反应体系的温度控制在 60~70 ℃。但 Herrera 等[40]用热碱法处理污泥样品时发现有机物质去除效果并不理想,只有 57%~67%。可能的原因是污泥中大量的难降解物质(如几丁质和纤维素)对 KOH 和 NaOH 具有较强的抵抗力,从而降低了热碱法的效率;而且部分材质的微塑料如聚对苯二甲酸类(polyethylene terephthalate, PET)会降解或表面性质发生变化而影响后续鉴定。因此,热碱法适用范围较小。

1.2.1.4　酶消解法(Enzymatic digestion)

酶是一类极为重要的生物催化剂,可以在温和的条件下高效地消化基质内的有机物。Mintenig 等[41]采用蛋白酶进行消解,成功鉴定出大小为 20 μm 的微塑料颗粒,并且没有对其造成影响。但是,目前酶试剂成本高,不适宜处理大样品量。此外,对于污泥及进水这类复杂样品,一方面酶的特异性高,需要多种酶的共同参与才能分解其中不同种类的有机杂质,成本及时耗明显上升;另一方面酶的易变性高,容易受样品组分(酸、碱及重金属等)的影响而失活[42]。因此,该方法在实际污水处理厂样品的消解中使用较少。

不同消解方法的适用性及优缺点列于表 2 中。在消解方法选择上,有机杂质的去除效率及对微塑料的损伤程度是 2 个最重要的参照点[43-44];同时也要进一步考虑方法的成本及时效。相对而言,酶消解法过高的成本和高的易变性,导致其难以推广。此外,上述消解方法对有机物的去除效果依次为:Fenton 试剂和高浓度酸>H_2O_2 和热碱>低浓度酸。对微塑料的影响依次为:热碱>高浓度酸>低浓度酸>H_2O_2 和 Fenton 试剂。而不同材质微塑料对消解方法的敏感程度依次为:PET、PA 和聚甲基丙烯酸甲酯(PMMA)类>PS>聚乙烯(PE)和 PP。在实际应用中,酸消解试剂氧化性强,对目标物的损伤较大,而且还会产生污染环境的氮氧化物,因此不推荐使用该方法。相对而言,Fenton 消解法既有高的有机杂质去除率,而且对微塑料的损伤相对较小,同时所需试剂安全易得,故推荐 Fenton 消解法作为污水厂中微塑料有机杂质预处理的首选方法。

1.2.2　无机物分离方法(Inorganic separation method)

1.2.2.1　密度分离法(Density separation)

密度分离法最早由 Thompson 等[45]使用在微塑料的提取上。该方法利用微塑料密度(0.8~1.4 $g \cdot mL^{-1}$)比沙子等无机杂质的密度(约 2.65 $g \cdot mL^{-1}$)小这一特点,采用高浓度盐溶液将微塑料分离出来,多用于处理沙滩样品及土壤样品等无机杂质为主的环境样品[45-46]。其中,氯化钠(NaCl)因其价格低廉且易于获取而成为最常用的分离试剂,但饱和 NaCl 溶液的密度约为 1.2 $g \cdot mL^{-1}$,难以分离一些高密度塑料,例如 PET(密度为 1.29~1.41 $g \cdot mL^{-1}$)或聚氯乙烯塑料(polyvinyl chloride, PVC;密度为 1.19~1.35 $g \cdot mL^{-1}$)。有研究人员尝试使用碘化钠(NaI)、氯化钙($CaCl_2$)和氯化锌($ZnCl_2$)等试剂代替 NaCl[47-49],盐溶液密度增大,进而提高了分离效果。但这些试剂也存在各自的不足。例如,NaI 不仅成本较高,而且碘离子很容易在使用过程中被氧化产生有毒的碘单质,降低了试剂回收率而且污染环境;$CaCl_2$ 与 $ZnCl_2$ 相对便宜,但是钙离子易与有机物作用沉淀在微塑料的表面而影响后续鉴定,而 $ZnCl_2$ 的腐蚀性及毒性也在一定程度上限制了其使用。

此外,Nuelle 等[35]开发了一种基于浮选与密度分离相结合的空气诱导溢流分离法。通过在容器底部引入气流,将 NaCl 溶液中的样品流化,使样品中较轻粒子更快速地移动到溶液的顶层,最终通过收集溢流液实现基质分离。一方面,该方法所用试剂安全易得,成本低,而且样品杂质去除效率高,可达 80%以上,可用于大量样品的预处理;另外一方面,可与高密度盐溶液联用,进行二次分离,提高了微塑料的回收率,能达到 91%~99%。

1.2.2.2 油萃取法(Oil extraction)

油萃取法是由 Crichton 等[50]提出的以微塑料的亲油特性为基础替代基于密度差的分离方案。该方法在操作上与液液萃取类似,微塑料会更倾向于分布在油相内从而实现与沉降在水相中的无机杂质分离,适用于无机杂质为主的少量样品的预处理,如沙滩样品[45]。经加标测试,该方法对微塑料的回收率可达 96% 以上。加之,所用试剂廉价、易得且安全性高,使得该方法有较广的适用性。但该方法使用前,需要尽可能地去除样品中的有机杂质。

上述无机物分离方法的优劣汇总在表 2 中。油萃取法处理后,油渍难以彻底清洗,微塑料表面会有残留,一定程度上影响后续鉴定。而密度分离法主要变量是所用盐溶液种类。但在试剂的易得性、安全性以及对后续塑料鉴定的潜在影响等方面,Ca^{2+} 易沉淀在微塑料表面而影响后续鉴定,$ZnCl_2$ 有一定危险性,而 I^- 容易被氧化,因此推荐 NaCl 作为首选试剂。为了提高 NaCl 溶液密度分离效率及适用范围,应进一步完善及规范浮选与密度分离相结合的空气诱导溢流方法中的试剂、装置及操作步骤,提高该方法的可操作性及经济性。

2 观察和鉴定方法(Observation and identification methods)

2.1 目视检测法(Visual detection)

目视检测法是最基础的微塑料鉴别方法,通过操作人员肉眼观察将样品中的疑似颗粒挑拣出来,适用于粒径大、特征明显的微塑料颗粒的初步筛选。该方法不需大型仪器,操作简单,Eriksen 等[51]便成功利用目视检测法完成了对加拿大劳伦湖水样品中大粒径塑料微珠(>1 mm)的筛分。但值得注意的是污水厂样品中微塑料粒径大多<500 μm[52-53],裸眼很难识别,需要借助显微镜对样品中的疑似颗粒物逐一筛查,费时费力;而且实际微塑料样品形貌多样,加上操作人员的主观偏差,导致误判率高达 70%[54-56]。为提高该方法的准确率及对污水处理厂样品的适用性,研究人员尝试使用了几种简单的辅助方法:一种是利用塑料的物理特性(如硬度高及热熔特性)[57-58],将微塑料与杂质颗粒物(如脂肪颗粒、植物纤维及沙粒等)区分开。如 Zhang 等[58]将样品在 130 ℃加热 3~5 s,通过对比前后照片的差异筛选微塑料,其粒径下限可达 20 μm。另一种则是基于微塑料的疏水性,通过脂溶性荧光染料对其染色,借助荧光显微镜进行识别。现有研究表明,经尼罗红荧光染料染色后,不同大小和聚合物类型的微塑料在蓝光下清晰可见,可以轻易地与其他杂质颗粒区分开[59]。总的来说,这 2 种方法均可在一定程度上提高目视法的检测速率及准确率。

2.2 光谱法(Spectral method)

目前,傅里叶变换红外光谱法(FTIR 法)及拉曼散射光谱法(Raman 法)是 2 种最常用于微塑料材质的定性分析方法[60]。该类方法可以在不接触与不破坏样品的前提下,对样品化学成像;不仅能表征化学成分,还能获得更多的样品信息:单个颗粒的形态(表面形貌、尺寸及颜色等)和不同聚合物颗粒的丰度[61]。FTIR 光谱属于吸收光谱,是基于化合物分子振动时因其特征结构而吸收特定波长的红外光而产生的,通过其所含特征官能团而鉴别样品组分,理论上能测定粒径>20 μm 的塑料颗粒[13]。Song 等[60]利用 FTIR 法显著提高了小粒径微塑料(< 50μm)的检出率,是目视法的 1.6 倍。值得注意的是水分会影响检测,需要将样品充分干燥。而且常规的透射模式很难满足对较厚及颜色较深的微塑料颗粒的测定要求[62]。因此,可用傅里叶变换衰减全反射红外光谱法加以代替。

Raman 光谱是基于分子极化率变化诱导产生的一种散射光谱,原则上可以鉴别粒径达 1 μm 的微塑料。最新研究通过 Raman 映射与扫描电镜图像相同结合的方法识别出粒径达 100 nm 的 PS 颗粒[63]。此方法对于样品制备没有特殊要求,而且不受颗粒的形状、大小和厚度的影响,但对样品预处理的要求高,需要去除样品中的荧光物质,否则会影响测定结果。与 FTIR 法相比,Raman 法空间识别度更高。因此,Raman 光谱是鉴定小粒径微塑料(< 20 μm)的首选方法[64],但测量时间比 FTIR 法要高得多。此外,这 2 种光谱方法可以互补,如两者结合使用才能完整可靠地表征有色颗粒的化学成分。

值得注意的是,在环境中长期暴露的微塑料,因受到多种因素(热、氧、机械摩擦及生物作用等)影响会发生老化,表面含氧官能团、粗糙度及色度等发生变化,使得光谱测定结果与标准谱图存在差异,导致误判。因此,有必要建立环境样品中真实微塑料的谱图库[65]。此外,光谱法仍以目视检测为基础,人力及时间成本较高。为解决这一问题,有研究提出研发基于光学软件与光谱相结合的检测仪器,实现对样品中颗粒物的自动鉴别。Tagg 等[66]使用加标废

表 2 微塑料预处理方法汇总

Table 2 Summary of microplastics pretreatment methods

方法 Method		简述 Description	优缺点 Advantages and disadvantages	参考文献 References
过氧化氢消解法 H_2O_2 solution	H_2O_2 试剂 H_2O_2 reagent	体系加热至 60～70 ℃以提高反应效率,反应时长多为 12～24 h The system was heated to 60～70 ℃ to improve the reaction efficiency, and need mostly 12～24 h	对微塑料性质影响小,适用于杂质较少的样品;但常温下反应时间长,去除效果差,而且微塑料长时间暴露在 H_2O_2 中会有一定程度的降解 It has little effect on the microplastics, suitable for samples with less impurities; however, under normal temperature, the reaction time is long and the removal effect is poor, and the microplastics will degrade when exposed to H_2O_2 for a long time	[34-35]
	Fenton 试剂 Fenton reagent	以 Fe(II)离子为催化剂,与 H_2O_2 体积比 1∶1 加入,体系 pH 在 3～5 之间,反应时间多为 1 h 以内 Fe(II) as the catalyst, H_2O_2 addition with the volume ratio of 1∶1, the pH of the system is between 3 and 5, and the reaction time is mostly within 1 h	反应时间短,去除效率高;但反应放热明显,且反应需控制在酸性条件下 Short reaction time and high removal efficiency; but the exothermic reaction was obvious, and the reaction should be controlled under acidic conditions	[36-37]
酸消解法 Acid digestion		常用酸是硫酸、硝酸与盐酸,体系会短时间(约 30 min)加热至 80～100 ℃,提高效率 Sulfuric acid, nitric acid and hydrochloric acid are commonly used; the system will be heated to 80～100 ℃ in a short time (about 30 min) to improve efficiency	有机物去除效果明显;但反应温度偏高,加之试剂的强氧化性,对聚酰胺和聚苯乙烯等塑料有损伤 The removal effect of organic matter is obvious; however, the high reaction temperature and the strong oxidation of the reagent caused damage to the polyamide and polystyrene plastics	[38-39]
热碱消解法 Alkali digestion		常用碱是氢氧化钠、钾,浓度多在 2～10 $mol \cdot L^{-1}$,反应温度为 60～70 ℃,时长 24 h 左右 Sodium hydroxide and potassium hydroxide are commonly used, with concentrations ranging from 2 to 10 $mol \cdot L^{-1}$ and reaction temperatures ranging from 60 to 70 ℃ for about 24 h	对蛋白质及纤维素类有机物有很强的水解能力,但对难降解有机物去除效果差,且与碱浓度及温度有关;会引起聚对苯二甲酸乙二醇酯(PET)、聚乙烯(PE)等降解及颜色变化 It has strong hydrolysis ability to protein and cellulose organic matter, but has poor removal effect to refractory organic matter, and is related to alkali concentration and temperature; polyethylene terephthalate (PET), polyethylene (PE) will degrade and change color	[40]

续表 2

方法 Method		简述 Description	优缺点 Advantages and disadvantages	参考文献 References
酶消解法 Enzymatic digestion		室温下，以生物酶作催化剂，促进有机物降解，需要控制反应条件(如温度、pH 及重金属) At room temperature, biological enzymes are used as catalysts to promote degradation of organic compounds, requiring controlled reaction conditions (like temperature, pH and heavy metals)	去除效率高，高达 97% 的有机物去除率，对微塑料没有影响，但污水样本组成复杂，需要多种酶，耗时、成本高且容易失活 High removal efficiency, up to 97%, has no impact on microplastics; but the composition of sewage samples is complex, requires a variety of enzymes, time-consuming, costly and easy to deactivate	[41-42]
密度分离法 Density separation	NaCl 溶液 NaCl solution	饱和食盐水密度约为 1.2 g·mL^{-1}，是最常用的盐溶液 The density of saturated salt water is about 1.2 g·mL^{-1}, which is the most commonly used	试剂易得且成本低，但许多高密度塑料不能分离，例如聚对苯二甲酸乙二醇酯(PET)或聚氯乙烯(PVC) Reagents are readily available and low cost, but many high-density plastics, such as polyethylene terephthalate (PET) or polyvinyl chloride (PVC), cannot be separated	[45-46]
	$CaCl_2$ 溶液 $CaCl_2$ solution $ZnCl_2$ 溶液 $ZnCl_2$ solution NaI 溶液 NaI solution	氯化钙溶液密度为 1.3~1.35 g·mL^{-1}，氯化锌溶液密度为 1.5~1.7 g·mL^{-1} 及碘化钠溶液密度为 1.6~1.8 g·mL^{-1} The density of calcium chloride solution was 1.3~1.35 g·mL^{-1}, the density of zinc chloride solution was 1.5~1.7 g·mL^{-1}, and the density of sodium iodide solution was 1.6~1.8 g·mL^{-1}	溶液密度更大，分离效率提高，但成本总体上升，且钙离子易沉淀在微塑料表面而影响后续鉴定，而 $ZnCl_2$ 有一定危险性，碘离子容易被氧化产生碘单质，回收率低 The higher solution density improved separation efficiency, but the overall cost increases; calcium ions are easy to precipitate on microplastics and affect the identification; $ZnCl_2$ has a certain risk; iodide ion is easy to be oxidized and the recovery is low	[47-49]
	空气诱导溢流 Air-induced overflow	密度分离的基础上加空气诱导溢流装置 Density separation based on the addition of air-induced overflow device	气浮与密度分离相结合，提高分离的效率，但装置相对复杂 The combination of air floatation and density separation improves the efficiency of separation, but the device is relatively complex	[35]
油萃取法 Oil extraction		以微塑料的亲油特性为基础，采用液液萃取操作步骤 Based on the oil-wet characteristic of microplastics, the liquid-liquid extraction operation procedure was adopted	操作简单且回收率高，可达 96%，且不受微塑料的形状影响，但微塑料表面残留的油类会影响后续检测 The operation is simple and the recovery rate is high, up to 96%, and is not affected by the shape; but the residual oil on microplastics will affect the detection	[50]

水样品验证了该方法,微塑料回收率为 98%,而且将通常耗时几天的映射样品在不到 9 h 内成像,大大提高了微塑料的检测效率。但相关技术仍处研发阶段,其检测成本相对较高。如何进一步降低检测成本以达到塑料样品常规检测分析的应用要求,是极具研究价值的。

2.3 热分析法(Thermal analysis method)

热分析是在程序控温下,基于物质的热力学参数或物理参数随温度变化的关系进行分析的方法,可用于微塑料成分及性质的鉴别,更适用于组成较为单一的样品。Majewsky 等[67]借助差式扫描量热与热重分析联用仪对废水样品中微塑料含量进行了测定,但只有 PE 被清楚地识别出来(约 81 ~257 mg $\cdot m^{-3}$),其他聚合物因相变信号发生了相互重叠而无法识别。由此可见,单纯的热分析在污水厂的微塑料检测中受到了限制。

现有研究使用较多的检测方法的是以热分析为基础,结合以色谱技术和质谱分析,测定样品裂解产物的组成,进而达到对微塑料定性及定量分析的目的[68-69]。根据热解方式的不同又分为 2 类:一类是借助高温将样品热解为气体,随后导入气相色谱仪进行鉴定,但需要注意的是控制热解及进样器温度。Hermabessiere 等[68]用热解-气质联用法不仅快速对微塑料含量进行了测定,还完成了对光谱法难以识别的塑料颗粒(如含颜料颗粒及多材质共聚物)的分析。另一类则是将样品在甲苯中热解沉降后在乙腈中重构,借助液相色谱测定,多用于检测微塑料中微量的添加剂(如光稳定剂[70])。该类方法检出限低(可达 1 μg),不受微塑料粒径影响,且对样品预处理要求低。最新研究表明,热解-气质联用法还可区分微塑料以其他类型的有机物成分(如腐殖质)[71],适用于污水厂及淤泥等组成复杂样品的检测。Ter Halle 等[72]成功利用该方法测出了北大西洋中纳米塑料的存在。但该类方法属于破坏性测定,样品无法回收,同时还会损失微塑料的颜色、形状及尺寸等方面的信息。

微塑料的观察和鉴定方法优缺点列于表 3 中。总的来说,目视检查法较为基础,所需设备简单,但是误判率高且无法判定材质,因此实用性不高。此外,光谱法和热分析法均可对微塑料样品进行定性及定量检测。光谱法可以从材质、数量和图像信息(颜色、粒径及形状等)反映样品中微塑料的组成情况,而热分析法则偏重于材质和质量 2 个方面的信息。两者检测结果具有可比性[73],同时还可以相互补充。但除了会损失微塑料的形貌信息外,热分析法的最大不足是仪器设备昂贵且普及率不高,而且可重复性有待提高[74]。因此,推荐光谱法作为检测的首选方法。而光谱法的不足主要是以目视检查法为基础,耗时耗力。完善以光谱法为基础的自动化颗粒检测技术来提高检测时间效益及降低经济成本,将能更快地推动微塑料在污水厂中赋存特征的研究。

3 总结和建议(Summary and suggestions)

本文从污水厂中微塑料的样品采集、预处理及检测 3 个方面对现有文献进行了总结。就样品采集来说,污泥中微塑料含量高且难以浓缩,应采取大样本法进行收集;而进水杂质较多,含量波动大,可选用分级过滤收集以提高采集的量及减少过滤时间;二沉池出水与最终出水较为清洁,适合于现场过滤收集以提高微塑料的检出率。对于样品预处理方法来说,污水厂进水及污泥样品无机和有机杂质都比较丰富,应采取先消解再密度分离的方法,其中 Fenton 消解法是去除有机物的较为合适的一种选择;而无机物分离可采用以 NaCl 溶液为基础的空气诱导溢流法。而二沉池出水及最终出水样品无机杂质少,可以仅采用有机物消解的方法进行样品预处理。对于微塑料的检测,考虑到检测的准确率、信息量及成本,推荐光谱法作为主要的检测方法。

目前污水处理厂中微塑料的分析方法日益丰富,而为了提高微塑料的检测结果的可信度与可比性,以下几个方面值得关注。

(1)规范采样方法。污水厂中样品采样方法种类多,不同方法采样量及所需器材不同,会在一定程度上影响不同样品间的可比性。因此,应进一步规范采样方法,优化采样体积、筛网孔径等相关参数,提高样品的代表性及横向可比性。

(2)建立标准化的分析方法。采用较为统一的分析方法有利于不同研究的结果进行横向对比;现有方法有着各自优缺点,应尝试建立一套针对污水厂样品的标准化分析方法,并进一步优化相关参数(如消解试剂种类及反应温度和检测方法等)以提高方法的适用性。

(3)统一微塑料的特征描述。污水厂中微塑料的尺寸、颜色、形态和化学组成等特征差异显著,导致不同研究对微塑料的描述出入较大,结果的可比性不高。因此,统一微塑料尺寸的定义、形态的划分等特征描述,有助于提高不同研究中微塑料检测结果的可比性。

表3 微塑料检测方法汇总

Table 3 Summary of microplastics detection methods

方法 Method		简述 Description	优缺点 Advantages and disadvantages	参考文献 References
目视检测法 Visual detection	简单目视 Simple visual	借助显微镜,操作人员凭借肉眼观察将样品中的疑似颗粒挑拣出来 The operators screen for suspected particles by the microscope	操作方便,设备简单,但主观性高,误判率高达70%;工作量大,耗时耗力,无法确定微塑料材质 Easy operation and simple equipment, but high subjectivity leads to high misjudgment rate, up to 70%; the heavy workload, time-consuming and labor-consuming, and it is impossible to determine the material	[54-56]
	物理辅助 Physical auxiliary	通过简单的物理方法(如针压、加热等),辅助目视检查以排除一些假性微塑料颗粒 Assisted visual inspection by physical methods (extrusion, heating, etc.) to exclude pseudomicroplastics	提高目视法准确率,但仅为辅助方法,适用性小 Improve the accuracy of visual method, but it is only an auxiliary method and has little applicability	[57-58]
	荧光染色 Fluorochrome stain	样品经荧光染料染色,借助荧光显微镜,将发荧光的微塑料与背景分开 The samples were dyed with fluorescent dyes, separated from the background by a fluorescence microscope	检测效率提高,但有些杂质也可染上荧光,存在误判 The detection efficiency is improved, but some impurities can also be stained with fluorescence, which leads to misjudgment	[59]
光谱法 Spectral method	FTIR 光谱 FTIR spectrum	基于化合物分子振动时因其特征结构而吸收特定波长的红外光而产生的吸收光谱 The absorption spectrum based on the characteristic structure of a compound molecule that absorbs infrared light at a specific wavelength when it vibrates	定性分析,不损伤样品,空间分辨率可达20 μm,但过厚及不透光颗粒及样品中水分对测定有影响 Qualitative analysis, no damage to microplastics, and recognizable up to 20 μm, but the thickness, opaque particles and moisture will influence on the determination	[60-62]
	Raman 光谱 Raman spectrum	基于分子极化率变化诱导产生的散射光谱 The scattering spectrum induced by a change in molecular polarizability	定性分析,不损伤样品,空间分辨率高,可达1 μm,但荧光杂质会影响检测,因此对样品预处理要求高 Qualitative analysis, no damage to microplastics, high spatial resolution, up to 1 μm, but fluorescence impurities will affect the detection, so high requirements for sample pretreatment	[61,63-64]
热分析法 Thermal analysis method	简单热重 Simple thermal method	在程序控制温度下,根据目标物热力学参数或物理参数随温度变化的关系进行分析的方法 A method of analysis according to the relationship between the thermodynamic parameters or physical parameters of the target with temperature under program control temperature	操作简单,易于与其他方法联用,但样品检测量小,且无法区分多种微塑料共存的样品 Simple and easily combined with others, but the amount is small, and could not distinguish different kinds of microplastics	[67]
	热分析-色谱联用 Thermal analysis-chromatographic method	将样品进行热解后,使用气相色谱-质谱或液相色谱-质谱对热解产物的组分及含量进行定性及定量分析 After pyrolysis, the components and contents of pyrolysis products were analyzed qualitatively and quantitatively by gas chromatography-mass spectrometry or liquid chromatography-mass spectrometry	快速、高效且检测限低(可达1 μg),预处理简单,但破坏性分析,样品无法回收;且会造成信息损失(如粒径、颜色和形状等) Fast, efficient and low detection limit (up to 1 μg), simple pretreatment; but destructive analysis, cannot be recycled, and information loss (size, color, shape, etc.)	[68-73]

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